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Boryl Azides in 1,3-Dipolar Cycloadditions

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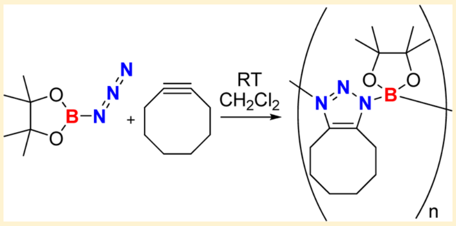
Ⓢ *Supporting Information*

ABSTRACT: The 1,3-dipolar cycloaddition reaction of boron azides with alkynes has been investigated experimentally and computationally. At room temperature $pinBN_3$ (pin = pinacolato) reacts with the strained triple bond of cyclooctyne with formation of an oligomeric boryl triazole. Alcoholysis of the oligomer yields the parent 4,5,6,7,8,9-hexahydro-2*H*-cyclooctatriazole, which could be characterized as a hydrate by X-ray crystallography. A computational analysis of the reaction of tri- and tetracoordinate boron azides R_2BN_3 (R = H, Me, pin, cat; cat = catecholato) and *I*Me·H_2BN_3 (*I*Me = 2,6-dimethylimidazole-2-ylidene) reveals significant differences in the reactivity depending on the coordination number: tricoordinate boron azides behave as type II 1,3-dipoles, while the tetracoordinate *I*Me·H_2BN_3 is an electron-rich 1,3-dipole (type I) that strongly prefers reactions with electron-poor alkynes.



■ INTRODUCTION

Huisgen's dipolar cycloaddition between azides and alkynes is an important reaction for the synthesis of [1,2,3]-triazoles,[1−3] and its copper-catalyzed version[4−7] is a prime example of "click chemistry".[8] Aureggi and Sedelmeier reported in 2007 the formation of tetrazoles from organoaluminum azides R_2AlN_3 (R = Me, Et) and nitriles.[9] This reaction has considerable scope, as a number of less reactive nitriles can be transformed under mild conditions and in the presence of a number of different functional groups. Aureggi described in a Ph.D. thesis that the related azidoborane 2-azido-1,3,2-benzodioxaborole ($catBN_3$, cat = catecholato) does not react with a small subset of reactive nitriles.[10] We had earlier been using $catBN_3$ for the generation of the corresponding borylnitrene by photochemical cleavage of the azide under cryogenic matrix isolation conditions and have subsequently studied the reactivity of borylnitrenes.[11−17] We also had probed the feasibility of 1,3-dipolar cycloadditions of $catBN_3$ and found the negative report by Aureggi to be in agreement with our own investigations of the 1,3-dipolar cycloaddition of $catBN_3$ with nitriles and alkynes.[18]

Merling et al. showed in 2012 that the adduct between an N-heterocyclic carbene (NHC, *I*Pr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene) and azidoborane *I*Pr·H_2BN_3 (Chart 1) can undergo 1,3-dipolar cycloadditions with electron-poor alkynes, nitriles, and alkenes at elevated temperatures (80−180 °C).[19] The authors thus suggested that *I*Pr·H_2BN_3 behaves as an electron-rich 1,3-dipole: the interaction between its HOMO and the LUMO of the dipolarophile is most important.[19] Similarly, Yao et al. showed that tetracoordinate azidoboranes, lithium tetraazidoborate $LiB(N_3)_4$, and Lewis base stabilized triazidoboranes, such as py·$B(N_3)_3$, undergo cycloadditions with nitriles (Chart 1).[20] A successful 1,3-dipolar cycloaddition of the tricoordinate azidoborane Cy_2BN_3 (Cy = cyclohexyl) and certain alkynes was reported by Melen and Stephan last year (Chart 1).[21] Reaction at room temperature occurs only with electron-poor alkynes that bear oxygen-containing substituents. Melen and Stephan invoked a Cy_2BN_3 dimer with two tetracoordinate boron centers,[21,22] even though there was no evidence for the existence of such a dimer in solution.

