

One-Pot Synthesis of 1,6-Diiodo-2,3,4,5-tetracarba-*nido*-hexaboranes(6) and Mechanistic Studies on the Reaction System Alkynes/ BI_3 / $\text{NaK}_{2.8}$

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Dedicated to Professor José Vicente on the occasion of his 60th birthday

Keywords: Boron / Boranes / Carboranes / Heterocycles / Iodine bridges

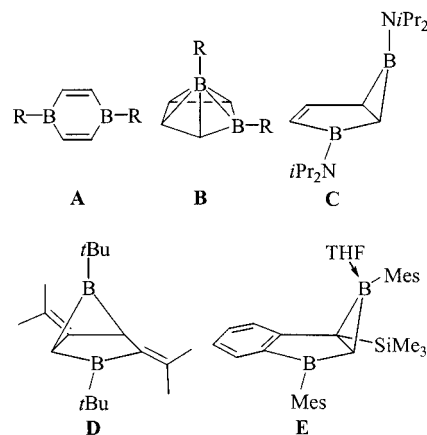
Attempts to prepare the tetracarba-*nido*-octaborane(8) derivative $(\text{EtC})_4(\text{BI})_4$ (**4**) by treatment of 3-hexyne with BI_3 (2 equiv.) and $\text{NaK}_{2.8}$ led to 2,3,4,5-tetraethyl-1,6-diiodo-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**2a**) as the predominant product with trace quantities of **4** as well as 2,3-diethyl-1,4,5,6,7-pentafluoro-2,3-dicarba-*closo*-heptaborane(7) (**5**). Starting at -78°C , reactions of 3-hexyne, 2-butyne or diphenylacetylene, respectively, with BI_3 (1 equiv.) and $\text{NaK}_{2.8}$ afforded the corresponding 1,6-diiodo-2,3,4,5-tetracarba-*nido*-hexaboranes(6) **2a–c** as the single carborane products. In the cases of 3-hexyne and diphenylacetylene, the formation of hexaorganylbenzene derivatives was also detected. To confirm the formation of **4** and **5**, the independent dehalogenation of *cis*-3,4-bis(diiodoboryl)-3-hexene (**3**) with $\text{NaK}_{2.8}$ has been studied, which indeed affords **4** and **5**, with the

former being the predominant product. A mechanism for the formation of **2a** has been proposed, which involves iodoboration of the alkyne to give the borylalkene **1a**. This is followed by deiodination, presumably yielding the iodoborirene derivative **7**, which easily dimerizes to form the 1,4-diboracyclo-2,5-hexadiene derivative **8**. Subsequent rearrangement leads to the final C_4B_2 -*nido*-carborane **2a**. To determine the stereochemistry of **1a**, its pyridine adduct **9** (and the isomer **9'**) and catechol derivative **10** (and the isomer **10'**), and the diisopropylamino derivative **11** have also been prepared. The new compounds have been characterized by MS and NMR spectroscopy, and the structures of **2a**, **3**, **9** and **9'** were confirmed by single-crystal X-ray analyses. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

The $(\text{HC})_4(\text{BR})_2$ organoborane/carborane system (**A**, **B**) has attracted considerable interest because the structures observed depend on the substituents (**R**) which attached to the boron atoms. Apart from the classical 1,4-diboracyclo-2,5-hexadienes **A**,^[1] and non-classical 2,3,4,5-tetracarba-*nido*-hexaboranes(6) **B**,^[2] the compounds **C**,^[3a] **D**,^[3b] **E**^[3c] in between these two limits have also been reported. Peralkylated 2,3,4,5-tetracarba-*nido*-hexaboranes(6), known since the mid-1960s, are more stable than the parent compound $\text{C}_4\text{B}_2\text{H}_6$ [4] but their reactivities have only recently been studied.^[5,6]

In order to investigate substitution reactions of **B**, functional groups (**R**) other than alkyl groups are needed at the boron atom(s). In 1994 we reported the formation of a 1,6-dichloro-2,3,4,5-tetracarba-*nido*-hexaborane(6)^[7] derivative by photochemical transformation of 1,4-dichloro-2,3,5,6-tetrakis(isopropylidene)-1,4-diboracyclohexane. The low yield of the $(\text{alkylC})_4(\text{BCl})_2$ carborane did not allow further reactivity studies to be carried out. Wrackmeyer et al. were



able to obtain 1,6-dibromo-2,3,4,5-tetracarba-*nido*-hexaboranes(6)^[5a] in high yield by treating 1,4,6,9-tetraalkyl-3,8-diethyl-2,7-bis(diethylboryl)-5-stannaspiro[4.4]nona-1,3,6,8-tetraenes with BBr_3 . They also studied the reactions between the peralkylated 2,3,4,5-tetracarba-*nido*-hexaboranes(6) and an excess of BBr_3 (and BI_3), whereby the corresponding B6-halo substituted carboranes were formed.^[5b] Nucleophilic substitution reactions of such B-halo carboranes were found to replace the basal B6-halogen atom to give the corresponding carboranes with organyl,^[5c] stan-

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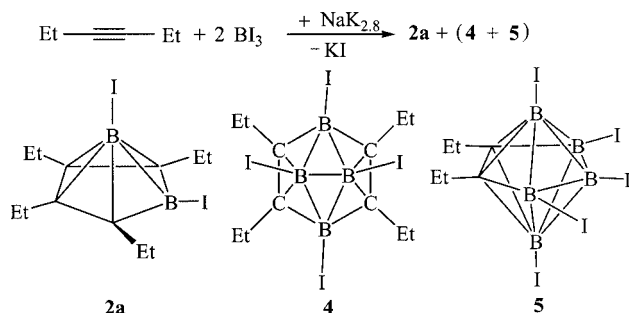
nyl^[5d] and diphenylphosphanyl^[5e] groups as well as, in the 1,6-dibromo case, an *N*-bonded $[\text{Fe}_2(\text{CO})_6(\mu\text{-SN})]$ substituent in the 6-position.^[5f] Currently there is no easy pathway to such B-functionalized C_4B_2 -*nido*-carboranes.

