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Main-Group Chemistry

Straightforward Formation of Borirenes from Boroles and Dialkynes

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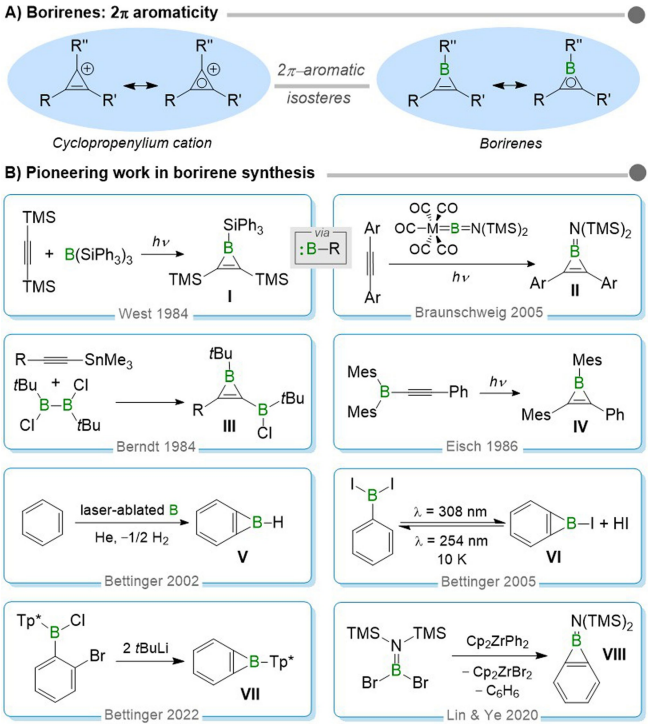
Abstract: We report a selective one-step synthesis of perarylated borirenes by reaction of antiaromatic boroles with 1,4-diarylbuta-1,3-diynes. Mechanistic studies, both experimental and computational, reveal key intermediates, including boranorbornadiene and 7-borabicyclo[4.1.0]heptadiene species, which are all in equilibrium with each other, ultimately leading to borirene formation by migration of the boranediyl bridge from the cyclohexadiene ring to the remaining exocyclic alkyne residue.

Introduction

Despite being the smallest possible carbocycle, the cyclopropenium cation, $[C_3H_3]^+$, is significantly more stable than its protonated cyclopropene analogue, owing to its 2π aromaticity.[1] Since the isolation of a stable $[C_3Ph_3]^+$ salt and the observation of the parent $[C_3H_3]^+$ cation by Breslow in 1958 and 1967, respectively,[2] cyclopropenium salts have moved from laboratory curiosity to becoming versatile organic reagents, catalysts, polyelectrolytes or ionic liquids.[3]

In recent years, boron-containing isosteres of π-conjugated carbocycles have attracted increasing attention, as the replacement of an endocyclic carbon atom by an electron-deficient boron atom renders these boracycles far more reactive than their all-carbon counterparts.[4] As isoelectronic and isosteric to the cyclopropenium cation, boracyclopropenes, also known as borirenes, are the smallest aromatic boron heterocycle exhibiting 2π-aromatic character (Scheme 1A).[1b,5] In 1983, van der Kerk and co-workers observed the first borirene from the [2+1] cycloaddition of di-*tert*-butylacetylene and methylborylene, generated in situ from the two-electron reduction of $MeBBr_2$.[6] This cycloaddition strategy was later adapted by West and Braunschweig, using borylenes generated in situ by photolysis from triphenylsilylborylene[7] and metal borylene complexes, re-



Scheme 1. Aromaticity and established approaches for boriene synthesis. TMS = $SiMe_3$, Mes = 2,4,6-trimethylphenyl = mesityl; Tp* = 2,6-bis(tri*iso*propylphenyl)phenyl, Cp = cyclopentadienyl.

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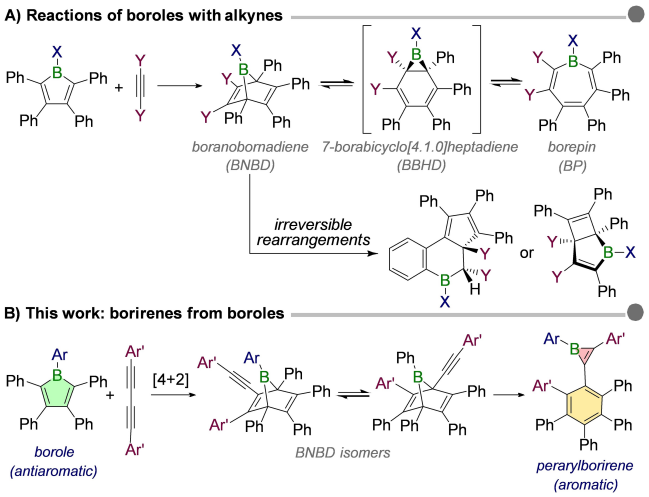
spectively (Scheme 1B).[8] Other known synthetic routes to borirenes involve the reaction of trimethylstannylalkynes and 1,2-di-*tert*-butyl-1,2-dichlorodiborane(4) via Me_3SnCl elimination and subsequent rearrangement (Scheme 1B),[9] or the photoisomerization of diaryl(arylethynyl)boranes (Scheme 1B, **IV**).[10] The parent borirene, which can be generated from ethylene and laser-ablated boron atoms, has only been detected spectroscopically.[11]