The successful reactions between the electron-poor Cy_2BN_3 and electron-poor alkynes prompted us to reinvestigate the 1,3-dipolar cycloaddition using a less electrophilic boryl azide, 2-azido-4,4,5,5-tetramethyl-1,3,2-dioxaborole (**1**; $pinBN_3$, pin = pinacolato),[12] as this should be a more suitable 1,3-dipole for an electron-poor alkyne. We[16] and others[23−25] have previously observed a difference in the reactivity between the electronically related catB and pinB groups, and we wondered if such a difference may also be observed in 1,3-dipolar cycloadditions. We here summarize our investigations of the 1,3-dipolar cycloaddition between $pinBN_3$ and alkynes of different electronic structures and give a computational analysis of boryl azide and NHC−boryl azide reactivity in cycloadditions.

■ RESULTS AND DISCUSSION

Experimental Investigations. Attempts to react $pinBN_3$ with alkynes RCCR′ (R = R′ = Ph, $SiMe_3$) at room temperature did not produce any triazole according to NMR and MS analyses, in agreement with previous observations using $catBN_3$ and Cy_2BN_3.[18,21] In contrast to Cy_2BN_3, investigated by Melen and Stephan,[21] $pinBN_3$ did not react at room temperature with electron-poor acetylenes that carry a Lewis basic center, such as acetylenedicarboxylic acid dimethyl ester (R = R′ = CO_2CH_3). Likewise, no product was observed with propargyl alcohol (R = CH_2OH, R′ = H) at room temperature.

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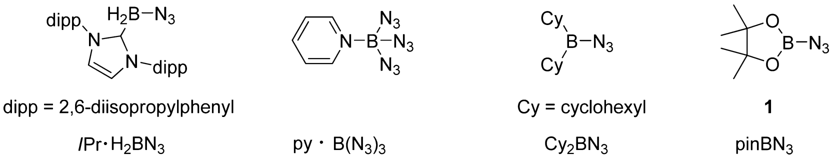
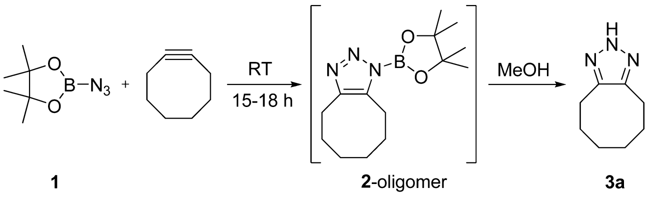
Chart 1. Azidoboranes Considered Previously (IPr·H_2BN_3, py·$B(N_3)_3$, and Cy_2BN_3) and in the Present Work (pinBN$_3$)



As the limited thermal stability of **1** makes successful dipolar cycloadditions unlikely at elevated temperatures, we investigated the reaction with cyclooctyne. The strain of the triple bond in this cyclic system is well-known to enhance the rate of azide cycloaddition reactions considerably.[26,27] Indeed, the reaction of **1** with cyclooctyne proceeded readily with formation of a colorless insoluble solid in a number of solvents (hexane, dichloromethane, THF, acetonitrile). The solid is a polymer of the expected cycloadduct **2** (Scheme 1) that could not be isolated in monomeric form.

Scheme 1. 1,3-Dipolar Cycloaddition between 1 and Cyclooctyne



Electron impact mass spectrometry (EI-MS) showed only the $M^{\bullet+}$ signal of monomer **2** as the highest mass signal, but at much higher temperatures than expected on the basis of the structure and molecular weight of **2**. This indicates that the polymer decomposed into monomers **2** on the probe tip of the MS instrument. The solid-state ^{13}C-CPMAS-NMR of the oligomer shows the presence of the alkoxy carbon atoms (83.0 ppm) of the pin group and the triazole carbon atoms (142.2 ppm) in the expected spectral region, in addition to the alkyl carbon atoms between 22.5 and 32.3 ppm (see the Supporting Information, Figure S6). A signal in the solid-state $^{11}B\{^1H\}$ NMR spectrum (see the Supporting Information, Figure S7) at 2.5 ppm ($h_{1/2}$ = 376 Hz) that essentially lacks quadrupolar coupling is a strong indication for the presence of a tetracoordinate boron center. The conceivable signal of a tricoordinate boron center as the terminus of an oligomeric chain is expected to show a broad and complex spectral shape in the solid state due to quadrupolar coupling. It would not have been possible to resolve such a signal due to the small amount of such centers in the presence of a larger amount of tetracoordinated boron atoms.