In our efforts to prepare the iodo analog of the tetracarba-*nido*-octaborane(8) $(\text{EtC})_4(\text{BCl})_4$ ^[8] we have developed a one-pot route to 1,6-diiodo-2,3,4,5-tetracarba-*nido*-hexaboranes(6) involving alkynes, BI_3 and $\text{NaK}_{2,8}$ alloy. In this paper we report the synthesis and characterization of the resultant C_4B_2 -*nido*-carboranes, and a possible mechanism for their formation is proposed.

Results and Discussion

Synthesis of 1,6-Diiodo-2,3,4,5-tetracarba-*nido*-hexaboranes(6)

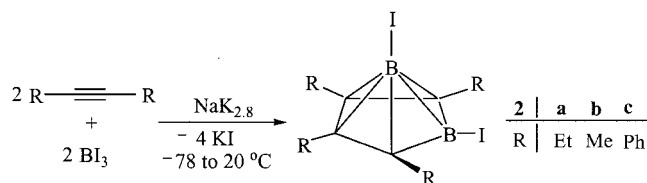
The reaction between 3-hexyne, BI_3 (2 equiv.) and $\text{NaK}_{2,8}$ alloy at room temperature, in a one-pot manner (Scheme 1), gave a mixture of products. Its ^{11}B NMR spectrum shows two dominant signals at $\delta = 5.5$ and -52.7 ppm in a 1:1 ratio, typical of C_4B_2 -*nido*-carboranes^[2] (type **B**). The EI-MS spectrum exhibits the molecular ion pattern with the correct isotopic distribution for the formula $(\text{EtC})_4(\text{BI})_2$ (**2a**). The other peaks can be assigned to *nido*-($\text{EtC})_4(\text{BI})_4$ (**4**) and the novel species *closo*-($\text{EtC})_2(\text{BI})_5$ (**5**), respectively, both exhibiting the expected isotopic patterns. Compounds **4** and **5** were formed only in trace amounts.



Scheme 1

Starting at low temperature (-78°C) the same reaction gave **2a** as the single product in 51% yield as a yellow, sensitive and viscous oil. The yield can be increased to 66% when a 1:1 ratio of 3-hexyne and BI_3 was used (Scheme 2). In the latter case a very small amount of hexaethylbenzene could also be detected. The ^{11}B NMR spectrum of **2a** exhibits two signals at $\delta = 5.5$ and -52.5 ppm. The ^1H NMR spectrum shows an ABX_3 spin pattern for the methylene protons of the ethyl groups, and the ^{13}C NMR spectrum exhibits the corresponding four signals for the two different ethyl groups. The signals responsible for the skeletal carbon atoms non-adjacent to the basal boron were observed, while the signals for the other two skeletal carbon atoms (expected at ca. 105 ppm^[5a]) were not observed. It should be noted that the formation of **2a** was first reported by Wrackmeyer et al.,^[5a] (see Introduction) when they carried out

reactions on a small scale for NMR spectroscopic studies. On standing at room temperature, yellow crystals of **2a** (vide infra) were obtained whereas the bromo compounds are oils.^[5a,5b]



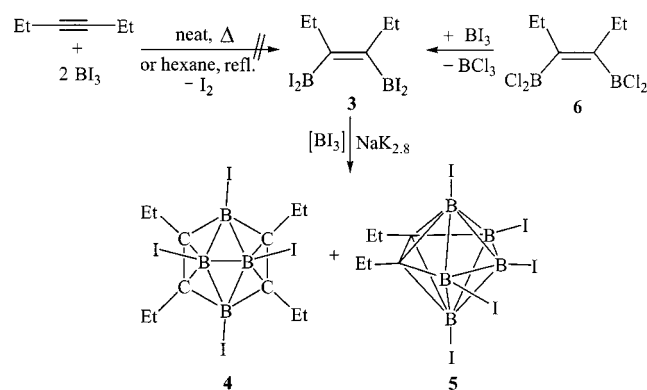
Scheme 2

The analogous reaction with 2-butyne proceeded smoothly but the yellowish *nido*-($\text{MeC})_4(\text{BI})_2$ (**2b**) was obtained only in low yield. The ^{11}B NMR spectrum exhibits two signals at $\delta = 5.7$, -48.6 ppm and the ^1H NMR spectrum shows two singlets for the two different methyl groups. The ^{13}C NMR spectrum gives the corresponding signals for the methyl and the skeletal carbon atoms non-adjacent to the basal boron, while the signal for the other two skeletal carbon atoms was not observed. In the mass spectrum the molecular ion peak with the expected isotopic pattern was found.

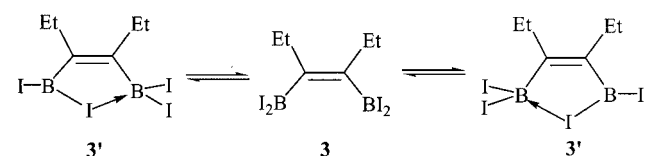
Whereas calculations^[10] suggest that such *nido*-carboranes bearing halogen substituents at the boron atom(s) would prefer a classical type **A** structure, we have found that **2a** and **2b** are perfectly stable like the bromo analogs.^[5a,5b] The reaction of diphenylacetylene with $\text{BI}_3/\text{NaK}_{2,8}$ also proceeds but the orange-yellow *nido*-($\text{PhC})_4(\text{BI})_2$ (**2c**) was also obtained in low yield. It was characterized by ^{11}B NMR spectroscopy ($\delta = 7.9$, -50.1 ppm), and the high-resolution mass spectrum exhibits the molecular ion peak having the correct isotopic distribution. Unfortunately, the formation of a significant amount of hexaphenylbenzene hampered the successful isolation and the recording of satisfactory NMR spectra. Moreover, it was found to be unstable at room temperature even when stored under nitrogen, as indicated by its color which turned from orange-yellow to pale yellow. This instability is different from the cases of **2a** and **2b**, and reminiscent of the instability of the iodoboration product of diphenylacetylene with BI_3 , which leads to a 9,10-dihydro-9-boraanthracene derivative.^[9]

