

Bistriazoles Connected Through a B–B Bridge, Synthesized by Highly Selective Dipolar Cycloaddition Reactions of a Diazido-diborane(4)

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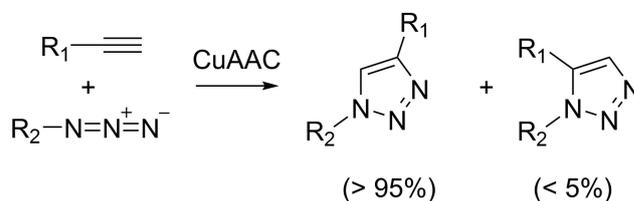
Abstract: In this work we report the first cycloaddition reactions between a diazido diborane(4) and terminal alkynes, providing unique access to bis-1,2,3-triazoles connected by a B–B bridge. The catalyst-free reactions are highly selective, yielding exclusively the thermodynamically disfavored bis-1,4-triazoles. The reactions are enabled by the high thermal

stability of the diazido-diborane [B(hpp)(N₃)₂] (hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2- α]pyrimidin-2-ylidene). Due to the tetra-coordinate boron atoms in this reagent, the reactions are tolerant with respect to the introduction of Lewis-basic groups at the alkyne. The scope and limitations of the new reactions are discussed.

Introduction

Reactions between organic azides and alkynes to give 1,2,3-triazoles are classical examples of [3 + 2] cycloaddition reactions. The uncatalyzed reaction, typically termed “Huisgen 1,3-dipolar cycloaddition”, requires high temperature and is unselective, leading to an equimolar mixture between the 1,4- and 1,5-disubstituted 1,2,3-triazole regioisomers.^[1–3] Later, the copper-catalyzed azide-alkyne [3 + 2] cycloaddition (CuAAC) was developed, that proceeds fast at mild conditions and with high selectivity to the 1,4-disubstituted 1,2,3-triazole (see Scheme 1).^[4–6] Since 2002, CuAAC has been developed to an extremely useful tool in synthetic chemistry.^[7–11] While the “Huisgen 1,3-dipolar cycloaddition” is a one-step reaction, CuAAC is a multistep process; its mechanism involves a complex between the azide and a copper(I) acetylide. Consequently, the classical CuAAC is limited to terminal alkynes. However, several groups developed alternative reaction protocols that allow the use of internal alkynes and especially 1-iodoalkynes^[12] in 1,3-dipolar cycloadditions with azides.^[13]

In addition, many transition metal azide complexes were applied in [3 + 2] cycloaddition reactions.^[14] In 2007, Sedelmeier et al. showed that reaction between aluminum azides and nitriles could be used to synthesize 5-substituted tetrazoles in good yield, the required temperature depending on the alkyne.^[15] Therefore, it was obvious to also try the use of boron



Scheme 1. Copper-catalyzed azide-alkyne [3 + 2] cycloaddition (CuAAC), yielding selectively 1,4-disubstituted 1,2,3-triazoles.

azides. To anticipate the difficulties of such reactions, that proceed without catalyst, we first briefly summarize some results on the synthesis and thermal stability of boron azides, before turning to examples for their reactions with alkynes. Indeed, boron azides were studied for a long time, as they have a rich and fascinating chemistry. Some of these compounds, like dichloro boron azide,^[16] crystallizing as the trimer (Cl₂BN₃)₃ with bridging (μ -bound) N₃ groups,^[17] or dimethyl boron azide, Me₂BN₃,^[18,19] are amenable to explosion upon solvent removal or sublimation, but several diaryl and dialkyl boron azides (e.g., diphenyl boron azide or dibutyl boron azide) were found to be stable and thermally quite robust. They are usually synthesized by reaction between diorganyl boron chlorides and lithium azide.^[20,21] Like the trimer (Cl₂BN₃)₃, dimeric bis(pentafluorophenyl)boron azide ([C₆F₅)₂BN₃)₂ exhibits bridging azido groups between the boron atoms.^[22] Also, mononuclear compounds with more than one azido group attached to the same boron atom are known, for example the tetraazidoborate anion [B(N₃)₄][−] and several boron triazide adducts.^[23]