Running the reaction in toluene did not result in precipitation of an insoluble polymer. On the other hand, the polymer obtained in the solvents mentioned above did not dissolve in toluene, indicating that the polymer length depends on the solvent used in the reaction. The product obtained in toluene was studied by NMR spectroscopy. In addition to unreacted azide **1** (25.2 ppm), two signals at 21.9 ppm ($h_{1/2}$ = 93.4 Hz) and 7.0 ppm ($h_{1/2}$ = 156.8 Hz) were observed in a ratio of 1:3 (see Figure 1).

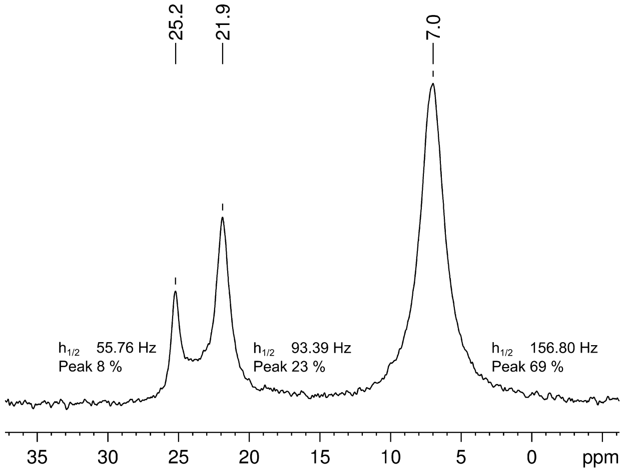
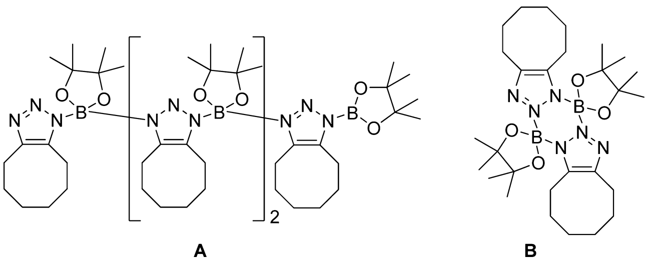


Figure 1. $^{11}B\{^1H\}$ NMR spectrum of the product obtained from reaction between **1** and cyclooctyne in toluene solution.

This excludes the formation of a cyclic oligomer and indicates a linear oligomer consisting of four monomeric units. The oligomerization of 1-triazolylboranes is known to form either oligomers/polymers of undefined structure or, in the case of boron carrying small organyl groups (Me, Et), cyclic tetramers with 1,3-connectivity according to X-ray crystallography.[28,29] Thus, formation of an oligomer of **2** with 1,3-connectivity (**A** in Chart 2) is in line with previous reports; a conceivable 1,2-product is unlikely, as the latter would be prone to formation of the dimer **B** (see Chart 2) with a six-membered B_2N_4 ring. Such dimers are well-known to form from 1-pyrazolylboranes.[30]

Chart 2. (Left) Suggested Structure of Oligomer A Obtained from Reaction of 1 with Cyclooctyne in Toluene and (Right) Alternative Dimeric Structure B, Not Observed



While the oligomer did not crystallize, crystals of a partially hydrolyzed monomer could be obtained: the triazole unit coordinates to the anhydride pinBOBpin (Figure 2). The formation of such a complex with the electron-rich boron center of pinBOBpin demonstrates the strong Lewis basisicity of the triazolyl group.

Treatment of the oligomers/polymers with the nucleophilic solvent MeOH resulted in alcoholysis and gradual dissolution. After Kugelrohr distillation of the crude product, a colorless oil was obtained that crystallized slowly. The product could be unequivocally identified as the 2*H* isomer **3a** by ^{13}C NMR spectroscopy (Scheme 1). The yield of **3a** ranges between 68

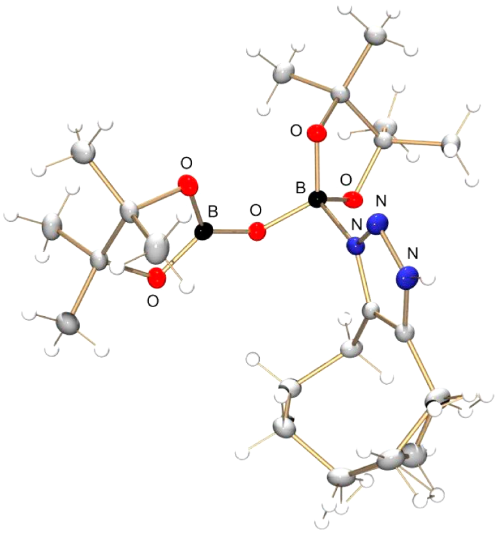


Figure 2. Structure of the pinBOBpin−triazole complex in the solid state as determined by X-ray crystallography.