By far the most work in this field has been carried out by the group of Bettinger, starting with the landmark gas-phase generation of the elusive parent benzoborirene **V** from benzene and laser-ablated boron atoms.[12] This was followed by the reversible photochemical generation of benzo-(iodo)borirene (**VI**) from diiodoborylbenzene in an argon matrix at 10 K,[13] and most recently, the first structural characterization of a kinetically stabilized terphenylbenzoborirene (**VII**).[14] Lin and Ye reported an alternative strategy for the synthesis of a benzoborirene via a zirconocene benzyne intermediate (**VIII**).[15] Borirenes exhibit a variety of reactivity patterns, including Lewis adduct formation at the electron-deficient boron center, ring opening by polar 1,2-addition of H–E bonds to the endocyclic B–C bond, and ring expansion reactions by insertion of unsaturated small molecules into the endocyclic B–C bond-(s).[16,17] However, their chemistry remains relatively underexplored as the known synthetic routes to stable borirenes are limited by a rather small range of mostly symmetrical substitution patterns.

In contrast, the synthesis and chemistry of boroles and their annulated derivatives, which are isoelectronic to the cyclopentadienylium cation and thus 4π-antiaromatic,[18] has greatly advanced in the last decade. The high reactivity of boroles arises from their highly Lewis-acidic boron center and antiaromatic character, making them particularly prone to the insertion of multiple bonds, heterocumulenes, nitrenes or phosphinidenes into one endocyclic B–C bond to generate larger, more stable aromatic heterocycles.[4c,d,19] With internal alkynes boroles react like activated cyclopentadienes, undergoing Diels-Alder reactions, which yield boranorbornadienes (BNBD, Scheme 2A).[20] At room temperature, the latter are in equilibrium with their seven-membered 6π-aromatic borepin (BP) isomers via bicyclic 7-borabicyclo[4.1.0]heptadiene (BBHD) intermediates, as confirmed both experimentally and computationally.[21,22]

Depending on the electronic nature of the alkyne substituents and the sterics/electronics of the boron substituent, the boranorbornadienes may also undergo complex, irreversible rearrangements to fused bicyclic or tricyclic boron heterocycles through sigmatropic rearrangements, *retro*-Diels-Alder reactions, and intramolecular *ortho*-C–H activation of a peripheral phenyl substituent.[20c,22,23]

Given the versatile rearrangement reactivity of BNBDs, we wondered whether their bridging BX boranediyl moiety could be transferred to an exocyclic unsaturation, a process which would be driven by the aromatization of the BNBD cyclohexa-2,5-diene ring to a benzene ring. Herein, we show that alkynyl-substituted BNBDs, straightforwardly obtained from the reactions of boroles with 1,3-dialkynes, undergo a series of complex rearrangements, ultimately leading to



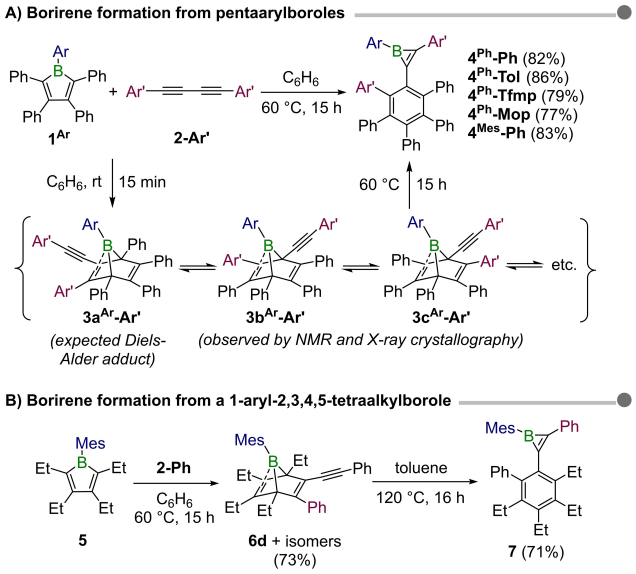
Scheme 2. Reactions of boroles with alkynes.

otherwise inaccessible perarylated borirenes (Scheme 2B). Experimental and computational investigations highlight the mobility of the borole-derived BX moiety, which easily migrates around the BNBD cyclohexadiene ring, before shifting to the exocyclic alkyne functionality, thereby generating two unsymmetrically substituted aromatic rings – a benzene and a borirene – in a single step.

