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Article

# Divergent Reactivity of Perfluoropentaphenylborole with Alkynes[§]

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The reactions of perfluoropentaphenylborole (**1**) with the symmetrical internal alkynes RCCR (R = $C_6F_5$, $C_6H_5$, $CH_2CH_3$) have been explored. For R = $C_6F_5$, a slow reaction occurs via a Diels–Alder pathway established for the non-fluorinated system to give the new borane perfluoroheptaphenylborepin **2**. The new perfluoroarylborane **2** and its pyridine adduct **2-py** were characterized crystallographically. In contrast, the reaction of **1** with diphenylacetylene is dominated by a reaction path in which the borole electrophilically attacks the alkyne, triggering a 1,2 phenyl migration and borole ring expansion to deliver the boracyclohexadiene **3** as the major product. Minor products in this reaction were identified as diphenyl-substituted borepins resulting from the Diels–Alder reaction channel. Finally, 3-hexyne reacts with **1** via the Diels–Alder pathway, but the kinetic products are not the expected diethyl borepins but rather one of the initial Diels–Alder adducts formed prior to ring-opening to the seven-membered borepin ring. This intermediate was fully characterized and provides concrete evidence for the pericyclic reaction sequence proposed by Eisch for the reaction of pentaphenylborole with diphenylacetylene.

## Introduction

Materials containing $\pi$-conjugated boron heterocycles at their core exhibit potentially exploitable photophysical, redox, and anion-binding properties.[1–13] However, although interest in applications has recently arisen, these heterocycles have been the subject of investigation for decades[14–19] because of their isoelectronic relationship to hydrocarbons of theoretical significance and their relevance to concepts of aromaticity.[20] Thus, five-membered borole rings **I** are antiaromatic $4\pi$ rings that are isoelectronic to the fleetingly stable cyclopentadienyl $[C_5R_5]^+$ cations, while the neutral, aromatic $6\pi$ borepin systems **II** are related to the tropylium cation.[21,22] The aromaticity of **II**[23] contributes to the stability of the unsubstituted parent,[24] but the unsubstituted $C_4H_5B$ borole **I** is not isolable. Typically, more substituted derivatives of both heterocycles are required to bolster stability. In the case of **I**, substituted[14,16,25,26] or ring-annulated[27–29] derivatives are

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required to prevent Diels–Alder dimerization pathways, while for **II**, photochemical reactions that extrude "BR" and substituted benzenes are a principle reactivity mode[30] disfavored by substitution on the ring.

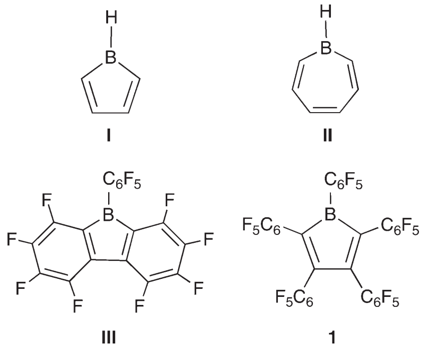
In terms of Lewis acidity, boroles are typically more Lewis acidic than their borepin analogues due to their antiaromaticity. In particular, the Lewis acid strength of perfluoroaryl boranes has been augmented in this way. For example, the quintessential perfluoroaryl borane $B(C_6F_5)_3$, a strong, protically stable organometallic Lewis acid,[31–34] is a slightly weaker Lewis acid than the perfluorinated 9-phenyl-9-borafluorene derivative **III**,[35,36] which has at its core an antiaromatic five-membered borole ring. While steric effects and relief of ring strain may also play a role in this Lewis acid strength enhancement of **III** over $B(C_6F_5)_3$, undoubtedly the disruption of antiaromaticity is also a significant driver behind the increased Lewis acidity of **III**. Thus, both antiaromaticity and perfluorination enhance the Lewis acid strength of boron-containing compounds.[37–39]

In accordance with this assertion, the recently prepared perfluorinated pentaphenylborole, **1**,[40] was found to be a powerful Lewis acid in comparison to $B(C_6F_5)_3$ and its unfluorinated analogue.[14,25] For example, in a competition for the weak Lewis base $CH_3CN$, the adduct of compound **1** was exclusively formed, leaving $B(C_6F_5)_3$ completely free of coordination despite its propensity to form a strong adduct with $CH_3CN$.[41] We have thus begun to explore the reactivity of **1**, and given the propensity of the unfluorinated pentaphenylborole to undergo Diels–Alder reactions with alkynes,[30] herein we report on the reactivity of **1** with three symmetrically substituted alkynes, RCCR (R = $C_6F_5$, $C_6H_5$, $CH_2CH_3$), with varying electronic properties. These studies reveal competing pathways for the reactivity of **1** with alkyne substrates involving conventional Diels–Alder reactivity or electrophilic attack by the potently Lewis acidic boron center.

## Results and Discussion

Perfluoropentaphenylborole, **1**, reacts slowly with electron-poor dienophile $C_6F_5CCC_6F_5$[42] at 110 °C in toluene over the course of a week to form a new product, identified as the perfluorinated heptaphenylborepin **2** (Scheme 1). Eisch has detailed the "paradigm of pericyclic reactions"[30] that characterize the reaction of the unfluorinated pentaphenylborepin with diphenylacetylene to form heptaphenylborepin; presumably the perfluorinated reactants engage in an analogous reaction pathway to give **2**, as depicted in Scheme 1. Thus, a 1,3-suprafacial sigmatropic shift from the initial Diels–Alder intermediate **A** yields the unstable, homoantiaromatic[43] 7-borabicyclo[4.1.0]heptadiene intermediate **B**,[44,45] which undergoes electrocyclic ring-opening to yield the observed heptaarylborepin product.

**Chart 1**



The course of the reaction was followed visually via the loss of the intensely purple-colored **1** in favor of the white suspension of **2**, in a light yellow liquor, that results upon complete conversion. The new perfluoroarylborane **2** was isolated by filtration in 82% yield. Monitoring by NMR spectroscopy was made difficult as a consequence of the poor solubility of both **1** and **2** in common solvents even at higher temperatures; indeed spectroscopic characterization of **2** was to a large degree precluded by its insolubility. It was unambiguously identified when crystals were harvested from a 1:1 reaction of **1** and $C_6F_5CCC_6F_5$ in $CH_2Cl_2$ at 50 °C that took place over the period of about four weeks with no stirring.