The controlled thermal or photolytic decomposition of boron azides often leads to boron imides RBNR by dinitrogen elimination followed by migration of an R-group from boron to nitrogen; the boron imides subsequently dimerize or oligomerize (see Figure 1a), for example Ph₂BN₃ is eventually converted to (PhBNPh)₂.^[20,24] Diamino and dialkoxy boron azides were also

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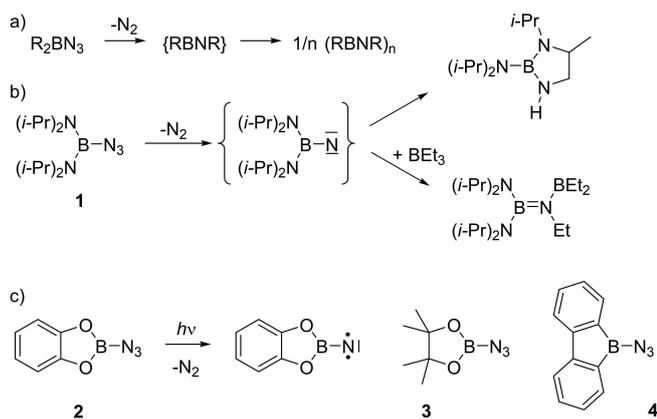


Figure 1. a) Decomposition of azidoorganoboranes to give oligomeric boron imides. b) Formation of a borylnitrene from decomposition of an azidoborane (work of Paetzold et al.) and its reaction with triethylborane. c) Photolytic formation of a borylnitrene in a matrix by Bettinger et al., together with other azido-boranes studied in the course of these investigations.

synthesized^[25] and their decomposition studied. An example is bis(diisopropylamino)-azido-borane ($B(N(i\text{-Pr}))_2N_3$ (**1**), Figure 1b), synthesized by Paetzold et al.^[26] Dinitrogen elimination from diamino boron azides with sterically demanding amino groups at higher temperatures gives reactive borylnitrene intermediates. For example, the borylnitrene formed in the course of thermal decomposition of **1** undergoes an intramolecular insertion process into the C–H bond of one of the *i*-Pr groups (Figure 1b); in the presence of BEt_3 , insertion into the B–C bond was observed (Figure 1b). Also, azido-(*o*-phenylenedioxy)-borane, $catBN_3$ (**2**),^[27] and 2-azido-4,4,5,5-tetramethyl-1,3-dioxaborolane, $pinBN_3$ (**3**),^[28] could be photochemically converted to borylnitrene intermediates.^[29–31] Bettinger et al. studied the nitrene generated by photochemical dinitrogen elimination from **2** in a solid Ar matrix (reaction in Scheme 1c); its EPR spectrum revealed a triplet ground state, in line with quantum-chemical calculations. Its special reactivity was first probed in inert-gas matrices (reactions with CO and O_2); then reactions were carried out on a preparative scale. Photo-induced reactions of **2** with methane and cycloalkanes gave new access to amines and amides,^[28] and similar reactions were then extended to **3** and other dialkoxy boron azides. In this context it is also worth mentioning that thermal decomposition of 9-azido-9-borafluorene (**4**)^[32] leads to a 1,2-azaborine that cyclo-tetramerizes to a B_4N_4 ring compound.^[33,34]

Hence, boron azides are amenable to several thermally induced reactions, that have to be considered when they are applied in uncatalyzed 1,3-dipolar cycloadditions at higher temperatures. Indeed, most reactions between boron azides and alkynes proceed at high temperatures, and so far it was not possible to develop a catalytic reaction that might allow milder reaction conditions for a variety of boron azide substrates. For example, boryl azide **5** (Figure 2a), stabilized by an N-heterocyclic carbene,^[35] reacts with electron-poor alkynes, alkenes and nitriles.^[36] Figure 2a shows the reaction with ethylpropiolate in toluene at 110°C , giving selectively the 1,4-triazole in an excellent yield of 94%. Reactions of $LiB(N_3)_4$ and $Na(N_3)_4$ as well