and 80% and seems to be independent of the length of the oligomer. In contrast to a previous report,[31] **3a** was not oxidized by air upon storage for an extended period of time. Although the preference of the 2*H* over the 1*H* tautomer is well-known for triazoles, we investigated the cycloaddition reaction of cyclooctyne and azidotrimethylsilane or adamantyl azide (AdN_3) for comparison. As expected, $(CH_3)_3SiN_3$ produced **3a** after hydrolysis, while AdN_3 yielded the 1-adamantyl derivative.

Recrystallization from H_2O/MeOH gave crystals of **3a** that were suitable for X-ray single-crystal analysis. The molecule crystallized with one molecule of water in the asymmetric unit in the space group $P2_1/n$. The cyclooctyl group is disordered. A hydrogen-bonding network between water and triazole molecules results in ribbons (Figure 3).

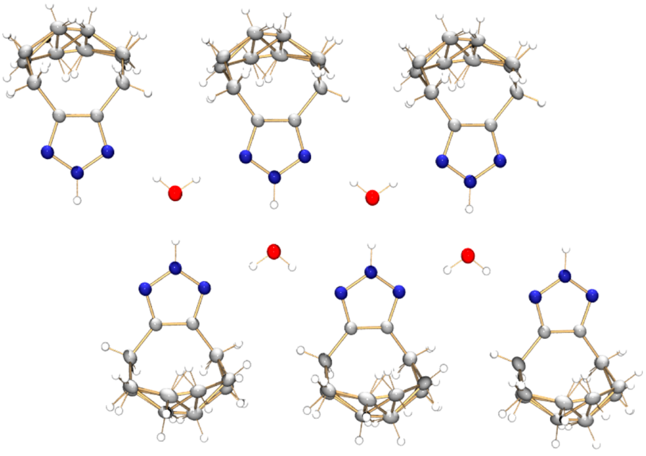


Figure 3. Ribbons of water-interconnected triazole **3a** in the solid state as determined by X-ray crystallography.

Computational Investigation of Boryl Azide Cycloadditions. We investigated the 1,3-dipolar cycloaddition of a number of boryl azides that differ in electronic structure: the parent H_2BN_3 and its NHC adduct *I*Me·H_2BN_3 as a model for *I*Pr·H_2BN_3 used in the experiments by Merling et al.,[19] $(CH_3)_2BN_3$ as a model for Cy_2BN_3 employed by Melen and Stephan,[21] and $catBN_3$ and $pinBN_3$, which each carry stronger electron donors than does $(CH_3)_2BN_3$. As alkynes, parent ethyne, propyne as a model for a terminal alkyne, electron-poor 3-butyn-2-one, and electron-rich aminoethyne as a representative electron-rich ynamine were chosen. For comparison, we also included the well-understood phenyl azide (PhN_3), for which Ess and Houk[27] provided computational results at the B3LYP/6-31G* level of theory. To allow direct comparison with the data of these authors, we also employed their level of theory, as it is appropriate for determining the trend of substituent effects (Table 1). To validate the computational approach, we computed the barrier for exo addition of phenyl azide to norbornene that was measured by Huisgen and coworkers.[32,33] The electronic barrier at the B3LYP/6-31G* level is 14.7 kcal mol^{-1}. This increases to 15.4 kcal mol^{-1} after inclusion of zero-point vibrational energy correction, while the activation enthalpy at 298.15 K is computed to be 15.1 kcal mol^{-1}, in very good agreement with the experimental value of 15.2 ± 0.3 kcal mol^{-1}.[33] The inclusion of solvent effects using CCl_4 in the computation ($\Delta H^{\ddagger}$ = 15.1 kcal mol^{-1}) does not change the agreement appreciably; hence, the data reported in Table 1 refer to gas-phase values.