Spectroscopic confirmation of borepin **2** was carried out indirectly via formation of its pyridine adduct **2-py**. A $CH_2Cl_2$ suspension of **2** went clear upon addition of one equivalent of pyridine, forming the more soluble adduct, which could be probed by the usual spectroscopic techniques. The $^1$H NMR spectrum shows three downfield shifted signals for the coordinated pyridine at 9.35 (broadened by coupling to the $^{10}B/^{11}B$ nuclei), 8.42, and 7.93 ppm for the *ortho*, *para* and *meta* protons, respectively. The $^{11}$B NMR chemical shift observed for **2-py** is at −2.3 ppm, consistent with a neutral, four-coordinate boron center. The $^{19}$F NMR spectrum is complex in the *ortho* and *meta* fluorine regions due to rotational stasis in some of the rings, but shows four *para* fluorine resonances in the expected 2:2:2:1 ratio at −150.4, −151.5, −153.9, and −154.7 ppm.

The solid-state structures of both **2** and **2-py** were determined by X-ray crystallography; thermal ellipsoid diagrams of each are shown in Figure 1, along with selected metrical parameters. Compound **2** crystallizes with two independent molecules in the unit cell (only molecule A is shown in Figure 1); the metrical parameters are similar for both molecules of **2**, the primary differences being the intraring boron–carbon distances and the extent of puckering in the

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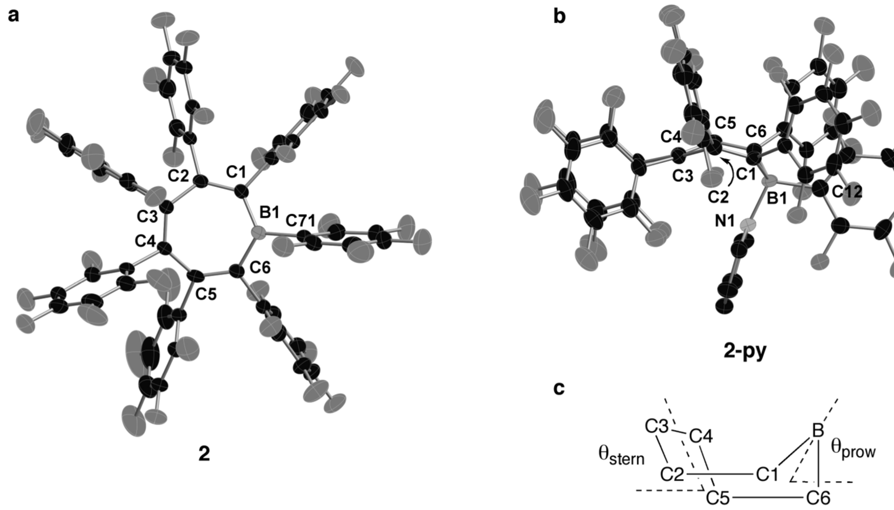
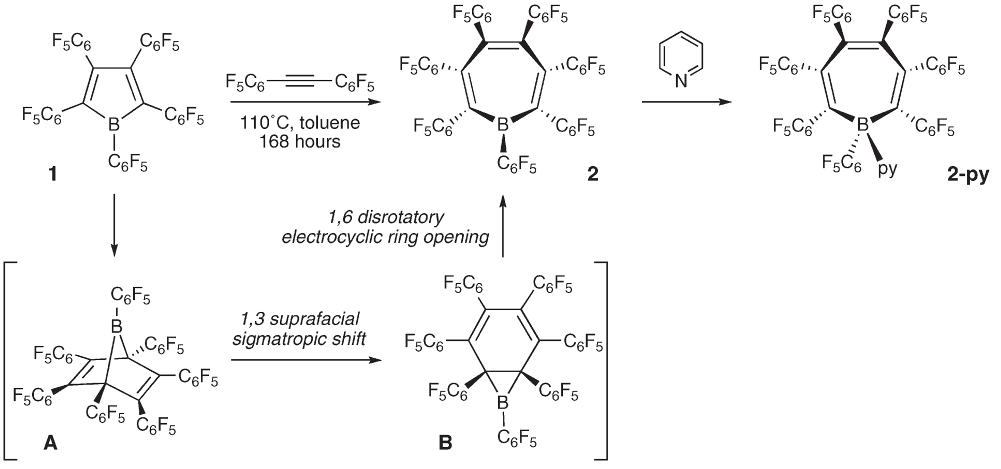


**Figure 1.** (a) Thermal ellipsoid diagram (50%) of molecule A of compound **2**; view from above ring. Selected bond distances (Å): B1−C1, 1.502(4); C1−C2, 1.392(3); C2−C3, 1.465(3); C3−C4, 1.369(3), C4−C5, 1.465(4); C5−C6, 1.370(4); B1−C6, 1.510(3); B1−C71, 1.587(4). Selected bond angles (deg): C1−B1−C6, 122.4(2); C1−B1−C71, 118.7(2); C6−B1−C71, 118.3(2). Selected dihedral planes (deg): $\theta_{\mathrm{prow}}$, 23.1(2) (20.2(2) for molecule B); $\theta_{\mathrm{stern}}$, 25.2(1) (23.2(1) for molecule B). (b) Thermal ellipsoid diagram (50%) of compound **2-py**; view from side of ring. Selected bond distances (Å): B1−C1, 1.604(7); C1−C2, 1.358(7); C2−C3, 1.492(6); C3−C4, 1.357(7), C4−C5, 1.480(7); C5−C6, 1.359(7); B1−C6, 1.640(7); B1−C12, 1.655(8); B1−N1, 1.604(7). Selected bond angles (deg): N1−B1−C1, 111.2(4); N1−B1−C6, 108.9(4); C1−B1−C6, 104.4(4); N1−B1−C12, 107.4(4); C1−B1−C12, 113.2(4); C6−B1−C12, 111.8(4). Selected dihedral planes (deg): $\theta_{\mathrm{prow}}$, 45.8(4); $\theta_{\mathrm{stern}}$, 31.8(3). (c) Diagram illustrating the dihedral planes $\theta_{\mathrm{prow}}$ and $\theta_{\mathrm{stern}}$ defining the deviation of the ring from planarity into a boat-like conformation.