In order to verify the formation of compounds **4** and **5**, the independent dehalogenation of **3**^[11a] (Scheme 3) was carried out. Attempts to obtain **3** through a redox reaction of 3-hexyne and two equivalents of BI_3 were not successful.^[11b] However, the halogen exchange reaction of **6**^[12] with BI_3 led to **3**, a yellow crystalline solid, which is extremely sensitive to air and moisture. In solution it exhibited a ^{11}B NMR signal at $\delta = 11.8$ ppm. No change in the chemical shift was observed upon cooling the sample to -30°C but only broadening of the signal. The significant shift to high field compared with that of **6** ($\delta = 53.9$ ppm) indicates some additional intra- or intermolecular interaction. An X-ray structural determination revealed that **3** forms an intramolecular $\text{B}-\text{I}-\text{B}$ bridge to yield **3'**. In solu-

tion a fast equilibrium is present as shown in Scheme 4, which explains the single ^{11}B NMR signal.



Scheme 3



Scheme 4

The dehalogenation of **3** starting at $-65\text{ }^{\circ}\text{C}$ gave compound **4** in 29% yield. When the same reaction was carried out at room temperature, the yield was lower. Compound **4** exhibits two ^{11}B NMR signals at $\delta = -10.5$ and -13.4 ppm, which are shifted to lower frequencies in comparison with *nido*-($\text{EtC})_4(\text{BCl})_4$ [$\delta = -1.5$ and -5.5 ppm]. In the mass spectrum, the molecular ion at $m/z = 716$ is the base peak and has the correct isotopic distribution, while the formation of **5** was only detected by a cutoff peak at $m/z = 771$ [M^+] of very low intensity.

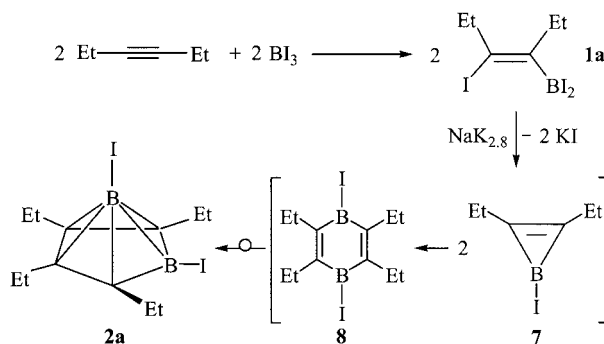
To further study the scope and limitations of this approach, a series of other alkynes has been studied using the same or similar procedures. In the cases of 5-decyne, di-*tert*-butylacetylene, bis(trimethylsilyl)acetylene, and di-*p*-tolylacetylene, all the reactions led to decomposition products. The debromination reaction of 3-hexyne and BBr_3 (1 equiv.) afforded the known *nido*-($\text{EtC})_4(\text{BBr})_2$ [5a] in 49% yield, together with a small amount of hexaethylbenzene, while the analogous reaction using BCl_3 gave a mixture of unidentified boron-containing species, and a significant amount of hexaethylbenzene. Surprisingly, the reaction system of diphenylacetylene- $\text{BBr}_3/\text{NaK}_{2.8}$ led only to decomposition irrespective of whether the one-step or step-wise procedures were used. Efforts to produce the corresponding *nido*- C_4B_2 carboranes with CH cluster atoms, starting from ethyne or phenylacetylene, and BI_3 (or BBr_3), respectively, were not successful.

Mechanistic Considerations

There have been two similar dehalogenation reactions reported. One is the early study of the diphenylacetylene/

PhBBr_2/K system by Lappert et al.,^[13] in which they claimed to have obtained a perphenylated 1,4-diboracyclohexadiene derivative or an unknown carborane species. These results, however, could not be reproduced by Eisch et al.^[14] The other system involves the alkynes/ $\text{MeBBr}_2/\text{C}_8\text{K}$ reaction reported by van der Kerk et al.,^[15] who claimed to have obtained stable peralkylated 1,4-diboracyclohexadiene derivatives as the main products through a borylene mechanism, while Wrackmeyer et al.^[16] (in the cases of 3-hexyne and 5-decyne) obtained the corresponding C_4B_2 -*nido*-carboranes. No 1,4-diboracyclohexadiene derivatives could be detected.

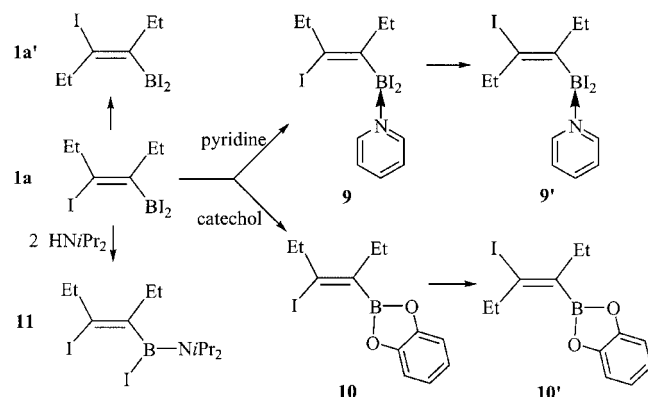
In order to get an insight into the formation of **2**, we selected **2a** as our target compound. A possible pathway to **2a** is shown in Scheme 5. Iodoboration of 3-hexyne with BI_3 afforded **1a**, its dehalogenation presumably yielded the iodoborirene intermediate **7**, which might dimerize^[1d,17] to give 1,4-diboracyclohexadiene **8** or the bicyclic analog of type C (see Introduction) with iodine at boron and ethyl at carbon atoms as intermediates to rearrange to the carborane **2a**.