In agreement with experiment, the formation of the 1,4-disubstituted [1,2,3]triazole isomer is in most cases kinetically slightly more favorable for the electron-poor alkyne (R = $COCH_3$) and that of the 1,5-disubstituted [1,2,3]triazole isomer is more favorable for the electron-rich (R = NH_2) alkyne (HCCR).[33] Notable exceptions are the ynamine reactions of H_2BN_3 and Me_2BN_3, which show a slight preference of 0.2−0.3 kcal mol^{-1} for formation of the 1,4-isomer over the 1,5-isomer (see Table 1).

The data for phenyl azide indicate that introduction of a methyl group increases the barrier in comparison to ethyne and that both electron-donating and electron-accepting substituents decrease the barrier with respect to the terminal alkyne. This trend is in qualitative agreement with the reactivity of PhN_3 established from experiments with alkenes and alkynes.[33,34] Phenyl azide was thus classified as an ambiphilic dipole of type II by Sustmann.[35]

A very similar trend is obtained for tricoordinate boron azides: in comparison to the terminal alkyne, the barriers drop for reactions with the electron-rich and the electron-poor alkyne. The computed barrier heights for the reactions of the various alkynes with boron azides R_2BN_3 are within 2 kcal mol^{-1} of those of PhN_3. This suggests that the tricoordinate boron azides should show reactivity very similar to that of phenyl azide. The lack of reactivity observed by us and others[21] can thus be ascribed to the rather high barriers that necessitate elevated temperatures, a requirement that is not compatible with the thermal instability of these boryl azides.[21]

The barriers toward electron-rich and electron-poor alkynes qualify the boron azides as type II dipoles. The computed frontier molecular orbital (FMO) energies (B3LYP/6-31G* data) reveal that the energy gap is smaller (5.8 eV) between the LUMO of the azide H_2BN_3 and the HOMO of ethyne than between the HOMO of the azide and the LUMO of ethyne (9.7 eV). Hence, the azide H_2BN_3 acts as an electron-poor 1,3-dipole. As expected, the LUMO (azide)−HOMO (alkyne) gap becomes smaller for the electron rich ynamine (3.99 eV), while the HOMO (azide)−LUMO (alkyne) gap becomes larger (9.9 eV). For the electron-poor alkyne, the LUMO (azide)−HOMO (alkyne) energy difference is still the smaller (6.2 eV) one, but the HOMO (azide)−LUMO (alkyne) gap is of

Table 1. Lowest Barriers ($E^‡$, in kcal mol^{-1}) for 1,3-Dipolar Cycloadditions between Azides and Alkynes and Distortion and Interaction Energies Computed at the B3LYP/6-31G* Level of Theory[a]

azide	R in HCCR	$\Delta E^‡$	$\Delta E_d(\text{az})^‡$	$\Delta E_d(\text{alk})^‡$	$\Delta E_d^{‡}$ [b]	$\Delta E_i^{‡}$ [c]
H_2BN_3	H	13.8	16.9	5.4	22.3	−8.5
	CH_3	16.0[d]	17.9	7.0	24.9	−8.9
	$(CO)CH_3$	13.5	14.9	6.1	21.0	−7.5
	NH_2	14.4[e]	17.6	7.3	24.9	−10.5
*I*Me·H_2BN_3	H	18.4	19.3	6.9	26.2	−7.8
	CH_3	21.3	20.1	8.6	28.7	−7.4
	$(CO)CH_3$	11.7	16.6	8.8	25.4	−13.7
	NH_2	17.2	9.2	9.1	18.3	−1.1
Me_2BN_3	H	15.6	17.5	6.1	23.6	−8.0
	CH_3	18.0	18.5	7.8	26.3	−8.3
	$(CO)CH_3$	14.8	15.4	6.9	22.3	−7.5
	NH_2	16.9[f]	18.4	8.7	27.1	−10.2
catBN_3	H	16.9	19.6	6.3	25.9	−9.0
	CH_3	19.3[g]	20.8	8.2	29.0	−9.7
	$(CO)CH_3$	16.7	17.7	7.1	24.8	−8.1
	NH_2	16.1	22.1	6.8	28.9	−12.8
pinBN_3	H	17.2	19.4	6.3	25.7	−8.5
	CH_3	19.9[h]	20.5	8.1	28.6	−8.7
	$(CO)CH_3$	16.0	16.9	7.0	23.9	−7.9
	NH_2	16.4	21.2	7.7	28.9	−12.5
	cyclooctyne	9.1	14.7	1.6	16.3	−7.2
PhN_3	H	16.2	18.1	6.0	24.1	−7.9
	CH_3	18.7[i]	19.3	7.9	27.2	−8.6
	$(CO)CH_3$	15.9	16.7	6.9	23.6	−7.7
	NH_2	14.7	19.9	5.5	25.4	−10.7