**Scheme 1**



ring conformation. In molecule A, the B−C distances are 1.502(4) and 1.510(3) Å for B1−C1 and B1−C6, respectively, while in molecule B the analogous values are somewhat shorter at 1.475(3) and 1.475(4) Å. This may be due to the somewhat more planar seven-membered ring in molecule B, resulting in more $\pi$ delocalization in the seven-membered ring in molecule B. Nevertheless, in both molecules of **2** the seven-membered ring is nonplanar,[46] with both B1 and C3/C4 rising out of the plane defined by C1−C2−C5−C6; the angles between this plane and those defined by C1/B1/C6 and C2/C3/C4/C5 ($\theta_{\mathrm{prow}}$ and $\theta_{\mathrm{stern}}$, see Figure 1c) are 23.1(2)° and 25.2(1)°, respectively, in molecule A, but slightly smaller at 20.2(2)° and 23.2(1)° for molecule B. There is distinct bond alternation within the ring, with C1−C2, C3−C4, and C5−C6 exhibiting shorter distances than the C2−C3 and C4−C5 lengths. The boron center is essentially planar, with the sum of angles about B1 being 359.4(3)°; the intraring C1−B1−C6 is larger than the extra-ring angles by about 4°. The nonplanar nature of **2** contrasts with the structure observed for the unsubstituted chloroborepin reported by Ashe et al.,[23] where the ring is highly planar. Thus, the lack of planarity in **2** must be largely a consequence of the need to accommodate the large $C_6F_5$ substituents around the ring.

Coordination of pyridine to the boron center results in a tetrahedral boron center; the side view of **2-py** depicted in Figure 1b illustrates more clearly the puckering of the borepin ring. Indeed, the $\theta_{\mathrm{prow}}$ and $\theta_{\mathrm{stern}}$ angles are considerably larger in **2-py** than in **2** at 45.8(4)° and 31.8(3)°, respectively. The occupation of the empty orbital on boron by the pyridine base also serves to enhance the localization of

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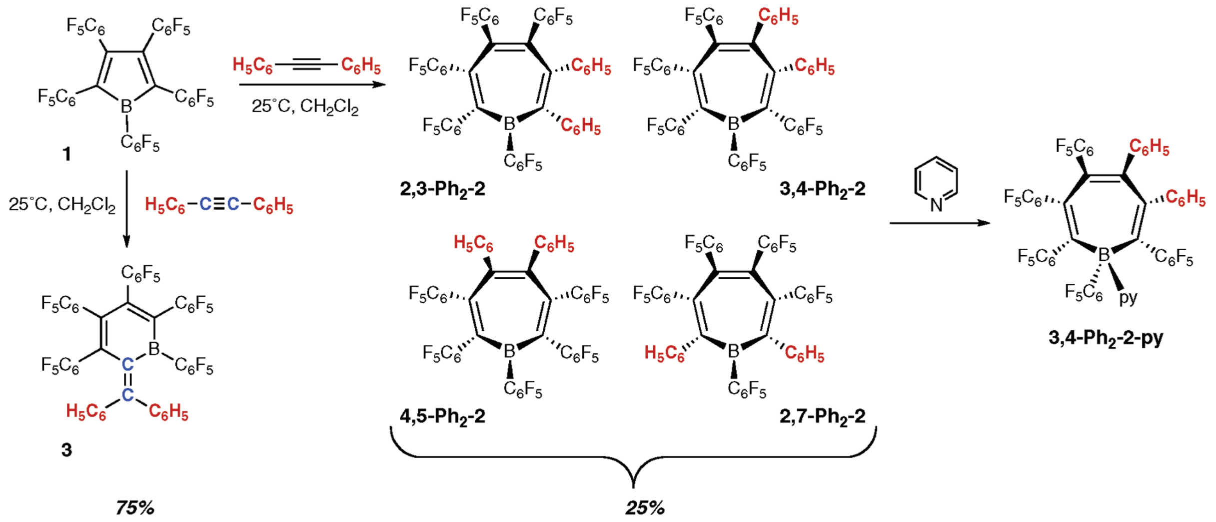
Scheme 2



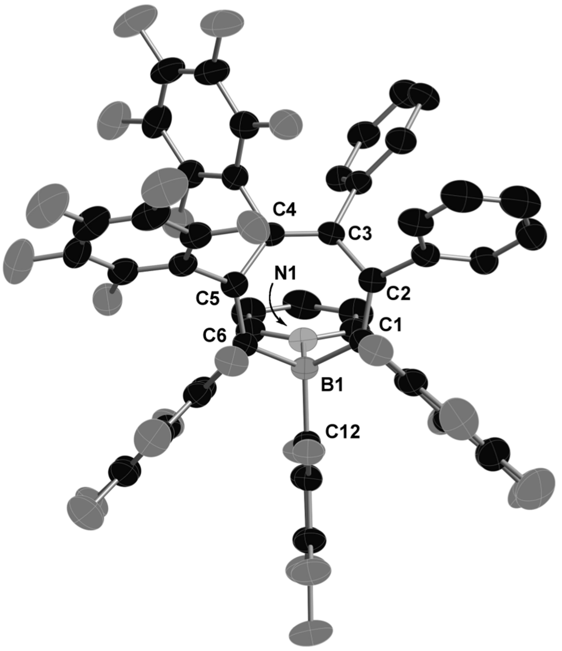


**Figure 2.** Thermal ellipsoid diagram (50%) of compound **3,4-Ph$_2$-2-py**; view from above ring. Selected bond distances (Å): B1−C1, 1.612(5); C1−C2, 1.361(5); C2−C3, 1.480(5); C3−C4, 1.351(5), C4−C5, 1.474(5); C5−C6, 1.361(5); B1−C6, 1.646(5); B1−C12, 1.653(5); B1−N1, 1.639(4). Selected bond angles (deg): C1−B1−N1, 108.9(3); C1−B1−C6, 105.3(3); N1−B1−C6, 109.3(3); C1−B1−C12, 113.0(3); N1−B1−C12, 107.9(3); C6−B1−C12, 112.4(3). Selected dihedral planes (deg): $\theta_{\text{prow}}$, 47.3(2); $\theta_{\text{stern}}$, 34.9(3).