Scheme 5

The first step is the iodoboration of 3-hexyne to yield **1a**. In a study involving this step for the preparation of the 2,5-dihydro-1,2,5-thiadiborol,^[9,18] the iodoboration product was reported to be a *cis/trans* mixture (ca. 2:3 *cis/trans* ratio) based on acetolysis which is an established method^[19] for determining the stereochemistry of haloboration products (we repeated the acetolysis reaction and a ratio of 1:1 was obtained). The problem is that at room temperature the ^1H NMR spectrum shows two sets of ethyl signals and the ^{13}C NMR spectrum exhibits only six signals, whereas a *cis/trans* mixture should give more signals. Moreover, the ^{11}B NMR spectrum exhibits only one signal at $\delta = 40$ ppm. As a result of this^[20] some reactions were carried out with $[\text{Fe}_2(\text{CO})_9]$ and Me_2S but unfortunately neither complexation nor adduct formation was observed. Later, the very similar reaction of 3-hexyne and BBr_3 was studied by Wrackmeyer.^[21] Their results revealed that it is a stereoselective *cis*-addition, while the fast *cis-trans* isomerization led to a mixture. This allowed the assignment of both isomers by NMR spectroscopic methods. We tried to determine the stereochemistry of the present iodoboration products using a method more direct than acetolysis. It turned

out, in agreement with Wrackmeyer's findings, that the reaction of 3-hexyne and BI_3 gave the *cis* isomer **1a** (Scheme 6), which underwent a slow isomerization to the thermodynamically more stable *trans* isomer **1a'**, thus allowing the characterization and even separation of both isomers. The pyridine adduct **9** and the catechol derivative **10** showed much faster *cis*–*trans* isomerizations than the parent **1a**, while the amino derivative **11** did not isomerize at room temperature even over a timescale of weeks. The X-ray structural analyses of **9** (*cis*) and **9'** (*trans*) unequivocally confirmed the stereochemical assignments.



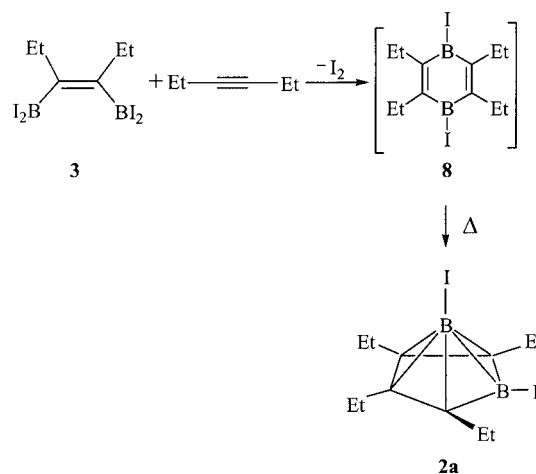
Scheme 6

The second step in the formation of **2a** is the dehalogenation of **1a**. Apart from the one-pot reactions, the stepwise reaction (see Exp. Sect.) also afforded **2a** in a somewhat lower yield (43%). Although we do not have direct evidence for the formation of the borirene intermediate **7**, we found ^{11}B NMR signals for the reaction mixtures which may be assigned to the corresponding 1,4-diboracyclohexadiene **8** (broad signals at ca. 68 and 67 ppm in the formation of **2a** and **2b**, respectively), near to the expected region for 1,4-diboracyclohexadienes (55–65 ppm).^[22]

The redox reaction of **3** with 3-hexyne shown in Scheme 7 (analogous to the preparation of the corresponding 1,3-diiodo-2,3-dihydro-1,3-diborol derivatives^[23] and the 1,4-diiodo-1,4-diboracyclohexene compounds^[24]) indeed afforded the expected carborane **2a**. The reaction mixture showed a broad ^{11}B NMR signal at $\delta = 66$ ppm. As suggested by Schleyer et al.^[17] the straightforward intramolecular rearrangement of 1,4-diboracyclohexa-2,5-dienes into carboranes is forbidden by symmetry and our attempts to separate **8** by distillation led gradually to **2a**, as evidenced by ^{11}B NMR spectroscopy and EI-MS (see Exp. Sect.). Although this redox reaction (Scheme 7) represents a new route to the corresponding 1,4-diboracyclohexadienes/ C_4B_2 -*nido*-carboranes, the difficult access to the *cis*-1,2-diborylalkene **3** prevents its practical application.

X-ray Structural Analyses of **2a**, **3**, **9** and **9'**

The structures of the C_4B_2 -*nido*-carboranes were previously examined by electron diffraction studies of the hexa-



Scheme 7

methyl derivative $(\text{MeC})_4(\text{BMe})_2$,^[25] and by microwave spectroscopy^[26] of the parent derivative $(\text{HC})_4(\text{BH})_2$.^[4] The structures were confirmed by X-ray diffraction analyses.^[3c,5f] In 1992, Berndt et al.,^[3c] reported the structure of a benzo-annulated derivative, and in 1996 Herberhold, Wrackmeyer et al.^[5f] published the structure of the first example of an “undisturbed” pentamethyl-*nido*- C_4B_2 carborane with an *N*-bonded $[\text{Fe}_2(\text{CO})_6(\mu\text{-NS})]$ complex fragment in the 6-position. Derivatives of a benzo compound^[3c] with transition metal complex fragments coordinated to the benzene ring have also been synthesized.^[6b]

The molecular structure of **2a** is shown in Figure 1. Its C_4B_2 skeleton adopts the expected *nido* structure (C_s symmetry) with an apical six-coordinate boron atom. The B–B bond length of 1.821 Å is similar to, but slightly shorter