Results and Discussion

The addition of 1 equiv. of diphenylbuta-1,3-diyne (**2-Ph**) to a solution of 1,2,3,4,5-pentaphenylborole ($\mathbf{1^{Ph}}$) in benzene led to a color change from deep blue to light yellow within the first 15 minutes of the reaction. The ^{11}B NMR spectrum of the reaction mixture showed a new resonance at −1.5 ppm, similar to that of known perarylated boranorbornadienes (BNBDs, $\delta_{11B} = -5$ to −2 ppm).[22,23] The resonance is unusually upfield-shifted for an sp^2-hybridized boron nucleus owing to the π interaction with an alkene double bond of the cyclohexa-2,5-diene ring. Examination of the ^1H NMR spectrum suggested a mixture of three BNBD isomers ($\mathbf{3^{Ph}}$-**Ph**) in a 44:42:14 ratio as determined by ^1H NMR spectroscopy (Scheme 3A). Mixtures of BNBD isomers ($\mathbf{3^{Ar}}$-**Ar′**) were also obtained when reacting a range of *para*-substituted 1,4-diarylbuta-1,3-diynes **2-Ar′** (Ar′ = Tol (*p*-tolyl), Tfmp (*p*-trifluoromethylohenyl), Mop (*p*-methoxyphenyl)) with $\mathbf{1^{Ph}}$, or **2-Ph** with the more sterically encumbered borole $\mathbf{1^{Mes}}$.

From the reaction of $\mathbf{1^{Ph}}$ with **2-Tol**, colorless crystals suitable for single-crystal X-ray diffraction (SC-XRD) analysis were obtained, revealing a 93:7 mixture of two cocrystallized BNBD isomers, $\mathbf{3b^{Ph}}$-**Tol** and $\mathbf{3c^{Ph}}$-**Tol**, overlapping in all but the disordered Ph/Tol substituents at C4 and C8 (Figure 1). Neither of the two isomers is the one expected from the Diels-Alder reaction between one of the alkyne moieties of **2-Tol** with the diene backbone of $\mathbf{1^{Ph}}$, compound $\mathbf{3a^{Ph}}$-**Tol**, in which the boron atom is π-stabilized by the 1-alkynyl-2-(*p*-tolyl)-ethylene moiety (Scheme 3).



Scheme 3. Reactions of boroles with diarylbuta-1,3-diynes. Ar = Ph, Mes; Ar′ = Ph, Tol (*p*-tolyl), Tfmp (*p*-trifluoromethylphenyl), Mop (*p*-methoxyphenyl).