double bonds in the seven-membered ring, as evidenced by the elongation of the single bonds and contraction of the double bonds of the ring relative to unligated **2**. Particularly, the B1−C1 and B1−C6 distances in **2-py** are ~0.1 Å longer than those in **2**, as conjugation between B1 and the alpha carbons is disrupted. The pyridine occupies an axial site on the prow of the boat and is slightly bent away from the *ortho*-fluorines on the $C_6F_5$ groups on C3 and C4, leaving the pentafluorophenyl group on boron to assume an equatorial conformation. The B1−N1 distance is comparable to those of other perfluoroarylborane-pyridine adducts[47] and slightly shorter than various imine adducts of $B(C_6F_5)_3$, which have B−N distances ranging from 1.627(3) to 1.658(6) Å.[48] Clearly, despite the steric crowding about the boron center, the perfluorination of the seven phenyl rings enhances the Lewis acidity of the boron in this new member of the perfluoroarylborane family of Lewis acids.[34]

Borole **1** is an electron-poor diene, and its slow reaction with the perfluorodiphenylacetylene dienophile suggests that a more electron-rich alkyne might react with **1** at a faster rate. Indeed, the reaction of **1** with diphenylacetylene proceeds essentially upon mixing at 25 °C in methylene chloride to produce a complex mixture of products as determined by $^{19}F$ NMR spectroscopy. The chemistry that occurs is summarized in Scheme 2. On the basis of an analysis of the products that would be produced via the Diels−Alder/pericyclic rearrangement pathway depicted in Scheme 1, four diphenyl-substituted heptaarylborepin isomers are expected: two $C_s$ symmetric isomers (**4,5-Ph$_2$-2** and **2,7-Ph$_2$-2**) and two unsymmetric isomers (**2,3-Ph$_2$-2** and **3,4-Ph$_2$-2**). (For a more complete depiction as to how these isomers arise, see Scheme S1 in the Supporting Information.) Since the $^{19}F$ NMR spectrum of the crude product mixture (see Figure S1 in the Supporting Information) indicates that the major product of the reaction has five inequivalent $C_6F_5$ groups, we initially surmised that one of the two unsymmetric isomers of **Ph$_2$-2** was the dominant product. However, an X-ray crystallographic analysis of a single crystal of this major product (which selectively crystallizes nicely from the crude product mixture) reveals its structure to be the boracyclohexadiene compound **3**, in which the diphenylacetylene reagent manifests itself as the *exo* diphenylmethylene unit shown in blue and red in Scheme 2. From the $^{19}F$ NMR spectrum (Figures S1 and S2), it can be estimated that **3** comprises approximately 75% of the product mixture; the rest is likely made up of the diphenyl borepins **Ph$_2$-2**, the major component being the **3,4-Ph$_2$-2** isomer. This was deduced through

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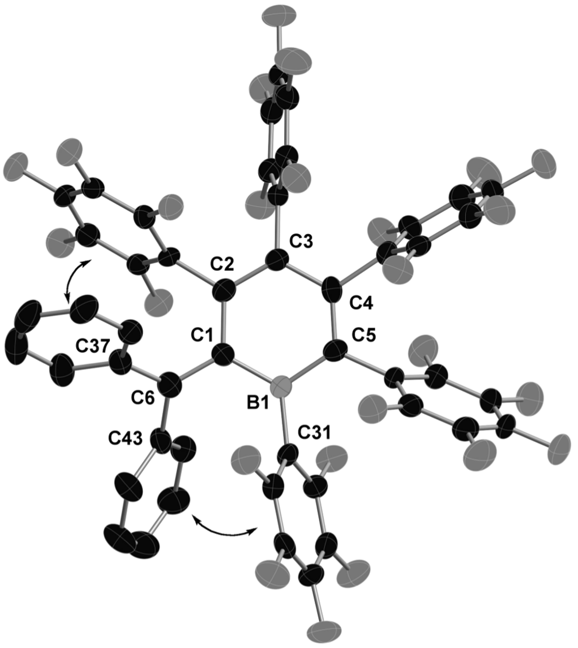
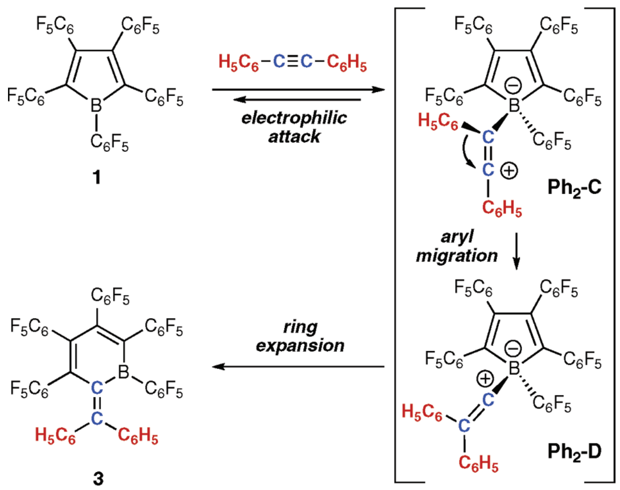