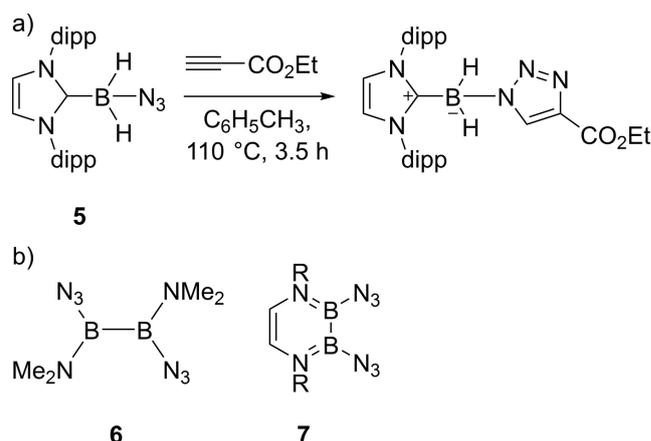
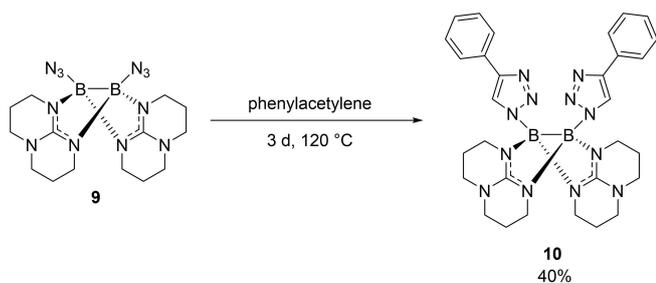


Figure 2. a) Example for a 1,3-dipolar cycloaddition between a boron azide and an alkyne. b) Examples for known diazido-diborane compounds.

as several adducts of $B(N_3)_3$ with nitriles to give tetrazoles were accomplished at $80\text{--}120^\circ\text{C}$.^[37] Five-membered N_3BC heterocyclic compounds resulted from reaction between the boron azide $(F_5C_6)_2BN_3$ and the boron alkyne $(F_5C_6)_2BC\equiv\text{CPh}$.^[38] Since reactions generally require high temperature, temperature-sensitive boron azides could only be applied in exceptional cases. For example, Melen and Stephan reported several cycloadditions between dimeric dicyclohexyl boron azide, $(Cy_2BN_3)_2$, and electron-poor alkynes, proceeding already at room temperature to new dibora-triazole compounds.^[39,40] Furthermore, Bettinger showed that compound **2** (see Lewis structure in Figure 1c), being an example of a relatively temperature-sensitive boron azide that does not react with most alkynes, reacts at room temperature with cyclooctyne to yield an oligomeric boryl triazole.^[41]

Hence, recent research showed that some boron azides could be used in cycloaddition reactions with alkynes. By contrast, cycloaddition reactions of azido diborane(**4**) or diazido diborane(**4**) compounds are completely unknown up to date. This is primarily due to the fact that only a few stable azido diborane(**4**) compounds are known so far, such as compounds **6** and **7** reported by Braunschweig et al. (Figure 2b).^[42] Further attempts by Braunschweig et al. to synthesize diazido diboranes failed and demonstrated a relatively high instability of these compounds.^[43]

Recently, we reported the reaction of the ditriflate diborane $[B(\text{hpp})\text{OTf}]_2$ (**8**) ($\text{hpp} = 1,3,4,6,7,8\text{-hexahydro-2H-pyrimido}[1,2-\alpha]\text{pyrimidin-2-ylidene}$)^[44] with $n\text{Bu}_4\text{NN}_3$ to give the diazido diborane $[B(\text{hpp})(N_3)]_2$ **9** (see Lewis structure in Scheme 2).^[45] Since test experiments showed that it has an exceptionally high temperature stability, we thought of evaluating the chemistry of this electron-rich diazido diborane(**4**). Here we focus on its reaction with alkynes, giving convenient, first access to bis-1,4-triazoles connected by a B–B bridge. We will show that the reaction tolerates Lewis-basic groups and also further alkynyl groups at the alkyne.