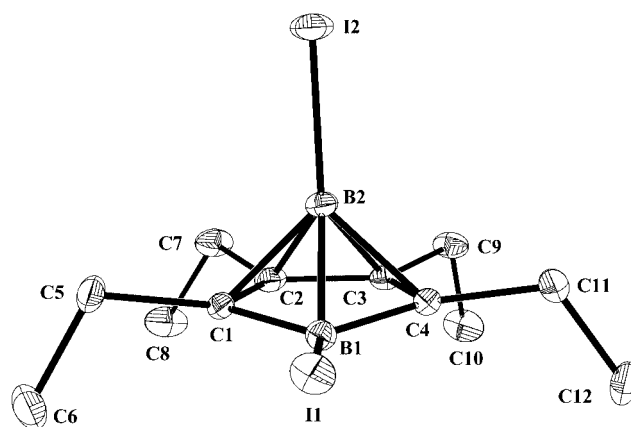


Figure 1. Molecular structure of **2a**, hydrogen atoms omitted for clarity, thermal ellipsoids are shown at the 40% probability level; selected bond lengths [Å] and angles [°]: I1–B1 2.155(3), I2–B2 2.126(3), C1–C2 1.457(4), C2–C3 1.437(4), C3–C4 1.459(3), C1–B1 1.522(3), C4–B1 1.526(4), C1–B2 1.705(4), C2–B2 1.713(4), C3–B2 1.713(4), C4–B2 1.708(4), B1–B2 1.821(4); C2–C1–B1 108.3(2), C1–B1–C4 104.1(2), B1–C4–C3 107.9(2), C4–C3–C2 109.6(2), C3–C2–C1 109.2(2), B2–B1–I1 130.0(2), B1–B2–I2 140.1(2)

than, the corresponding distances in the above-mentioned $(\text{MeC})_4(\text{BMe})[\text{B}(\mu\text{-NS})\text{Fe}_2(\text{CO})_6]^{[5f]}$ (1.836 Å), in the benzoannulated structure^[3c] (1.870 Å) and in the parent derivative $(\text{HC})_4(\text{BH})_2$ ^[26] (1.886 Å). The B2–C distances vary within a narrow range (1.705–1.713 Å), and are also slightly shorter than the values in the examples mentioned^[5f,3c] (1.720–1.743 and 1.673–1.865 Å, respectively), which can be attributed to the different steric environments around the skeleton. The skeletal C–C distances were found to be almost identical (av. 1.451 Å), and are also similar to the average of 1.438 Å in $(\text{MeC})_4(\text{BMe})[\text{B}(\mu\text{-SN})\text{Fe}_2(\text{CO})_6]$. The four skeletal carbon atoms are in one plane, and the four *exo*-polyhedral carbon atoms C5, C7, C9, C11 are bent out of the C_4 plane towards B2 by an average of 0.24 Å. The five-membered C_4B open face is not planar, with B1 lying ca. 0.15 Å below the C_4 plane. The dihedral angle between the C_4 plane and the $\text{C}_2\text{B1}$ plane is ca. 9°. The B–I bond lengths are 2.126 and 2.155 Å, respectively, and are similar to the reported values in some other B-iodinated polyhedral borane and carborane clusters, for example 2.133 Å (av.) in $\text{HNB}_{11}\text{Cl}_5\text{I}_6$,^[27a] 2.09–2.17 Å in polyiodinated *p*-carboranes,^[27b] and also similar to that of 2.10(4) Å in BI_3 .^[28]

The molecular structure of **3** is shown in Figure 2. The two BI_2 groups are in a *cis* arrangement, and the I1 atom is intramolecularly coordinated to B1, forming a unique B–I–B bridge. The boron atom B2 is tri-coordinate and the B2–I4 bond length of 2.107 Å is typical of an I–B(sp^2) distance. B1 is four-coordinate, however, and the B1–I2 and B1–I3 distances are 2.231 and 2.201 Å, respectively, and are very similar to the reported values for I–B(sp^3) bonds, e.g. 2.21(1) Å (av.) in $[\text{Ph}_2\text{PBI}_2]_2$ ^[29a] and 2.229 Å (av.) in $(\text{vi}_3\text{P})\text{BI}_3$ ^[29b] (where vi is vinyl). The B–I bond lengths involving the bridging I1 atom are 2.160 and 2.383 Å, respectively, and the latter is longer than the sum of the covalent radii of the two atoms, indicating that the interaction between B1 and I1 is weak.

Figure 3 (a and b) show the structures of **9** (*cis*) and **9'** (*trans*), respectively. In both structures the boron atom is four-coordinate, adopting a slightly distorted tetrahedral geometry. The bond lengths and angles in both structures are very similar. The B–I bond lengths are 2.269 and 2.306 Å in **9**, and 2.275(3) and 2.294(3) Å in **9'**, respectively, similar to the corresponding values in compound **3**. The corresponding B–N distances of 1.587 Å in **9** and 1.596 Å in **9'**, respectively, are similar to, but slightly shorter than, those found in other pyridine adducts.^[30]

Conclusion

We have developed a one-pot synthesis of 1,6-diiodo-2,3,4,5-tetracarba-*nido*-hexaborane(6) derivatives involving disubstituted alkynes, BI_3 and $\text{NaK}_{2.8}$. Considering the ready availability of the starting materials and the product **2a**, it has been convenient to study the reactivities of such B–I functionalized carboranes and dehalogenation is a practical method for the preparation of carboranes. The formation of **4** from the dehalogenation of **3** confirms that bis(boryl-