**Figure 3.** Thermal ellipsoid diagram (50%) of compound **3**; view from above ring. Selected bond distances (Å): B1−C1, 1.520(7); C1−C2, 1.469(6); C2−C3, 1.398(7); C3−C4, 1.438(6), C4−C5, 1.390(7); B1−C5, 1.497(7); B1−C31, 1.566(7); C1−C6, 1.411(7). Selected bond angles (deg): C5−B1−C1, 117.0(4); C5−B1−C31, 117.8(4); C1−B1−C31, 125.0(4); C1−C6−C43, 120.9(4); C1−C6−C37, 122.1(4); C43−C6−C37, 117.0(4). Selected dihedral angles (deg): B1−C1−C6−C43, 42.0(6); C2−C1−C6−C37, 37.2(7).

the isolation of its pyridine adduct via treatment of the mother liquor of a crude reaction mixture with pyridine *after* the bulk of compound **3** had been removed by precipitation. Crystals of **3,4-Ph$_2$-2-py** suitable for X-ray analysis were obtained from such an experiment, and a thermal ellipsoid diagram is shown in Figure 2, along with selected metrical data. Overall, the structure is very similar to that of **2-py**, except for the unfluorinated phenyl groups in the 3 and 4 positions of the ring. Here again, the pyridine occupies an axial position on the boron, tucked into the pocket formed by the prow and stern of the boat conformation of the borepin ring.

The molecular structure of boracycle **3** is shown in Figure 3, along with selected metrical data. The intraring bond distances reflect the localization of carbon−carbon double bonds between C2/C3 and C4/C5 (1.398(7) and 1.390(7) Å, respectively) and single bonds between B1 and the sp$^2$ carbons C1 and C5 (1.520(7) and 1.497(7) Å, respectively). Indeed the atoms of the six-membered boracycle are essentially coplanar, with deviations from the plane defined by the six atoms ranging from 0.010 to 0.033 Å. The *exo* double bond between C1 and C6 is somewhat elongated from typical values at 1.411(7) Å, a consequence of its distortion from coplanarity with the $\pi$ system of the intra-ring diene. This distortion is quite severe, as measured by the B1−C1−C6−C43 and C2−C1−C6−C37 torsion angles of 42.0(6)° and 37.2(7)° and the deviation of C6 from the plane defined by B1 and C1−C5 of 0.170 Å and likely arises due to steric interactions between the phenyl groups on C6 with adjacent C$_6$F$_5$ groups on B1 and C2. The C1−B1−C31 angle of 125.0(4)° is also impacted by this factor. However, the twisting of the C1−C6 double bond may also in part be driven by the assumption of $\pi$-stacking interactions between the C37 phenyl group with the C$_6$F$_5$ group on C2, and the C43 phenyl moiety with the boron C$_6$F$_5$ substituent (indicated by the double-headed arrows in Figure 3).

**Scheme 3**



Given the expectation of Diels−Alder-dominated chemistry in the reaction of **1** with diphenylacetylene, the formation of **3** as the major product is surprising. We postulate that it is a consequence of the very high Lewis acidity of **1**, which opens a new pathway for the reactivity of boroles with alkynes that involves electrophilic attack at the carbon−carbon triple bond, followed by rearrangement to a vinylidene-like group via 1,2-migration of the phenyl group as shown in Scheme 3. This alkyne-to-vinylidene sequence has ample precedence in transition metal chemistry;[49,50] usually, it involves terminal alkynes since the proton is an excellent migrating group, but there is also precedence for this isomerization in coordinated internal alkynes.[51] Here, the coordination of the alkyne to the electrophilic borole center is likely reversible, and Diels−Alder chemistry to yield borepins **Ph$_2$-2** is competitive with the rate-limiting migration of the phenyl group in zwitterionic intermediate **Ph$_2$-C** to irreversibly yield **Ph$_2$-D**. The reactivity of the highly electrophilic borole **1** with more electron rich alkynes thus takes two divergent, competitive pathways.

Compound **3** was synthesized separately via the reaction of the bromoborole **1-Br**[40] and diphenyl acetylene as shown in Scheme 4. Interestingly, **1-Br** reacts almost exclusively via the electrophilic attack pathway to produce **3-Br** as the sole boron-containing product; conversion of this material to **3** proceeds smoothly with prolonged heating at 100 °C using the bis-pentafluorophenyl zinc reagent[52] to install the −C$_6$F$_5$ group on boron. In this way, analytically pure samples of **3** (free of borepin side products) were obtainable.

Given these observations, it was of interest to attempt a reaction of **1** with an electron-rich internal alkyne substituted with groups that are less prone to migration, that is, those

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(51) Ikeda, Y.; Yamaguchi, T.; Kanao, K.; Kimura, K.; Kamimura, S.; Mutoh, Y.; Tanabe, Y.; Ishii, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16856–16857.

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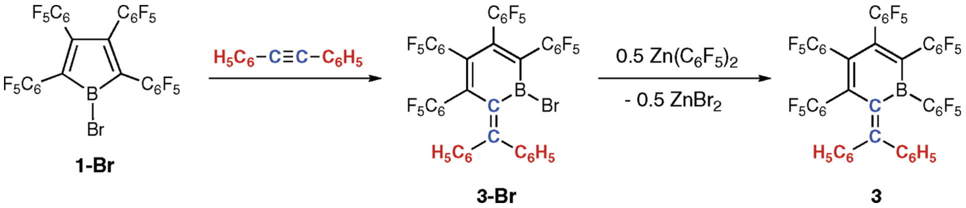
**Scheme 4**