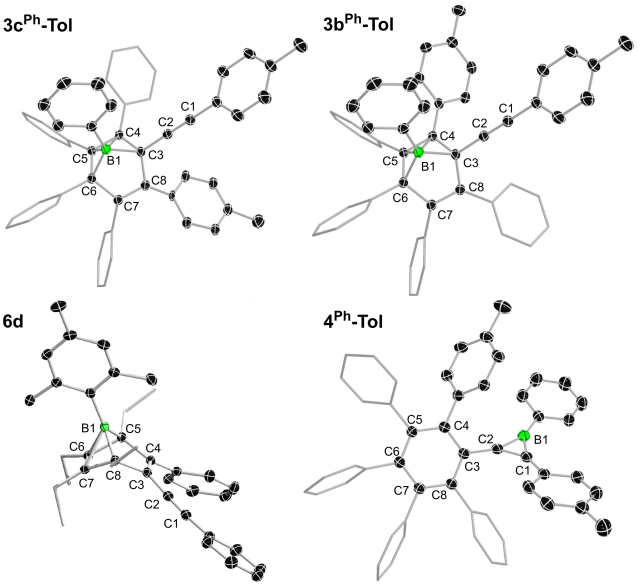


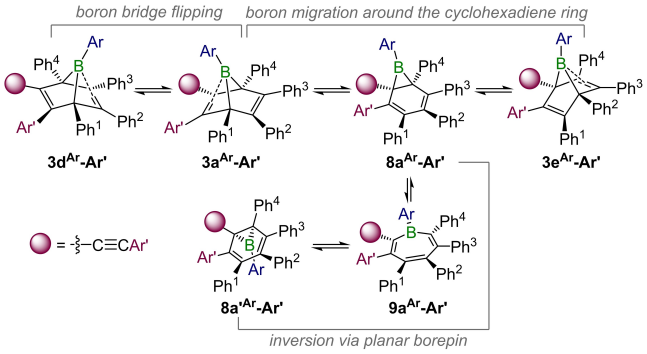
Figure 1. Crystallographically determined solid-state structures of **3b^{Ph}-Tol** and **3c^{Ph}-Tol** (superimposed in the asymmetric unit in a 93 : 7 ratio), **6d** and **4^{Ph}-Tol**. Thermal displacement ellipsoids at 50% probability. Ellipsoids of peripheral phenyl groups and hydrogen atoms omitted for clarity.

Instead, the alkynyl substituent in both **3b^{Ph}-Tol** and **3c^{Ph}-Tol** is positioned at the bridgehead carbon of the cyclohexa-2,5-diene ring, while the boron atom is inclined either away from or towards the adjacent *p*-tolyl substituent, respectively. The π interaction between the C4=C5 double bond and the empty p orbital at B1 is reflected in the elongation of the C4=C5 double bond (1.3907(17) Å) compared to the C7=C8 double bond (1.3406(18) Å), as well as the relatively short B1–C3 and B1–C4 distances (1.837(2) and 1.8446 (19) Å), consistent with other BNBD structures.[22,23]

Heating of solutions of in situ-generated **3^{Ar}-Ar′** (Ar = Ph, Ar′ = Ph, Tol, Tfmp, Mop; Ar = Mes, Ar′ = Ph) isomers at 60 °C for 15 h led to a color change to dark yellow in all cases (Scheme 3A). Monitoring of the reactions by NMR spectroscopy (see ESI for details) showed the gradual consumption of all BNBD isomers and quantitative formation of a single boron-containing product with an ^{11}B NMR resonance around 33–36 ppm, typical for arylborirenes.[8c,23] Work-up yielded the corresponding borirenes **4^{Ar}-Ar′** as colorless solids in good to excellent yields (77–86%). HMBC NMR spectra revealed two low-field quaternary carbon resonances in the 165–173 ppm range, corresponding to the boracyclopropene ring, which were not detectable in the ^{13}C{^{1}H} NMR spectra owing to broadening by the neighboring quadrupolar boron nucleus. The rearrangement of a BNBD to a benzene ring by migration of the bridging BAr fragment to an exocyclic position has been observed by Erker, whose B(C$_6$F$_5$)$_2$-substituted BNBD derivative underwent thermal rearrangement to an unsymmetrical diborane-(4) by insertion of the bridging BPh moiety into the exocyclic C$_{BNBD}$–B(C$_6$F$_5$)$_2$ bond.[24] Similarly, much older work by Eisch had shown that quaternization of the BNBD boron bridge with RLi leads to migration of the anionic BRR′ (R, R′ = Me, Ph) fragment to an exocyclic position or even insertion into an exocyclic C$_{BNBD}$–B$_{aryl}$ bond (R = R′ = Me) and aromatization of the former cyclohexadiene to a benzene ring.[20b]

The solid-state structures of **4^{Ph}-Ph**, **4^{Ph}-Tol** and **4^{Mes}-Ph** obtained by SC-XRD analysis confirmed the formation of the perarylated borirenes (see Figure 1 and Figures S48–S50 in the SI). The bond lengths within the C$_2$B rings (avg. C1–B1 1.47, B1–C2 1.48, C1=C2 1.36 Å) are similar to those observed in other perarylated borirenes.[8b,10] and reflect the delocalization of the two π electron over the entire ring.[5] The Ph/Mes substituent at B1 tends to coplanarity with the borirene ring (Ar∠B1 ca. 10–17°), whereas the large perarylphenyl substituent at C2 is significantly rotated out of the borirene plane (Ar∠C2 ca. 55–63°), while the rotation of the Ph/Tol substituent at C1 depends on the sterics of the B1 substituent (**4^{Ph}-Ph/Tol** 11–22°, **4^{Mes}-Ph** 42°).