[a] The barriers refer to formation of 1,4-isomers for R = CH_3, $(CO)CH_3$ and of 1,5-isomers for R = NH_2 and are lowest for these isomers, unless noted otherwise. For a definition of distortion and interaction energies, see Figure 4. [b] $\Delta E_d^‡ = \Delta E_d(\text{az})^‡ + \Delta E_d(\text{alk})^‡$. [c] $\Delta E_i^‡ = \Delta E^‡ - \Delta E_d^‡$. [d] Formation of 1,5-isomer: 15.9 kcal mol^{-1}. [e] Formation of 1,4-isomer: 14.1 kcal mol^{-1}. [f] Formation of 1,4-isomer: 16.0 kcal mol^{-1}. [g] Formation of 1,4-isomer: 18.5 kcal mol^{-1}. [h] Formation of 1,5-isomer: 19.2 kcal mol^{-1}. [i] Formation of 1,5-isomer: 18.1 kcal mol^{-1}.

the same order (6.6 eV). The observed reactivity trends may also be analyzed by the distortion model of 1,3-dipolar cycloadditions introduced by Houk and co-workers.[27,36−38] Ess and Houk concluded that the reactivity is controlled by the energy $\Delta E_d^‡$ required to distort reactants to their geometries in the transition states rather than by frontier molecular orbital (FMO) interactions.[36,37] The dissection of the barrier heights in the spirit of Ess and Houk[36,37] (see Figure 4 for an explanation) shows that the distortion energies $\Delta E_d^‡$ are smaller for the carbonyl derivative, while the absolute interaction energies $\Delta E_i^‡$ are larger for the electron-rich ynamine.

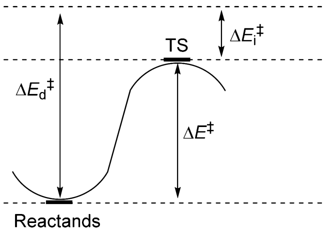


Figure 4. Definitions of overall energy barrier $\Delta E^‡$, distortion energy of reactands $\Delta E_d^‡$, and interaction energy $\Delta E_i^‡$.

The situation changes upon coordination of an N-heterocyclic carbene to the boron center. As the good σ-donating NHC saturates the vacant p atomic orbital at boron, the boryl azide becomes more electron rich. The smallest FMO gap in the *I*Me·H_2BN_3−ethyne system is between the HOMO of the azide and the LUMO of the alkyne. Hence, *I*Me·H_2BN_3 is an electron-rich 1,3-dipole toward the prototypical alkyne, in contrast to the case for H_2BN_3. Decreasing the electron density in the alkyne decreases the HOMO (azide)−LUMO (alkyne) gap and accordingly also the reaction barrier by almost 10 kcal mol^{-1}. In addition, a lower barrier in comparison to propyne is obtained for the ynamine, but the decrease is much less pronounced (4.1 kcal mol^{-1}). In contrast to the tricoordinated boron azides, the distortion energy is larger for the reaction with the electron-poor alkyne, but at the same time also the interaction energy is much stronger. The conclusion reached from this computational analysis is that the NHC-stabilized boron azide behaves primarily as an electron-rich 1,3-dipole (type I in Sustmann's[35] terminology), in full agreement with the experiments and conclusions of Merling et al.[19] As is known in carbene chemistry, where the prototypical electrophilic carbene CCl_2 can show nucleophilic behavior toward sufficiently electron poor alkenes,[39] NHC-stabilized boron azides should have lower barriers for reactions with very electron rich alkynes such as ynamines.