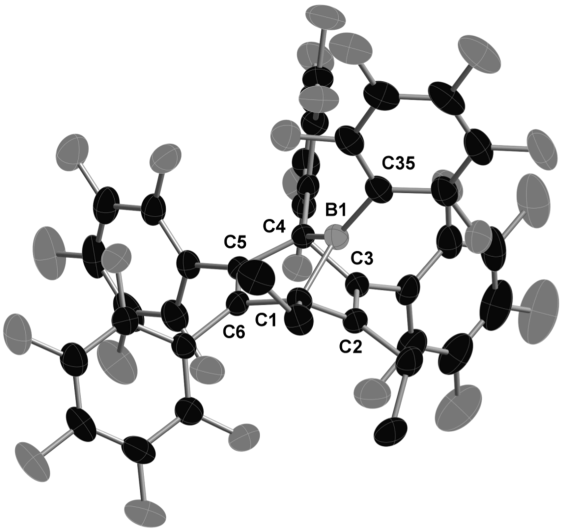


**Figure 4.** Thermal ellipsoid diagram (50%) of molecule A of compound **1,2-Et$_2$-4**. Selected bond distances (Å); bold parameters cited after are the corresponding values for molecule B: B1−C1, 1.651(4), **1.651(4)**; B1−C4, 1.628(4), **1.634(4)**; C1−C2, 1.504(4), **1.506(4)**; C2−C3, 1.388(4), **1.398(4)**; C3−C4, 1.534(4), **1.530(4)**; C4−C5, 1.517(4), **1.518(4)**; C5−C6, 1.329(4), **1.336(4)**; C1−C6, 1.513(4), **1.507(4)**; B1−C35, 1.574(4), **1.570(4)**. Selected nonbonding distances (Å): B1−C2, 1.835(4), **1.825(5)**; B1−C3, 1.812(4), **1.795(4)**. Selected bond angles (deg): C1−B1−C4, 96.5(2), **96.6(2)**; C1−B1−C35, 127.6(3), **127.6(3)**; C4−B1−C35, 135.0(3), **134.8(3)**. Selected dihedral planes (deg); plane 1 contains C1/B1/C4; plane 2 contains C1/C2/C3/C4; plane 3 contains C1/C6/C5/C4: angle between planes 1 and 2, 83.0(2), **82.0(2)**; angle between planes 1 and 3, 152.7(2), **152.5(2)**; angle between planes 2 and 3, 124.8(2), **125.5(2)**.

with sp$^3$-hybridized carbons. Accordingly the reaction of **1** with 3-hexyne was explored. Not surprisingly, a rapid reaction occurred upon mixing of these two reagents, as indicated by the immediate loss of the deep purple color of **1** when 3-hexyne was added, forming a light orange-yellow solution. Multinuclear NMR spectroscopy suggests the formation of a single product, **4**, with five inequivalent $C_6F_5$ groups and two inequivalent (or diastereotopic) ethyl groups, consistent with either of the reaction channels described above. However, the $^{11}$B NMR shows one broad signal at −10.3 ppm, a chemical shift inconsistent with either a borepin or a boracyclohexadiene structure, whose boron nuclei resonate at 40−50 ppm. The observed −10.3 chemical shift is generally associated with neutral (and perhaps anionic) four-coordinate boron centers.

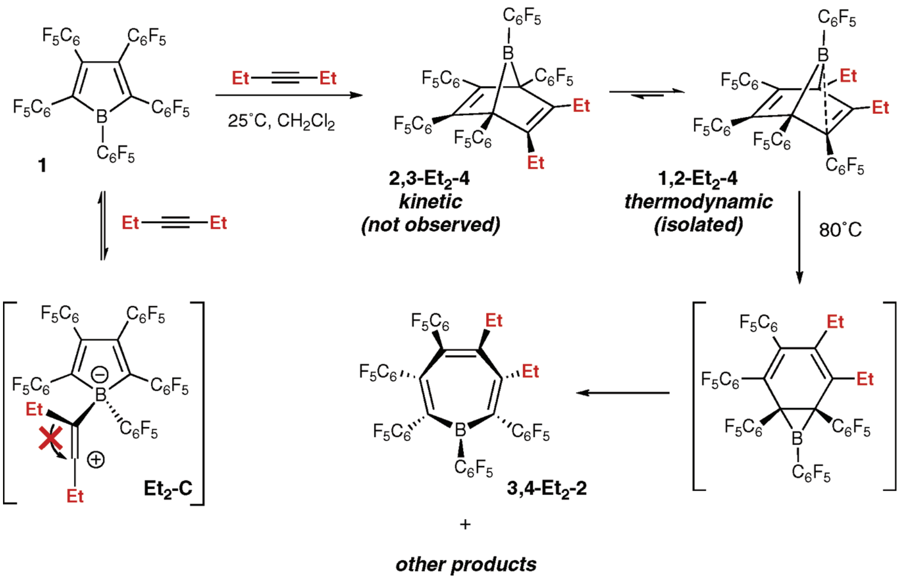
The nature of **4** was determined conclusively via X-ray crystallography; a thermal ellipsoid diagram is shown in Figure 4, along with selected metrical parameters, and the chemistry involved in this reaction is depicted in Scheme 5. Essentially, compound **4** is one of the two possible isomers of the 7-borabicyclo[2.2.1]heptadienes formed upon [4+2] Diels−Alder cycloaddition[30] between **1** and 3-hexyne. Interestingly, it is not the expected kinetic product with ethyl groups in the 2,3 positions of the borabicyclo[2.2.1]heptadiene ring, but rather the (apparently) more thermodynamically stable **1,2-Et$_2$-4** isomer as shown. While stable enough to isolate (in 59% yield) and fully characterize, this product is converted to a mixture of products upon heating in solution at 80 °C for 8 h, some of which are likely borepin isomers of **Et$_2$-2** on the basis of low-field boron signals in the $^{11}$B NMR spectrum.

While the precise nature of all of the products in this mixture was not determined, examination of the bond distances in the structure of **1,2-Et$_2$-4** reveals some nuances in the structure that suggest it is poised to undergo a suprafacial 1,3-sigmatropic shift that would lead to the 7-borabicyclo-[4.1.0]heptadiene intermediate and borepin **3,4-Et$_2$-2** shown in Scheme 5. The compound crystallizes with two molecules in the unit cell with similar metrical parameters; both are given in the caption for Figure 4 for comparison. The ethyl groups are on C1 and C2 in the view presented, and from this perspective, it is clear that the B($C_6F_5$) unit is tilted decidedly toward C2 and C3. The angle subtended between the planes defined by B1/C1/C4 and C1/C2/C3/C4 is acute (83.0(2)°), while the one between the former plane and that defined by C1/C6/C5/C4 is obtuse, at 152.7(2)°. Although the boron is not four-coordinate, this tilt toward the C2−C3 double bond may contribute to the unusual negative value of the chemical shift for boron; another potential factor is the nonideal C1−B1−C4 angle of 96.5(2)°. In any case, the double bond between C2 and C3 is 1.338(4) Å, slightly longer than the linkage between C5 and C6, which is 1.329(4) Å, by virtue of this interaction. The other bonds in the C1−C6 rings are clearly single bonds.