In contrast, the reaction of the tetraethylborole **5** with **2-Ph** at 60 °C yielded a 60 : 32 : 8 mixture of three BNBD isomers (δ_{11B} = –2.9 ppm), which could not be separated (Scheme 3B). It is noteworthy that upon heating the BNBD isomer mixture to 80 °C for a prolonged time, no conversion to the corresponding borirene was observed. Instead, the initial BNBD isomer ratio changed, highlighting the fact that all these isomers are in exchange with each other. Based on previous experimental and computational work,[21,22] we propose three main pathways for BNBD isomerization: i) flipping of the boron bridge coordination from one alkene moiety to the other, ii) migration of the boron bridge via 7-borabicyclo[4.1.0]heptadiene (BBHD) intermediates **8^{Ar}-Ar′**, and iii) inversion of the BBHDs via borepin intermediates **9^{Ar}-Ar′** (Scheme 4). The BNBD isomer **6d**, which results from the Diels-Alder adduct between **5** and **2-Ph** and flipping of the boron bridge to the C$_4$Et$_4$ side of the



Scheme 4. Proposed mechanisms of BNBD isomerization.

cyclohexadiene ring, was characterized by SC-XRD analysis (Figure 1). The main structural difference to the perarylated derivative **3b/c^{Ph}-Tol** derivative (see above) is the weaker boron-alkene interaction, which is visible in longer B1–C6/C7 distances (1.8548(16), 1.8650(16) Å) and a shorter C6=C7 double bond (1.3828(14) Å). Upon heating to 120 °C, however, a slow but selective rearrangement to the borirene **7** was observed (δ_{11B} = 33.9 ppm).

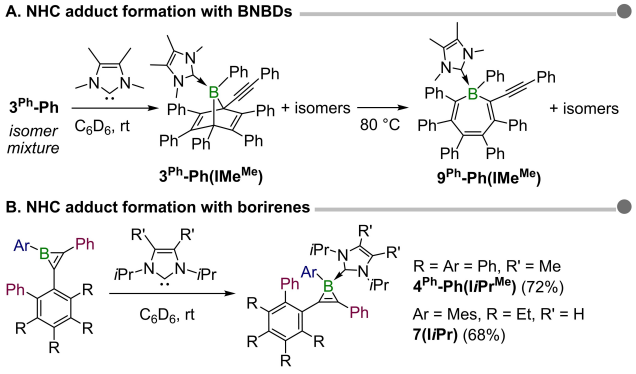
Previous studies have shown that some of the intermediates of borole-alkyne reactions can be trapped by adduct formation with a small N-heterocyclic carbene (NHC).[22,25] The room-temperature addition of IMe^{Me} (1,3,4,5-tetramethylimidazol-2-ylidene) to the BNBD isomer mixture **3^{Ph}-Ph** resulted in adduct formation at the boron atom (Scheme 5A). The ^{11}B NMR spectrum of this **3^{Ph}-Ph(IMe^{Me})** isomer mixture shows two major resonances at 14.6 and 11.6 ppm in a 10:1 ratio, in agreement with known NHC-BNBD adducts (δ_{11B} = 10.2–11.5 ppm).[22,25] The unexpected downfield shift compared to **3^{Ph}-Ph** (δ_{11B} = −1.5 ppm), despite the higher coordination number at boron, is owed to the loss of the alkene-boron π interaction and the bridging position of the boron atom. Heating of this mixture at 80 °C yielded a broad upfield-shifted ^{11}B NMR resonance at –11.8 with a shoulder at ca. −12.6 ppm, corresponding to the NHC adducts of the borepin isomers **9^{Ph}-Ph(IMe^{Me})**.[22,25] It is noteworthy that further heating of **9^{Ph}-Ph(IMe^{Me})** at higher temperatures (up to 120 °C) did not lead to rearrangement to the NHC-borirene adduct, **4^{Ph}-Ph(IMe^{Me})**, as NHC coordination seemingly makes the rearrangement to the borepin irreversible.

Given some difficulties in crystallizing **7** cleanly, presumably due to the multiple flexible ethyl groups and the rotation of the borirenyl substituent, the boron center was quaternized by adduct formation with the N-heterocyclic carbene (NHC) adduct I*i*Pr (1,3-di*iso*propylimidazol-2-ylidene) to yield **7(I*i*Pr)** in good yield (68 %) as a pale yellow crystalline solid (Scheme 5). Similarly, **4^{Ph}-Ph** underwent facile adduct formation with I*i*Pr^{Me} (1,3-di*iso*propyl-4,5-dimethylimidazol-2-ylidene) to yield **4^{Ph}-Ph(I*i*Pr^{Me})**. Both **7(I*i*Pr)** and **4^{Ph}-Ph(I*i*Pr^{Me})** display typically upfield-shifted ^{11}B NMR resonances at −21.2 and −19.7 ppm, respectively.[26] Their solid-state structures also confirm the adduct formation (Figure 2), reflected in a significant shortening of the C1=C2 bond (both 1.318(2) Å) and lengthening of the B1–C1 and B1–C2 bonds (1.588(2)-1.621(3) Å) in comparison to **4^{Ph}-Ph**.