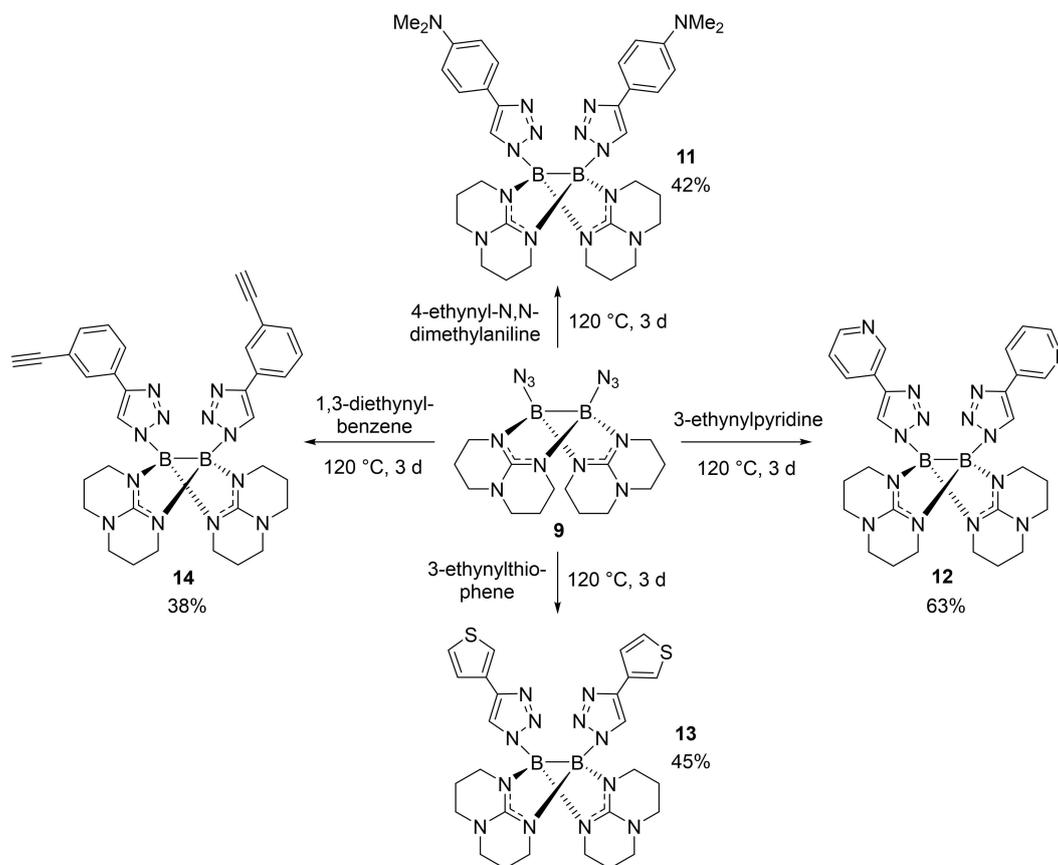
Scheme 2. Synthesis of the new triazole $B_2(hpp)_2(4\text{-phenyltriazolyl})_2$ (**10**).

Results and Discussion

In our first experiments, we tried to react diazido-diborane **9** with an equimolar amount of phenylacetylene in an organic solvent. In one such experiment, the alkyne was added to a solution of the diborane in 1,2-dichlorobenzene, and the reaction mixture was stirred for three days at 120 °C before the solvent was removed under vacuo. Despite of the long reaction time and high temperature, the NMR spectra showed no sign of any reaction. The diazido-diborane remained stable even under these harsh conditions. A thermogravimetric analysis (TGA) of the solid compound showed no sign of decomposition until

approximately 150 °C (see Supporting Information). Next, we suspended the diborane in the pure alkyne and stirred the reaction mixture again for three days at 120 °C. After 6 h, the pale-yellow reaction mixture turned into a red solution, indicating conversion of the diazido-diborane. Indeed, the ^{11}B NMR spectrum of the product isolated after three days reaction time showed only one new signal at $\delta=0.51$ ppm. Excess alkyne was removed under vacuo at 80 °C and unidentified byproducts formed from the alkyne at high temperatures were removed by washing the residue four times with tetrahydrofuran, yielding eventually the pure, new bistriazole **10** in a yield of 40% (Scheme 2). These experiments showed that a high temperature and a large excess of the alkyne are required for successful cycloaddition reactions.