■ CONCLUSIONS

The oxygen-substituted azidoborane pinBN_3 does not readily react with oxygen atoms carrying electron-poor alkynes at room temperature. Only the strained cyclooctyne undergoes a smooth reaction with pinBN_3, yielding an oligomeric product that can be cleaved into the expected triazole derivative by alcoholysis. The computational investigation identifies the tricoordinate boron azides as ambiphilic 1,3-dipoles but shows that coordination by an N-heterocyclic carbene turns H_2BN_3 into an electron-rich 1,3-dipole. The reason for the different reactivities of Cy_2BN_3 and $pinBN_3$ toward 3-butyne-2-one at room temperature most likely is not due to inherently different reaction barriers of the azides. The difference computed using the Me_2BN_3 model is only 1.2 kcal mol^{-1}, and this likely becomes smaller in the experimentally employed Cy_2BN_3 for steric reasons. The computational results for *I*Me·H_2BN_3 show that coordination strongly reduces the barrier for the reaction with an electron-poor alkyne. As an alternative to a dimeric form of Cy_2BN_3,[21] for which there is no experimental indication, a coordination of the carbonyl oxygen atom of the alkyne to the azide may be invoked.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

All experiments were performed under an inert atmosphere using argon or nitrogen as protective gas. Dry THF, Et_2O, toluene, DCM, and hexanes were taken from a MBraun SPS-800 solvent purification system, dry acetonitrile was purchased, and dry pentane was obtained by treating pentane with molecular sieves (4 Å). All commercially available chemicals were purchased and used as received.

NMR spectra were referenced to residual solvent signals (^1H, ^{13}C)[40] or to an external standard (^{11}B, $BF_3·OEt_2$) and measured at room temperature. The solid-state spectra were measured using TMS and $BF_3·OEt_2$ as primary and ^{13}C glycine (COOH, 176.03 ppm) and ^{11}B $NaBH_4$ (−42.06 ppm) as secondary references. The full width at half-maximum, $h_{1/2}$, was determined by a Lorentzian fit with TopSpin 2.1 (Bruker) and is given in hertz (Hz). TopSpin 2.1 was also used for the deconvolution of ^{11}B spectra. Compound **1** ($pinBN_3$)[12] and cyclooctyne[41] were synthesized as described previously.

Synthesis of 4,5,6,7,8,9-Hexahydro-2*H*-cyclooctatriazole (3a). Ca. 1.5 mmol of $pinBN_3$ (**1**) was dissolved in 10 mL of solvent (hexanes, toluene, dichloromethane, THF, and acetonitrile), and the solution was charged with 1.1 equiv of cyclooctyne. The colorless to slightly yellow solutions were stirred for 15−18 h at room temperature, forming a colorless precipitate within 2−3 h (except for toluene). Then the mixture was quenched by the addition of 20 mL of methanol and again stirred until the mixture cleared up (3−4 h). The solvent was evaporated, and the crude reaction oil was distilled via Kugelrohr distillation (1×10^{-3} mbar/120 °C). The product was obtained as a colorless, slowly crystallizing oil. The reaction yields were 77% (266 mg of **1**, 184 mg of **3a**, hexanes), 71% (275 mg of **1**, 212 mg of **3a**, toluene), 68% (241 mg of **1**, 148 mg of **3a**, dichloromethane), 71% (260 mg of **1**, 181 mg of **3a**, THF), and 71% (253 mg of **1**, 160 mg of **3a**, ACN).

Following the instructions above, the reaction of trimethylsilyl azide with cyclooctyne was performed, yielding a colorless oil after methanolysis and distillation whose spectral data are consistent with the aforementioned product.

^1H NMR (400 MHz, C_6D_6): δ 1.21 (m, 4 H), 1.51 (m, 4 H), 2.70 (m, 4 H); ^1H NMR ($CDCl_3$) 1.48 (m, 4 H), 1.77 (m, 4 H), 2.88 (m, 4 H). ^1H NMR (MeOH-d_4): δ 1.57 (m, 4 H), 1.88 (m, 4 H), 3.02 (m, 4 H). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 23.8, 25.6, 28.8, 145.3. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.6, 25.6, 28.5, 144.7. $^{13}C\{^1H\}$ NMR (MeOH-d_4): δ 22.6, 26.1, 27.7, 140.8. EI-MS (quadrupole, 70 eV, m/z): 151 [M], 136, 122, 108, 101, 95, 59. FAB-MS (quadrupole, glycerin, m/z): 152 [M + H]. ESI-MS (FTICR, MeOH, 1 μg mg^{-1}): exact mass for $C_8H_{14}N_3$ 152.118224, found 152.118289. IR (KBr, cm^{-1}) 553 w, 633 w, 677 w, 883 w, 1121 m, 1196 w, 1280 w, 1385 w, 1459 w, 1484 w, 1617 w, 2601 br s, 2856 m, 2935 s, 3424 br m.