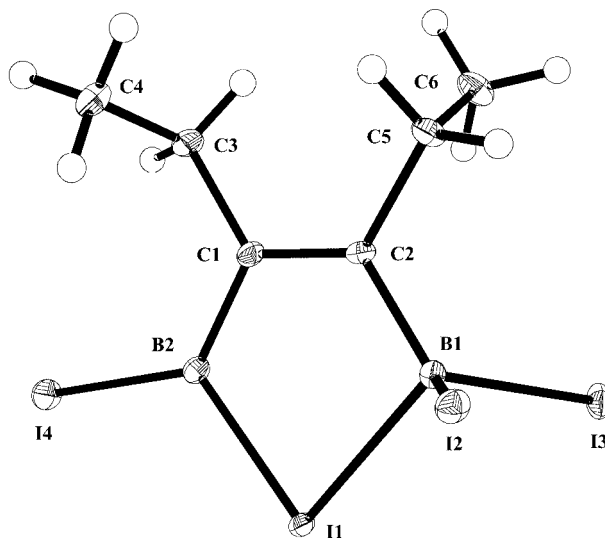


Figure 2. Molecular structure of **3**, thermal ellipsoids are shown at the 40% probability level; selected bond lengths [Å] and angles [°]: I1–B2 2.160(4), I1–B1 2.383(4), I2–B1 2.231(4), I3–B1 2.201(4), I4–B2 2.107(4), B1–C2 1.571(6), B2–C1 1.510(5), C1–C2 1.371(5), B2–I1–B1 81.1(2), C2–B1–I3 117.0(3), C2–B1–I2 111.0(3), I3–B1–I2 112.25(18), C2–B1–I1 102.8(2), I3–B1–I1 105.9(2), I2–B1–I1 106.8(2), C1–B2–I4 127.7(3), C1–B2–I1 113.8(3), I4–B2–I1 118.5(2), C2–C1–B2 118.5(3), C1–C2–B1 123.5(3).

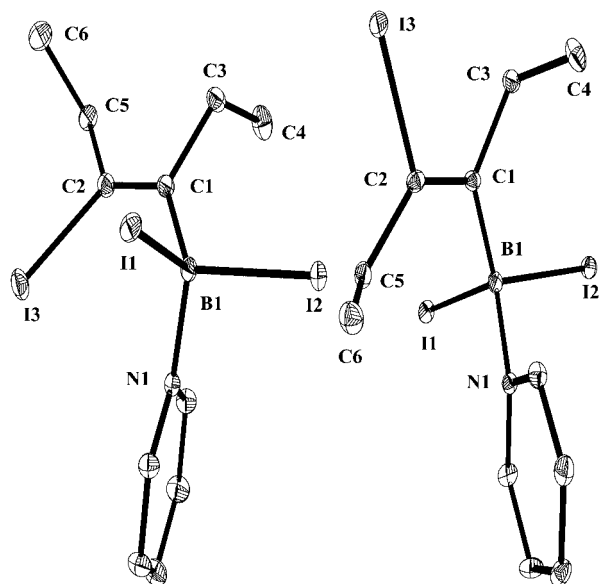


Figure 3. a) (left) Molecular structure of **9**, hydrogen atoms omitted for clarity, thermal ellipsoids are shown at the 40% probability level; selected bond lengths [Å] and angles [°]: I1–B1 2.269(3), I2–B1 2.306(3), I3–C2 2.141(3), N1–B1 1.587(4), B1–C1 1.600(4), C1–C2 1.343(4), N1–B1–C1 114.4(2), N1–B1–I1 111.8(2), C1–B1–I1 109.2(2), N1–B1–I2 101.4(2), C1–B1–I2 113.6(2), I1–B1–I2 106.1(1). b) (right) Molecular structure of **9'**, hydrogen atoms omitted for clarity, thermal ellipsoids are shown at the 40% probability level; selected bond lengths [Å] and angles [°]: I1–B1 2.275(3), I2–B1 2.294(3), I3–C2 2.160(3), N1–B1 1.596(4), B1–C1 1.607(4), C1–C2 1.342(4), N1–B1–C1 114.8(2), N1–B1–I1 111.3(2), C1–B1–I1 109.7(2), N1–B1–I2 100.8(2), C1–B1–I2 114.0(2), I1–B1–I2 105.7(1).

alkenes) are the precursors of *nido*-C₄B₄ carboranes. Such dehalogenation reactions at room temperature are more complex and give lower yields than at lower temperatures. A possible mechanism of the formation of C₄B₂-*nido*-hexaboranes(6) has been proposed and studied using **2a** as a representative example. The stereochemistry of the iodoboration product of the alkyne has been clarified as *cis*, using a more direct method than acetolysis, and the *cis-trans* isomerization exists in the addition product **1a** and some of the derivatives.

Experimental Section

All reactions and manipulations were performed in dry glassware under argon or nitrogen using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. NMR: Bruker DRX 200 spectrometer; Et₂O·BF₃ was used as the external standard for ¹¹B NMR spectroscopy; as internal references for ¹H and ¹³C NMR spectroscopy, the signals of the deuterated solvent (CDCl₃) were used and calculated relative to TMS. MS: ZAB-2F VH Micromass CTD spectrometer, and a JEOL MS Station JMS 700 spectrometer both using the EI ionization technique. Melting points (uncorrected) were measured with a Büchi apparatus, using capillaries which were filled under nitrogen and sealed.

2,3,4,5-Tetraethyl-1,6-diiodo-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**2a**). Formation from 3-Hexyne, BI₃ (1 equiv.) and NaK_{2.8}