In order to elucidate the mechanism of these reactions and rationalize the experimental observation of multiple **3^{Ar}-Ar′** isomers leading selectively to the borirene **4^{Ar}-Ar′**, DFT calculations were carried on the reaction of **1^{Ph}** and **2-Tol** in benzene, as using Ar′ ≠ Ph enables the exploration of BNBD isomerization pathways. Geometry optimizations of reagents, intermediates, products and transition states were carried out at the B3LYP-D3(BJ)/def2-SVP level of theory and Gibbs free energies computed at the B3LYP-D3(BJ)/def2-TZVPP-COSMO(benzene) level of theory at 298 K (see details in the SI).

Figure 3 presents the two major reaction routes with their corresponding intermediates and products (see Figure S53 in the Supporting Information for a comprehensive overview of all explored pathways, including those leading to the reversible formation of borepin species). 3D representations of all transition states involved in these two reaction routes are shown in Figure S54 in the SI.

The reaction begins with a Diels-Alder adduct formation between one alkyne moiety of **2-Tol** and the diene backbone of **1^{Ph}**, yielding the BNBD **3a^{Ph}-Tol** via the transition state **TS1** ($\Delta G_1^{\ddagger}$ = 19.2 kcal mol^{-1}). This step is exergonic (ΔG_1 = −13.2 kcal mol^{-1}) and achievable at room temperature, as observed experimentally. This is followed by the formation of the higher-energy BBHD intermediates **8a^{Ph}-Tol** and **8b^{Ph}-Tol**, in which the borirane ring is adjacent to the



Scheme 5. Quaternization of BNBDs and borirenes with small NHCs.

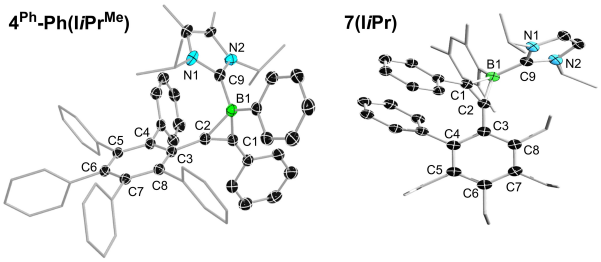


Figure 2. Crystallographically determined solid-state structures of **4^{Ph}-Ph(I*i*Pr^{Me})** and **7(I*i*Pr)**. Thermal displacement ellipsoids at 50 % probability. Ellipsoids of peripheral phenyl groups and hydrogen atoms omitted for clarity.