Coordination Polymer of the Triazole (2-oligomer). A solution of 250 mg (1.58 mmol) of $pinBN_3$ (**1**) in 10 mL of dioxane (absolute) at room temperature was charged with 176 mg (1.63 mmol) of cyclooctyne. In an overnight reaction, a colorless precipitate formed. The supernatant was discarded, and the solid was washed twice with fresh dioxane (absolute). The solid was dried and transferred into a glovebox (140 mg, 34 wt %).

$^{11}B\{^1H\}$ NMR (64 MHz, MAS, Rf 4 kHz): δ 2.5 ($h_{1/2}$ 370 Hz), $CaCO_3$ added. $^{13}C\{^1H\}$ NMR (50 MHz, MAS HP-Dec, Rf 10 kHz): δ 22.5, 23.6, 25.6, 27.7, 30.3, 32.3, 83.0, 142.2. EI-MS (quadrupole, 70 eV, m/z): 277 [M(monomer)], 152 [M(triazole + H)].

The reaction in toluene was run at room temperature with 250 mg (1.48 mmol) of $pinBN_3$ (**1**) in 15 mL of toluene (absolute) with addition of 176 mg (1.63 mmol) of cyclooctyne. After 20 h a NMR sample was taken out of the reaction mixture.

$^{11}B\{^1H\}$ NMR (80 MHz, C_6D_6): δ 7.0 ($h_{1/2}$ 156.80 Hz, 69%), 21.9 ($h_{1/2}$ 93.39 Hz, 23%), 25.2 ($h_{1/2}$ 55.76 Hz, 8%). $^{11}B\{^1H\}$ NMR (80 MHz, zgbsig): δ 7.0, 21.9, 25.3.

Synthesis of 4,5,6,7,8,9-Hexahydro-1-adamantylcyclooctatriazole. At room temperature, 120 mg (0.68 mmol) of 1-adamantylazide was dissolved in 10 mL of acetonitrile (absolute) and the colorless solution was charged with 107 mg (0.99 mmol) of cyclooctyne. The solution was stirred for 60 h, and then the solvent was evaporated. A colorless solid was obtained (195 mg, 100%).

^1H NMR (400 MHz, $CDCl_3$): δ 1.42 (m, 4 H), 1.71 (m, 2 H), 1.78 (m, 8 H), 2.24 (m, 3 H), 2.34 (m, 6 H), 2.80 (m, 2 H), 2.97 (m, 2 H). $^{13}C\{^1H\}$ NMR (101 MHz): δ 23.4, 25.0, 25.7, 26.1, 29.2, 29.8, 29.9, 36.3, 42.5, 61.5, 132.5, 147.0. FAB-MS (quadrupole, glycerin, m/z): 286 [M], 185, 93. ESI-MS (FTICR, MeOH, 1 μg mg^{-1}): exact mass for $C_{18}H_{28}N_3$ 286.227774, found 286.227574. IR (KBr, cm^{-1}): 818 w, 884 w, 947 w, 1000 w, 1024 m, 1101 m, 1193 w, 1246 m, 1261 w, 1307 w, 1356 w, 1370 w, 1454 m, 1475 w, 1554 w, 1660 w, 2851 s, 2923 s, 3443 br. Mp: 125−127 °C.

Computations. The computations were performed using Becke's[42] three-parameter hybrid functional and the Lee−Yang−Parr[43] correlation functional as implemented[44] in the Gaussian 09[45] program using the 6-31G* basis set. Geometries were fully relaxed using Gaussian's default convergence criteria, and the harmonic vibrational frequencies were subsequently computed analytically, providing thermodynamic parameters using the standard approximations and equations.

ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data for the pinBOBpin−triazole complex and **3a**, figures giving NMR and MS spectra of synthesized compounds, a table giving energy data at the B3LYP-D3/6-31G* level, tables giving Cartesian coordinates of computed structures, and text giving the full ref 45. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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