a) One-Pot Procedure: To a solution of BI₃ (872 mg, 2.23 mmol) in hexane (40 mL) at -78°C was added 3-hexyne (190 mg, 2.3 mmol) dropwise, and NaK_{2.8} (0.9 mL, excess) was then added with a syringe. The mixture was stirred for ca. 15 min, and the cooling bath was then removed. The reaction mixture was warmed to ambient temperature, stirred overnight, and then filtered (G4 frit) and the residue washed with hexane (2 × 15 mL). The solvent of the yellow filtrate was removed in vacuo, leaving a yellow viscous oil. Distillation at $80^{\circ}\text{C}/2 \times 10^{-3}$ Torr gave **2a** (326 mg, 66%) as a yellow, air-sensitive oil, which slowly solidified. For reactions with up to 28 mmol of BI₃, longer reaction times (1 week) were needed (av. yield > 60%, m.p. 52°C). ¹H NMR (CDCl₃, 200 MHz): δ = 1.20 (t, ³J_{H,H} = 7.6 Hz, 6 H, CH₃), 1.26 (t, ³J_{H,H} = 7.6 Hz, 6 H, CH₃), 1.87–2.04 (m), 2.11–2.38 (m, 8 H, CH₂) ppm. ¹¹B NMR (CDCl₃, 64 MHz): δ = 5.5 (s, B_{basal}, 1 B), -52.5 (s, B_{apical}, 1 B) ppm. ¹¹B NMR (C₆D₆, 64 MHz): δ = 5.9 (s, B_{basal}, 1 B), -52.4 (s, B_{apical}, 1 B) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ = 13.5, 14.2 (CH₃), 18.9, 20.4 (CH₂), 114.2 ppm (skeletal carbon atoms non-adjacent to the basal boron), the signals for the other basal carbon atoms not observed. EI-MS: m/z (%) = 440 (100) [M⁺], 313 (20.3) [M⁺ – I]. HR-MS (EI): m/z = 439.9842 [M⁺]. Calcd. For ¹²C₁₂¹H₂₀¹¹B₂¹²⁷I₂ 439.9840 (Δm = 0.2 mmu).

b) Stepwise Procedure: To a solution of BI₃ (2.165 g, 5.53 mmol) in hexane (50 mL) was added dropwise 3-hexyne (470 mg, 5.7 mmol) at -50°C , and the resultant solution was warmed to ambient temperature. The resultant red solution (¹¹B NMR: δ = 40.5 ppm) was cooled to -60°C again and NaK_{2.8} (2 mL) was added with a syringe. The workup procedure which followed was similar to that of the one-pot procedure and yielded **2a** (520 mg, 43%).

Reactions of 3-Hexyne with BI₃ (2 equiv.) and NaK_{2.8} at Different Temperatures

a): A solution of BI₃ (858 mg, 2.19 mmol) in hexane (35 mL) was added dropwise to a mixture of 3-hexyne (90 mg, 1.1 mmol) and

NaK_{2.8} (0.9 mL) at room temp. The reaction mixture became gray in ca. 20 min, and was stirred for 1 day, then filtered (G4 frit). The residue was washed with hexane (2 × 15 mL), and the slightly pink filtrate was dried in vacuo, leaving a red-brown oil (238 mg), which was a mixture of **2a**, **4** and **5**. EI-MS: m/z (%) = 440 (100) (**2a**), 716 (3.35) (**4**), and 771 (44.83) (**5**). HR-MS (EI): m/z = 439.9847 (**2a**); calcd. for ¹²C₁₂¹H₂₀¹¹B₂¹²⁷I₂ 439.9840 (Δm = 0.6 mmu), m/z = 715.8150 (**4**); calcd. for ¹²C₁₂¹H₂₀¹¹B₄¹²⁷I₄ 715.8116 (Δm = 3.4 mmu), m/z = 715.6464 (**5**); calcd. for ¹²C₆¹H₁₀¹¹B₅¹²⁷I₅ 715.6472 (Δm = -0.8 mmu).

b): To a solution of BI₃ (3.126 g, 7.98 mmol) in hexane (30 mL) at -78°C was added 3-hexyne (332 mg, 4.04 mmol) dropwise. The mixture immediately became yellow-brown, and NaK_{2.8} (2 mL) was then added with a syringe. The reaction mixture was stirred at -78°C for ca. 10 min, the cooling bath was removed, and the mixture was warmed to ambient temperature and stirred for 1 day. The mixture was then filtered (G4 frit), and the residue washed with hexane (2 × 15 mL). The yellow filtrate was dried in vacuo, leaving a yellow viscous oil, which was distilled to give **2a** (455 mg, 51%) as the single carborane product. In this case, no hexaethylbenzene was detected.

Formation of 2a from the Redox Reaction of 3-Hexyne and 3: 3-Hexyne (196 mg, 2.3 mmol) was added dropwise to a solution of **3** (1.357 g, 2.22 mmol) in hexane (25 mL) at -60°C . The mixture was warmed to ambient temperature during which time it became deep brown indicating the formation of I₂. The ¹¹B NMR spectrum showed a signal at δ = 66 ppm. All the volatiles were removed in vacuo and the resultant red oil was distilled at $71^{\circ}\text{C}/8 \times 10^{-2}$ Torr to give a yellowish oil (533 mg, 55%), which gradually became deep red. The ¹¹B NMR (C₆D₆, 64 MHz) data of the original distillate: δ = 57.6 (s), 45.7, 5.9, -9.0 (BI₃), -52.4 ppm; after three days, the corresponding signals were: δ = 57 (s), 32, 5.9, -52.4 ppm; after three weeks, there were only two ¹¹B NMR signals: δ = 5.9, -52.4 ppm (**2a**). The EI-MS spectrum was identical to that of authentic **2a**.

1,6-Diiodo-2,3,4,5-tetramethyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (2b**):** Same procedures as described for **2a**. 2-Butyne (426 mg, 7.9 mmol), BI₃ (3.09 g, 7.9 mmol), NaK_{2.8} (2 mL). The final yellow viscous oil was distilled at $95^{\circ}\text{C}/3 \times 10^{-2}$ Torr to give **2b** (225 mg, 15%) as a yellowish solid; m.p. $92-94^{\circ}\text{C}$. ¹H NMR (CDCl₃, 200 MHz): δ = 1.72 (s, 6 H, CH₃), 1.87 (s, 6 H, CH₃) ppm. ¹¹B NMR (CDCl₃, 64 MHz): δ = 5.7 (s, B_{basal}), -48.6 (s, B_{apical}) ppm. ¹³C NMR (CDCl₃, 50 MHz): δ = 11.29, 12.55 (CH₃), 110.7 ppm (skeletal carbon atoms non-adjacent to basal boron), the signals for the other basal carbon atoms not observed. EI-MS: m/z (%) = 384 (94) [M⁺], 257 (100) [M⁺ – I]. HR-MS (EI): m/z = 383.9218 [M⁺]; calcd. for ¹²C₈¹H₁₂¹¹B₂¹²⁷I₂ 383.9215 (Δm = 0.3 mmu).