The B1−C distances in the molecule are interesting and foreshadow the propensity for the molecule to convert to the observed borepin, which involves a 1,3 shift that cleaves the B1−C1 bond and forms a bond between B1 and C3. In accord with this, the B1−C1 distance of 1.651(4) Å is slightly longer than the B1−C4 distance of 1.628(4) Å, and B1 draws slightly nearer to C3 (1.812(4) Å) than it is to C2 (1.835(4) Å); the differences are more pronounced in molecule B. We speculate that this isomer is the thermodynamic isomer because the developing positive charge on C2 as this occurs is more stabilized by an ethyl group than a pentafluorophenyl group.

Regardless of this apparent structural bias toward decomposition to yield borepin **3,4-Et$_2$-2**, the observation of other products in the crude mixture formed upon thermal decomposition of **1,2-Et$_2$-4** suggests that conversion to other isomers of **Et$_2$-2** and decomposition via other unidentified modes (possibly via the intermediate **Et$_2$-C**) are occurring in this dynamic system.

**Scheme 5**



## Summary

The reactions of the perfluorinated pentaphenylborole **1** with three symmetrical internal alkynes have been studied. These investigations show that, in addition to previously observed Diels−Alder reactivity patterns for the reactions of unfluorinated boroles with alkynes, the potent Lewis acidity of **1** opens a new channel of reactivity for certain alkynes involving electrophilic attack of the alkyne and the triggering of an alkyne rearrangement reminiscent of those long known for transition metal alkyne complexes. These two reaction manifolds are competitive, with the nucleophilicity of the alkyne and the ability of the alkyne substituent to undergo 1,2 migration being the main factors in determining the dominant pathway. For example, the electron-poor alkyne $C_6F_5CCC_6F_5$ exclusively takes part in Diels−Alder chemistry, yielding the new perfluoroaryl borane **2**. Diphenylacetylene, on the other hand, undergoes both reactions, but the electrophilic attack pathway dominates, because of its electron richness and the ability of the $sp^2$-hybridized aryl *ipso* carbon to lower the transition-state energy for 1,2 migration. 3-Hexyne, despite its electron-rich nature, does not suffer electrophilic attack in the dominant pathway, although a zwitterionic adduct akin to **Et$_2$-C** may form and undergo decomposition via mechanisms that do not involve ethyl group migration at higher temperatures. Instead, Diels−Alder chemistry occurs, but the product at room temperature is the diethyl-substituted 7-borabicyclo[4.1.0]heptadiene compound that represents a previously proposed intermediate in the reaction of boroles with alkynes. Characterization of **1,2-Et$_2$-4** provides solid experimental evidence for the proposals of Eisch regarding the mechanism of formation of borepins from boroles and alkynes, representing one of the proposed intermediates along this reaction path.

## Experimental Section

**General Procedures.** All operations were performed under a purified argon atmosphere using glovebox or vacuum line techniques. Toluene and hexane solvents were dried and purified by passing through activated alumina and vacuum distilled from Na/benzophenone. $CH_2Cl_2$, pyridine, and 3-hexyne were dried over and distilled from $CaH_2$ twice. Diphenylacetylene was purchased from Aldrich and used as received. Perfluoropentaphenylborole,[40] $C_6F_5C{\equiv}CC_6F_5$,[42] and $Zn(C_6F_5)_2$[52] were prepared as previously reported. All $^1$H, $^{11}$B, and $^{19}$F NMR spectra were recorded on a Bruker 400 MHz spectrometer (operating at 400 MHz ($^1$H), 128 MHz ($^{11}$B), and 376 MHz ($^{19}$F)) at 25 °C or as indicated. Chemical shifts reported were relative to $SiMe_4$ ($^1$H) or $BF_3$ ($^{11}$B and $^{19}$F) standards. Due to poor solubility and $^{13}$C−$^{19}$F coupling, $^{13}$C spectra were not obtained. X-ray crystallography analyses were performed on suitable crystals coated in Paratone oil and mounted on a Nonius Kappa CCD diffractometer.

**Synthesis of Perfluoroheptaphenylborepin, 2.** Perfluoropentaphenylborole (**1**) (123 mg, 0.14 mmol) and $C_6F_5C{\equiv}CC_6F_5$ (50 mg, 0.14 mmol) were mixed in toluene (3 mL). The suspended mixture was sealed in a flask and heated to 110 °C for one week. The white precipitate was filtered, washed by $CH_2Cl_2$ (3 × 3 mL), and dried *in vacuo*. Yield: 142 mg (82%). Anal. (%) Calcd for $C_{48}BF_{35}$: C 46.04. Found: 45.71.

**Synthesis of Compound 2-py.** Perfluoroheptaphenylborepin (**2**) (100 mg, 0.09 mmol) was suspended in $CH_2Cl_2$ (2 mL). Pyridine (7 mg, 0.09 mmol) was added. The mixture was stirred and heated to form a clear solution and maintained at room temperature overnight to form colorless crystals. The crystals were filtered and washed with hexane (3 × 3 mL) and dried *in vacuo*. Yield: 72 mg (70%). $^1$H NMR ($CD_2Cl_2$): 9.35 (d, 2H), 8.42 (t, 1H), 7.93 (t, 2H). $^{11}$B{$^1$H} NMR ($CD_2Cl_2$): −2.3 (br). $^{19}$F{$^1$H} NMR ($CD_2Cl_2$): −121.5 (m, 2F, *o*-$C_6F_5$), −133.8 (m, 2F, *o*-$C_6F_5$), −135.0 (m, 2F, *o*-$C_6F_5$), −137.6 (m, 2F, *o*-$C_6F_5$), −140.3 (m, 2F, *o*-$C_6F_5$), −141.6 (m, 2F, *o*-$C_6F_5$), −142.3 (m, 2F, *o*-$C_6F_5$), −150.4 (t, 2F, *p*-$C_6F_5$), −151.5 (t, 2F, *p*-$C_6F_5$), −153.9 (t, 2F, *p*-$C_6F_5$), −154.7 (t, 1F, *p*-$C_6F_5$), −160.2 (m, 2F, *m*-$C_6F_5$), −160.5 (m, 2F, *m*-$C_6F_5$), −161.0 (m, 2F, *m*-$C_6F_5$), −161.4 (m, 2F, *m*-$C_6F_5$), −161.9 (m, 2F, *m*-$C_6F_5$), −163.5 (m, 2F, *m*-$C_6F_5$), −164.6 (m, 2F, *m*-$C_6F_5$). Anal. (%) Calcd for $C_{35}H_5BF_{35}N\cdot CH_2Cl_2$: C 45.79, H 0.50, N 1.00. Found: C 45.79, H 0.64, N 1.27.