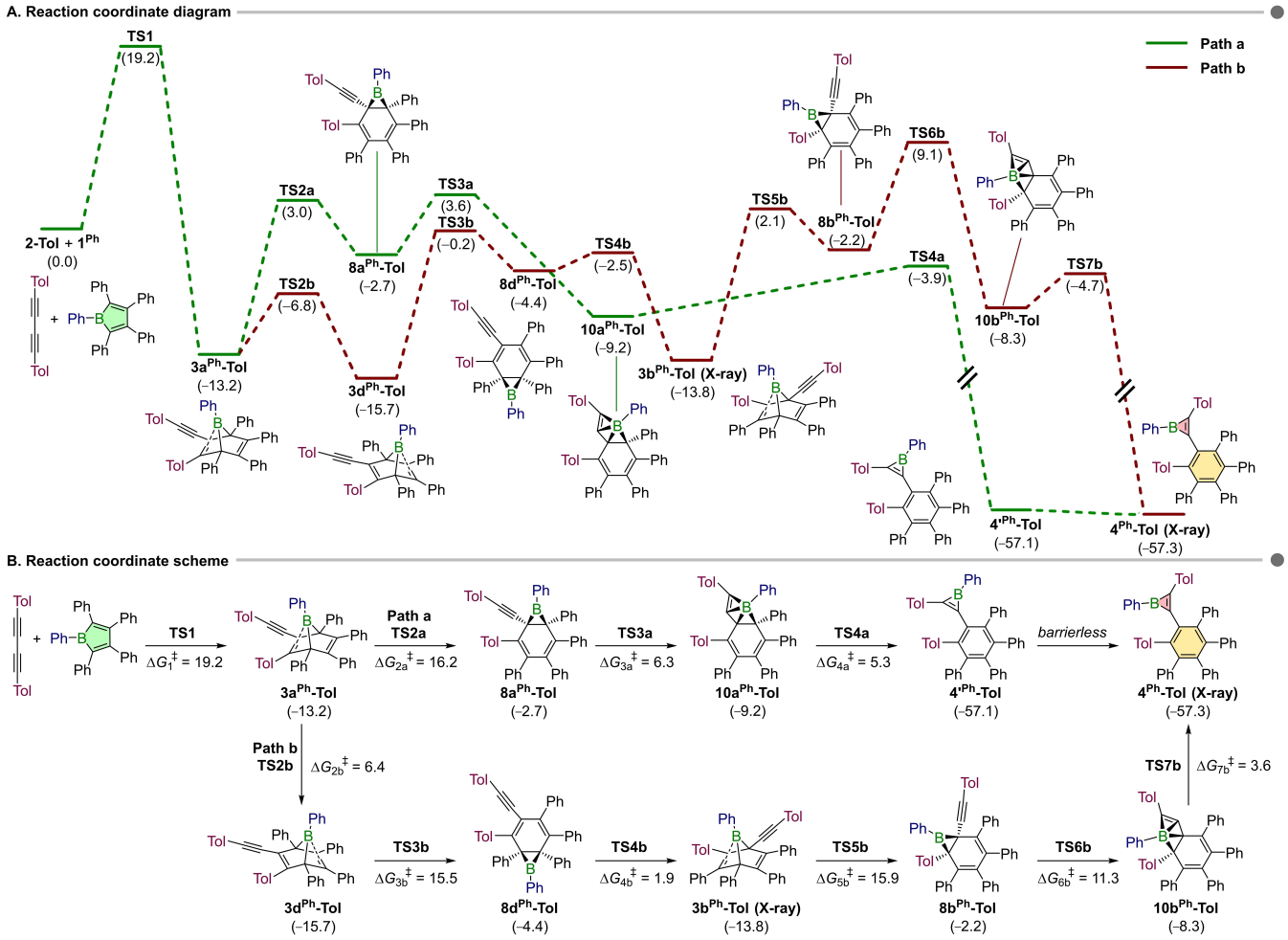


Figure 3. Computed mechanism of the primary reaction pathways for the formation of the borirene **4^{Ph}-Tol** from **1^{Ph}** and **2-Tol** in benzene at rt. Calculations were performed at the B3LYP-D3(BJ)/def2-TZVPP-COSMO(benzene)//B3LYP-D3(BJ)/def2-SVP level of theory. **(A)** Reaction coordinate diagram with Gibbs free energies (kcal mol^{-1}) for reagents, intermediates, transition states, and products given in parentheses. **(B)** Schematic representation of the reaction pathways, with activation free energies indicated below the corresponding reaction arrows.

alkynyl substituent, primed for BPh migration to the alkyne. **8a^{Ph}-Tol** is formed directly in an endergonic step ($\Delta G_{2a} = +10.5$ kcal mol^{-1}) from **3a^{Ph}-Tol** via **TS2a**, with a barrier of $\Delta G_{2a}^{\ddagger} = 16.2$ kcal mol^{-1}. The formation of **8b^{Ph}-Tol** from **3a^{Ph}-Tol**, however, requires several intermediate rearrangements.