Motivated by these results, we repeated the cycloaddition under the same conditions with other alkynes, namely 4-ethynyl-*N,N*-dimethylaniline, 3-ethynylpyridine, 3-ethynylthiophene and 1,3-diethynylbenzene. All four reactions gave the respective bistriazoles **11**, **12**, **13** and **14** in isolated yields of 42%, 63%, 45% and 38%, respectively (Scheme 3). Their synthesis demonstrates the tolerance of the reaction to the introduction of Lewis-basic groups at the alkyne. Certainly, the tetra-coordinated, saturated boron atoms of the diazido-diborane **9** are responsible for this unusual functional group tolerance. The absence of Lewis-acidic boron and the stabilizing



Scheme 3. Synthesis of the new triazoles $B_2(hpp)_2(4\text{-dimethylanilinotriazolyl})_2$ (**11**), $B_2(hpp)_2(4\text{-pyridyltriazolyl})_2$ (**12**), $B_2(hpp)_2(4\text{-thiophenyltriazolyl})_2$ (**13**) and $B_2(hpp)_2(4\text{-ethynylbenzyltriazolyl})_2$ (**14**).

effect of the two bridging guanidinate (hpp) units at the $B_2(hpp)_2$ core of diazido-diborane **9** prohibit nucleophilic attack by a functional group of the alkyne. Furthermore, the reaction tolerates a second ethynyl group without any signs of oligomerisation (reaction to bistriazole **14**). It is worth mentioning that for the reaction of the diazido-diborane with 1-ethynyl-4-fluorobenzene, the NMR spectra also indicate successful cycloaddition. However, it was not possible to isolate the product in pure form from the reaction mixture.

Crystals of the compounds **10**, **12** and **13** were grown by layering a saturated CH_2Cl_2 solution with *n*-pentane. Figure 3 illustrates the solid-state structures; selected bond lengths are collected in Table 1. The B–B bond lengths in the three crystallized bistriazoles (1.713 and 1.714 Å) fall into a typical region for B–B single bonds, being significantly longer than the B=B double bond in diborene compounds.^[45–48] The lengths of the B–N bonds to the triazole rings (1.552 and 1.557 Å) are similar to previously reported B–N bonds to triazole groups (1.567 Å),^[36] and only slightly larger than the lengths of B–N bonds to the bridging hpp substituents. Moreover, all B–N bond lengths fall into a typical range for sp^3 hybridized boron atoms.^[49–52] The N–B–B angles, involving the N atoms of the triazole rings, measure slightly more than 120° , being significantly larger than the value of 109.4° expected for an sp^3 -hybridized boron.

Although there are three possible regioisomers of the bistriazole products (Figure 4), the crystals only consist of the 1,4-isomer **A**. Furthermore, the NMR spectra of the pure compounds, as well as the crude product obtained directly from the reaction mixture (before washing with tetrahydrofuran), displayed only signals of a single specific bistriazole product (Figure 5). To demonstrate the regioselectivity of these reactions, Figure 5 shows the 1H NMR spectra of phenylacetylene (black) and of the pure bistriazole **10** (red). It is noticeable, that the product spectrum shows only one signal for the C–H proton of the triazole ring at $\delta=7.05$ ppm, and three defined multiplet signals for the aromatic protons, at $\delta=7.66–7.64$, $7.29–7.26$ and $7.18–7.15$ ppm. Considering the significant structural differences between the three possible regioisomers, these results indicate that the cycloaddition is

Table 1. Selected bond lengths (in Å) and angles (in $^\circ$) for the synthesized diboranes with two triazole units (standard deviations in parenthesis).