**Synthesis of Compound 3. 1-Br** (1 g, 1.24 mmol) and diphenylacetylene (0.22 g, 1.24 mmol) were mixed in toluene (20 mL) and stirred overnight to form a dark blue solution. $Zn(C_6F_5)_2$ (0.25 g, 0.62 mmol) was added, and the mixture was heated to 100 °C until complete conversion of **3-Br** to **3** was observed by $^{19}$F NMR spectroscopy (3−5 days). The volatiles were removed under reduced pressure, and the dark purple residue was then dissolved in $CH_2Cl_2$ and filtered. After the solvent was removed, the dark purple solid was recrystallized from hot toluene (6 mL) and dried *in vacuo*. Yield: 0.85 g (64%). $^1$H NMR

($CD_2Cl_2$): 7.62−7.57 (m, 2H, $C_6H_5$), 7.48−7.47 (m, 2H, $C_6H_5$), 7.41−7.33 (m, 4H, $C_6H_5$), 7.22−7.20 (m, 2H, $C_6H_5$). $^{11}B\{^1H\}$ NMR ($CD_2Cl_2$): 41.3 (br). $^{19}F\{^1H\}$ NMR ($CD_2Cl_2$): −131.4 (m, 2F, *o*-$C_6F_5$), −136.6 (m, 2F, *o*-$C_6F_5$), −138.7 (m, 2F, *o*-$C_6F_5$), −138.8 (m, 2F, *o*-$C_6F_5$), −140.8 (m, 2F, *o*-$C_6F_5$), −151.8 (t, 1F, *p*-$C_6F_5$), −152.0 (t, 1F, *p*-$C_6F_5$), −153.6 (t, 1F, *p*-$C_6F_5$), −155.3 (t, 1F, *p*-$C_6F_5$), −155.6 (t, 1F, *p*-$C_6F_5$), −161.1 (m, 2F, *m*-$C_6F_5$), −161.6 (m, 2F, *m*-$C_6F_5$), −162.4 (m, 2F, *m*-$C_6F_5$), −162.9 (m, 2F, *m*-$C_6F_5$), −163.3 (m, 2F, *m*-$C_6F_5$). Anal. (%) Calcd for $C_{48}H_{10}BF_{25}\cdot C_7H_8$: C 56.73, H 1.56. Found: C 57.08, H 1.88.

**Synthesis of Compound 4.** Perfluoropentaphenylborole (**1**) (500 mg, 0.56 mmol) and 3-hexyne (46 mg, 0.56 mmol) were mixed in toluene (10 mL). After the mixture was stirred for 4 h, all the volatiles were removed under vacuum. The orange solid was redissoved in hexane (5 mL) to obtain a yellow solution. Off-white crystals were allowed to grow at room temperature from the yellow solution over the course of five days and isolated by filtration. After washing with cold hexane (1 × 3 mL), the product was dried *in vacuo* to obtain an off-white solid. Yield: 320 mg (59%). $^1H$ NMR ($CD_2Cl_2$): 2.75 (m, 1H, $CH_2CH_3$), 2.47 (m, 1H, $CH_2CH_3$), 2.29 (m, 1H, $CH_2CH_3$), 1.72 (m, 1H, $CH_2CH_3$), 1.43 (m, 3H, $CH_2CH_3$), 0.87 (t, 3H, $CH_2CH_3$). $^{11}B\{^1H\}$ NMR ($CD_2Cl_2$): −10.3 (br). $^{19}F\{^1H\}$ NMR ($CD_2Cl_2$): −122.6 (br, 1F, *o*-$C_6F_5$), −130.4 (br, 1F, *o*-$C_6F_5$), −135.4 (m, 1F, *o*-$C_6F_5$), −137.4 (m, 2F, *o*-$C_6F_5$), −137.5 (m, 1F, *o*-$C_6F_5$), −137.8 (m, 1F, *o*-$C_6F_5$), −139.5 (m, 2F, *o*-$C_6F_5$), −139.9 (m, 1F, *o*-$C_6F_5$), −150.3 (t, 1F, *p*-$C_6F_5$), −151.2 (t, 1F, *p*-$C_6F_5$), −152.0 (t, 1F, *p*-$C_6F_5$), −152.6 (t, 1F, *p*-$C_6F_5$), −153.5 (t, 1F, *p*-$C_6F_5$), −159.5 (m, 1F, *m*-$C_6F_5$), −160.0 (m, 1F, *m*-$C_6F_5$), −160.6 (m, 1F, *m*-$C_6F_5$), −161.0 (m, 2F, *m*-$C_6F_5$), −161.7 (m, 3F, *m*-$C_6F_5$), −162.5 (br, 2F, *m*-$C_6F_5$). Anal. (%) Calcd for $C_{40}H_{10}BF_{25}\cdot 0.5C_6H_{14}$: C 50.67, H 1.68. Found: C 50.75, H 1.82.

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**Supporting Information Available:** Further details, including NMR spectra, schemes, and crystallographic data (CIF) for compounds **2**, **2-py**, **3,4-Ph$_2$-2-py**, **3**, and **1,2-Et$_2$-4**. This information is available free of charge via the Internet at http://pubs.acs.org.