First, facile flipping of the coordination of the boron bridge from one alkene moiety to the other via **TS2b** ($\Delta G_{2b}^{\ddagger} = 6.4$ kcal mol^{-1}) generates the slightly more stable BNBD isomer **3d^{Ph}-Tol** ($\Delta G_{2b} = -2.5$ kcal mol^{-1}). This is followed by boron migration around the cyclohexadiene ring via the higher-energy BBHD intermediate **8d^{Ph}-Tol** ($\Delta G_{3b}^{\ddagger} = 15.5$ kcal mol^{-1}; $\Delta G_{3b} = +11.3$ kcal mol^{-1}) to generate the BNBD isomer **3b^{Ph}-Tol** (identified experimentally by SC-XRD analysis; $\Delta G_{4b}^{\ddagger} = 1.9$ kcal mol^{-1}; $\Delta G_{4b} = -9.4$ kcal mol^{-1}), which then isomerizes to the desired BBHD intermediate **8b^{Ph}-Tol**. All these processes are achievable at room temperature and reversible, the steps with the highest barriers being the BNBD-to-BBHD rearrangements. From **8a^{Ph}-Tol** and **8b^{Ph}-Tol**, the phenylboranediyl moiety migrates from the cyclohexadiene ring to the exocyclic alkyne residue, first forming the BC_4 clusters **10a^{Ph}-Tol** and **10b^{Ph}-Tol**, respectively. These steps are mildly exergonic, with $\Delta G_{3a} = -6.5$ and $\Delta G_{6b} = -6.1$ kcal mol^{-1}, respectively, and feature low activation barriers of 6.3 (via **TS3a**) and 11.3 kcal mol^{-1} (via **TS6b**), respectively. Additionally, they are reversible, with $\Delta G^{\ddagger}$ values of +12.8 and +17.4 kcal mol^{-1}, respectively, for the backward reaction **10a/b^{Ph}-Tol→8a/b^{Ph}-Tol**. For both pathways, the final formation of the borirene rotamers **4'^{Ph}-Tol** and **4^{Ph}-Tol**, the latter being identified experimentally by SC-XRD analysis, proceeds via **TS4a** and **TS7b**, respectively, with very low activation barriers ($\Delta G_{4a}^{\ddagger} = 5.3$ kcal mol^{-1}, $\Delta G_{7b}^{\ddagger} = 3.6$ kcal mol^{-1}) and is irreversible. The rotamers **4'^{Ph}-Tol** and **4^{Ph}-Tol** interconvert without a barrier through rotation of the borirene substituent. Overall, the formation of **4'^{Ph}-Tol** and **4^{Ph}-Tol** from **1^{Ph}** and **2-Tol** is highly exergonic with $\Delta G_{reac} \approx -57$ kcal mol^{-1}. It is noteworthy that the 60 °C required to achieve conversion to the borirene end product is owed to the fact that, at room temperature, the various BBHD intermediates **8^{Ph}-Tol** isomerize spontaneously ($\Delta G_{8-9}^{\ddagger} = 1$ to 2 kcal mol^{-1}) to their much more stable borepin counterparts **9^{Ph}-Tol** ($\Delta G = -18$ to –21 kcal mol^{-1}), the reverse reactions being facilitated by heating ($\Delta G_{9-8}^{\ddagger} =$

17 to 23 kcal mol^{-1}; see Figure S53 in the Supporting Information).

The addition of an NHC to the initial mixture of BNBDs, **3^{Ph}-Ph**, is expected to stabilize all intermediates and raise all energy barriers, ultimately rendering the formation of the NHC-borepin adducts **9^{Ph}-Ph(IMe^{Me})** irreversible, as the barriers of the reverse rearrangement to the NHC-BBHD adducts **8^{Ph}-Ph(IMe^{Me})** become prohibitively high.

Conclusion

In summary, we have developed a highly efficient and versatile method for synthesizing perarylated borirenes with up to three different aryl substituents from simple borole and 1,3-dialkyne starting materials, enabling access to a broader range of substitution patterns than previously possible. Our mechanistic investigation, supported by both experimental and computational insights, revealed the involvement of complex equilibria between boranorbornadiene (BNBD) and 7-borabicyclo[4.1.0]heptadiene (BBHD) intermediates in borirene formation. Ultimately, the reaction is driven by the simultaneous formation of two aromatic (hetero)cycles, a fully substituted benzene and a borirene, both highly unsymmetrical, from the antiaromatic borole starting material via non-aromatic cyclohexadiene-containing BNBD and BBHD intermediates. Since terminal and alkylated alkynes are known to undergo similar reactions with boroles than diarylalkynes,[21,24,25,27] further work may focus on terminal and (di)alkylated 1,3-dialkynes to broaden the range of accessible borirene substituents. This study expands the synthetic scope of boron-containing heterocycles, opening up possibilities for further studies on borirene reactivity and on the formation of otherwise inaccessible, highly substituted benzenes from boroles.

Supporting Information

All synthetic procedures, analytical data, X-ray crystallographic,[28] and computational details are available in the supplementary material of this article. The authors have cited additional references within the Supporting Information.[29–42]

Acknowledgements

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Conflict of Interest

No conflicts of interest to declare.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Borirenes · Boroles · 1,3-diynes · Boron Chemistry · Cycloaddition reaction

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Research Article

Main-Group Chemistry

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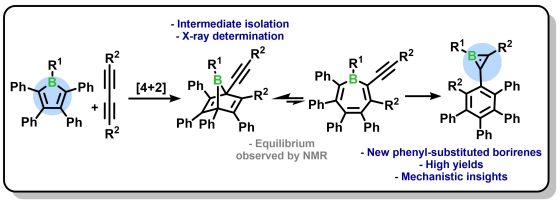
Straightforward Formation of Borirenes from Boroles and Dialkynes



The synthesis of unsymmetrical perarylated aromatic borirenes through a straightforward reaction between 1,3-diynes and boroles is reported. The study encompasses substrate scope exploration, X-ray studies and computational analysis. This work represents an illustration of the use of simplified reactions for the construction of three-membered systems containing boron.