Parameter	10	12	13
B–B	1.713(6)	1.714(3)	1.714(8)
B–N(hpp)	1.543(6)	1.539(3)	1.540(8)
B–N(triaz)	1.552(5)	1.557(3)	1.552(8)
N_1 (triaz)–B–B	122.8(3)	122.1(2)	125.2(5)
N_2 (triaz)–B–B	124.3(3)	121.3(2)	122.5(5)

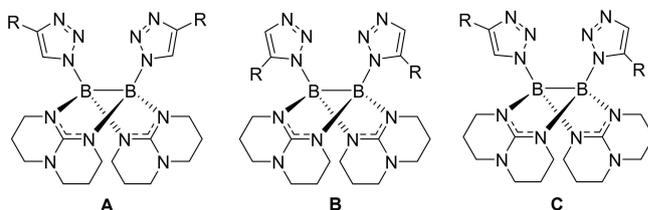


Figure 4. Illustration of the possible regioisomers A–C that could be formed in the dipolar cycloaddition reaction between diazido diborane **9** and a terminal alkyne RCCH. Only **A** is found in the experiments.

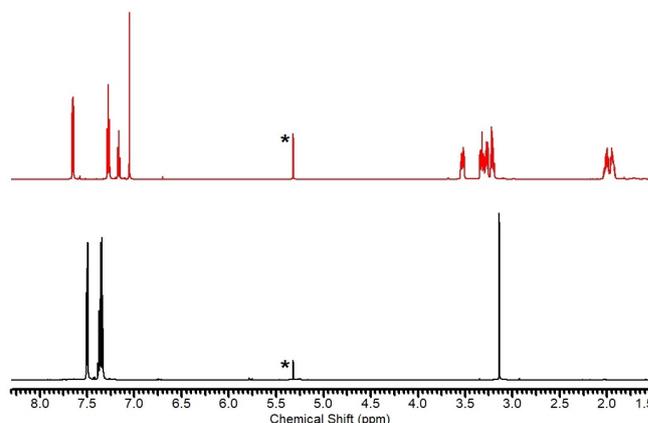


Figure 5. 1H NMR spectra (600 MHz) of phenylacetylene (black) and the bistriazole **10** (red) in CD_2Cl_2 solutions. Solvent signals are highlighted by asterisks.

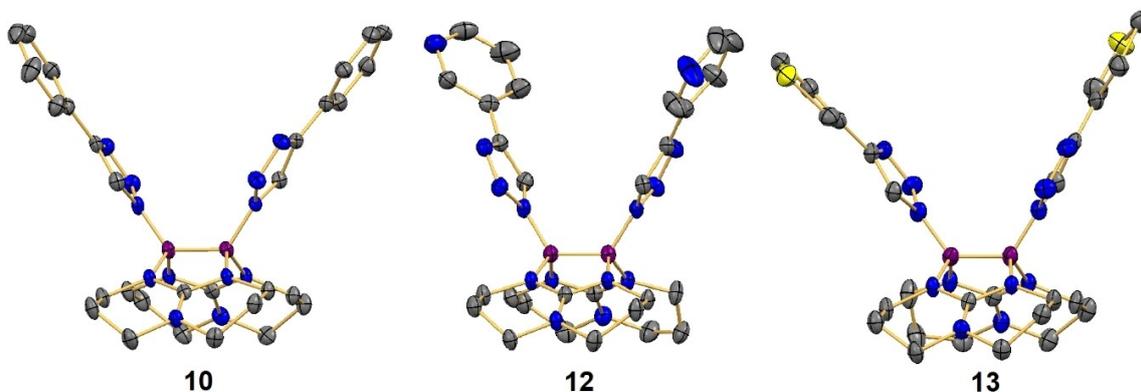


Figure 3. Illustration of the solid-state structures of **10**, **12** and **13**. Hydrogen atoms omitted. Displacement ellipsoids drawn at the 50% probability level. Colour code: B purple, C grey, N blue, S yellow.

highly regioselective. Probably, the steric demand of the hpp ligands prohibits the formation of the other two possible regioisomers **B** and **C** sketched in Figure 4.

To further evaluate the scope of the reactions and the possible steric constraints imposed by the presence of the hpp groups, we carried out experiments with the internal alkynes 1-phenyl-1-propyne and 1,2-diphenylethyne. The NMR spectra showed for both alkynes no sign of a reaction (Scheme 4). We conclude that the hpp substituents prohibit the formation of triazoles substituted in the 5-position.

Quantum-chemical calculations

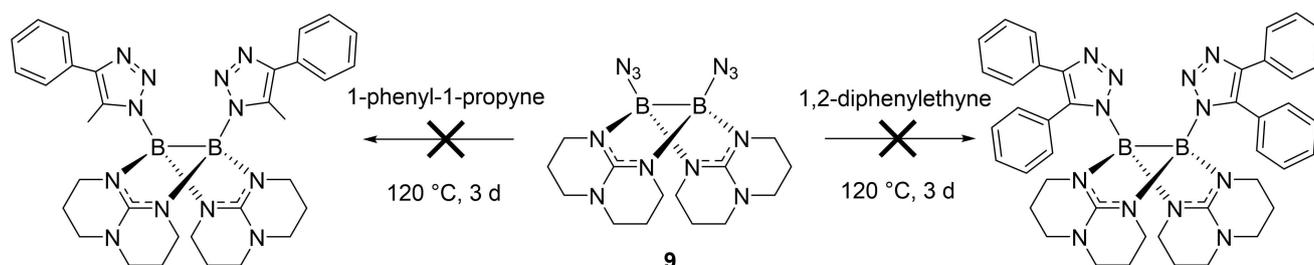
To complement our experimental results, some preliminary DFT calculations were carried out. In these calculations, we applied the B3LYP functional (with D3 corrections) in combination with the def2-TZVPP basis set.^[53–60] Table 2 compares the reaction Gibbs free energies ($\Delta_r G$) for the formation of the possible bistriazole products **A**, **B** and **C**, starting with the diazido-diborane **9** and the corresponding alkyne (see reaction equation in Scheme 5). Highly negative $\Delta_r G$ values were obtained for all examined alkynes, even for the internal ones. In consideration of the harsh conditions for a successful reaction, these results indicate a high activation energy for each cycloaddition. In Figure 6, the relative reaction Gibbs free energies $\Delta(\Delta_r G)$ are plotted, being defined as the differences between the reaction Gibbs free energies for reactions with the given alkyne (leading, in the case of terminal alkynes, to regioisomer **A**) and the $\Delta_r G$ value for the reaction of **9** with phenylacetylene to give **10**. One can see that reactions of electron-poor alkynes are more favored than those of electron-rich alkynes. Interestingly, the reaction between **9** and 1,2-diphenylethyne is

Table 2. Reaction Gibbs free energy changes ($\Delta_r G$ in kJ mol^{-1} at 273 K, 1 bar) for the bistriazole formation (regioisomers **A**, **B** and **C**) from the reaction between **9** and two equivalents of the given alkyne (B3LYP + D3/def2-TZVPP calculations).

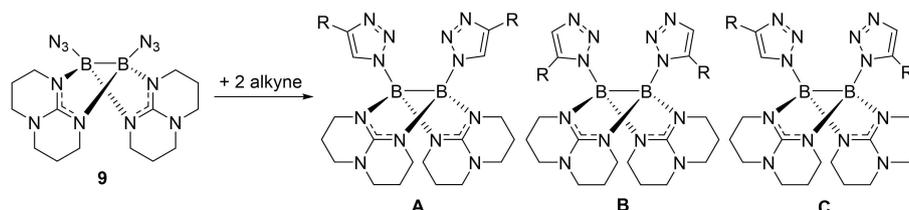
alkyne	regioisomer		
	A	B	C
phenylacetylene	−388.3	−397.8	−391.8
4-ethynyl-N,N-dimethylaniline	−375.8	−387.5	−384.9
1-ethynyl-4-fluorobenzene	−399.5	−402.1	−396.5
3-ethynylpyridine	−401.1	−405.2	−402.6
3-ethynylthiophene	−387.5	−399.2	−396.9
1,3-diethynylbenzene	−400.9	−400.8	−405.8
1-phenyl-1-propyne	−370.7 ^[a]	−375.4	−376.6
1,2-diphenylethyne	−	−460.1 ^[b]	−

[a] Phenyl group in 4-position of the triazole rings. [b] Only one regioisomer possible.

energetically especially favored (most negative $\Delta(\Delta_r G)$ value). Probably, the formation of an extended conjugated π -system is an additional factor here. Although the reactions exclusively lead to the 1,4-isomer **A**, the regioisomers **B** and **C** are energetically slightly favored. These results underline the high selectivity of the cycloadditions. They indicate that steric repulsion between the hpp substituents and the substituent in 5-position of the formed bistriazole ring in the transition state rather than in the product is responsible for the regioselectivity. Presumably, the reactions proceed in one step, like typical “Huisgen 1,3-dipolar cycloadditions” without catalyst. In this case, one expects a significant steric repulsion between the substituent at the alkyne and the hpp groups in the transition state leading to the 1,5-regioisomer. However, we abstained from calculations on the transition state.



Scheme 4. Hypothetical products of the reactions of the diazido-diborane **9** with the internal alkynes 1-phenyl-1-propyne and 1,2-diphenylethyne. The experiments show that these reactions do not occur.



Scheme 5. Reaction for the formation of the possible bistriazole products **A**, **B** and **C**, starting with the diazido-diborane **9** and the corresponding alkyne. The reaction Gibbs free energies ($\Delta_r G$) calculated for these reactions are collected in Table 2.

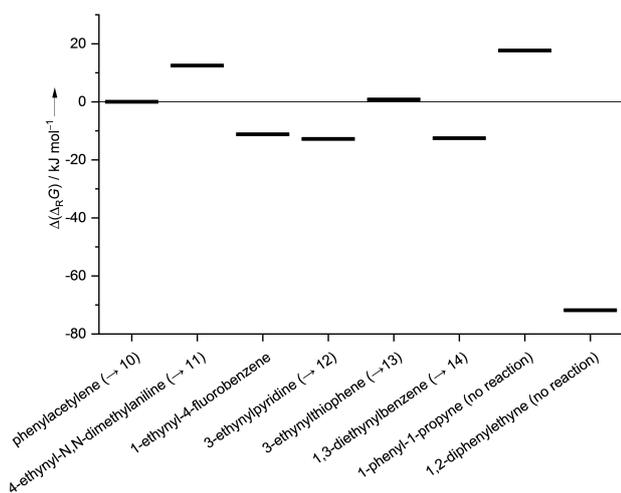


Figure 6. Plot of the calculated $\Delta(\Delta_rG)$ values (difference between the reaction Gibbs free energies for reaction between **9** and the given alkyne and the reaction Gibbs free energy for reaction of **9** with phenylacetylene to give **10**). For terminal alkynes, reaction to regioisomer **A** is considered. All Δ_rG values used for this plot are collected in Table 2.

Conclusions

The knowledge about the chemistry of diazido-diborane(4) compounds is scarce; only a few stable compounds are known up to date. The remarkable stability of $[B(hpp)(N_3)]_2$ (**9**), reported recently by our group,^[45] stands out and was used in this work to synthesize the first bistriazoles connected by a B–B bridge. At high temperatures (120 °C), terminal alkynes react with **9** in dipolar 1,3-cycloaddition reactions; the reactions are strictly regioselective, leading exclusively to the 1,4-substituted bistriazoles. Reactions with Lewis-basic groups and also additional alkynyl groups attached to the alkynes demonstrate the high functional-group tolerance of the reactions. The cycloaddition reactions reported in this work could be used to align two π -systems in close proximity to each other by an ethylene-like, but rigid, diborane linker.

Experimental Section

The synthetic details and analytical data for all compounds as well as the details of the quantum-chemical (DFT) calculations are included in the Supporting Information.

Deposition Number(s) 2169533 (**10**), 2169534 (**12**), and 2169535 (**13**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: azides · boron · cycloaddition · diborane · triazoles

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