1,6-Diiodo-2,3,4,5-tetraphenyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (2c**):** Same procedures as described for **2a**. Diphenylacetylene (1.38 g, 7.7 mmol), BI₃ (3.03 g, 7.7 mmol), NaK_{2.8} (1.6 mL). The yellow filtrate was cooled, and some yellow solid (mainly hexaphenylbenzene) was filtered, and the yellow filtrate was dried in vacuo to give **2c** (147 mg, ca. 5%) and a small amount of hexaphenylbenzene as an orange yellow solid. ¹¹B NMR (CD₂Cl₂, 64 MHz): δ = 7.9 (s, B_{basal}), -50.1 (s, B_{apical}), (δ = 8.2 and -49.6 ppm in CDCl₃) ppm. EI-MS: m/z (%) = 632 (100) [M⁺], 505 (69.6) [M⁺ – I]. HR-MS (EI): m/z = 631.9855 [M⁺]; calcd. for ¹²C₂₈¹H₂₀¹¹B₂¹²⁷I₂ 631.9841 (Δm = 1.4 mmu).

***cis*-3,4-Bis(diiodoboryl)-3-hexene (**3**):**^[11a] A portion of 3,4-bis(di-chloroboryl)-3-hexene (**6**) (2.13 g, 8.7 mmol) was added to BI₃

(4.653 g, 11.9 mmol) at room temperature. The resultant dark brown solution was stirred at room temperature for ca. 2.5 h. The reaction flask was connected to a condensation apparatus, the trap cooled to -78°C , and the system was kept at ca. 60 mbar overnight. All volatiles were then removed under high vacuum, and the resultant dark brown residue was recrystallized five times from hexane (ca. 20 mL), four times at -84°C , and the last time at -28°C . Compound **3** (2.53 g, 47.5%) was obtained as a yellow crystalline solid, which can be kept at -28°C for a long period of time, m.p. $70-72^{\circ}\text{C}$. ^1H NMR (C_6D_6 , 200 MHz): $\delta = 1.02$ (t, $^3J_{\text{H,H}} = 7.5$ Hz, 6 H, CH_3), 2.29 (q, $^3J_{\text{H,H}} = 7.5$ Hz, 4 H, CH_2) ppm. ^{11}B NMR (C_6D_6 , 64 MHz): $\delta = 11.8$ ppm. ^{13}C NMR (C_6D_6 , 50 MHz): $\delta = 14.8$ (CH_3), 26.2 (CH_2), 178.4 ($\text{C}=\text{C}$) ppm. EI-MS: m/z (%) = 485 (100) [$\text{M}^+ - \text{I}$]. HR-MS (EI): $m/z = 484.8128$ [$\text{M}^+ - \text{I}$]; calcd. For $^{12}\text{C}_6^{1}\text{H}_{10}^{11}\text{B}_2^{127}\text{I}_3$ 484.8103 ($\Delta m = 2.5$ mmu). $\text{C}_6\text{H}_{10}\text{B}_2\text{I}_4$ (611.4): calcd. C 11.79, H 1.65; found C 12.23, H 1.61.

Tetraethyltetraiodotetracarba-nido-octaborane(8) (4): To a solution of **3** (2.3 g, 3.76 mmol) in hexane (40 mL) at -65°C was added $\text{NaK}_{2.8}$ (1.5 mL, excess) dropwise with a syringe. After ca. 1 h the cooling bath was removed, and the reaction mixture was warmed to room temperature and stirred for 3 days. The reaction mixture was filtered (G4 frit) and the residue washed with hexane (2×15 mL), the light yellow filtrate dried in vacuo, leaving a yellow viscous oil which slowly solidified, containing **4** (385 mg, 28.6%) and a trace amount of **5**. ^{11}B NMR (CDCl_3 , 64 MHz): $\delta = -10.5$ (s, 2 B), -13.4 (s, 2 B) ppm. EI-MS: m/z (%) = 716 (100) [M^+] (**4**), 589 (91.7) [$\text{M}^+ - \text{I}$], 771(4.3) [M^+] (**5**). HR-MS (EI): $m/z = 715.8112$ [M^+]; calcd. For $^{12}\text{C}_{12}^{1}\text{H}_{20}^{11}\text{B}_4^{127}\text{I}_4$ 715.8117 ($\Delta m = -0.5$ mmu). $m/z = 771.6440$ [M^+]; Calcd. For $^{12}\text{C}_6^{1}\text{H}_{10}^{11}\text{B}_5^{127}\text{I}_5$ 771.6471 ($\Delta m = -3.1$ mmu).

cis-3-Diiodoboryl-4-iodo-3-hexene (1a):^[9,18] The procedure in the literature was slightly modified. To a solution of BI_3 (3.245 g, 8.3 mmol) in pentane (50 mL) was added 3-hexyne (681 mg, 8.3 mmol) dropwise at -25°C . The red mixture was warmed to ambient temperature and the deep pink solution was transferred to another flask, leaving a little black solid on the wall of the original flask. The solution was dried in vacuo to give analytically pure **1a** almost quantitatively as a deep red liquid. ^1H NMR (CDCl_3 , 200 MHz): $\delta = 1.08$ (t, $^3J_{\text{H,H}} = 7.4$ Hz, 3 H, CH_3), 1.22 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 3 H, CH_3), 2.15 (q, $^3J_{\text{H,H}} = 7.6$ Hz, 2 H, CH_2), 2.62 (q, $^3J_{\text{H,H}} = 7.4$ Hz, 2 H, CH_2) ppm. ^{11}B NMR (CDCl_3 , 64 MHz): $\delta = 40.0$ ppm. ^{13}C NMR (CDCl_3 , 50 MHz): $\delta = 14.2$, 15.0 (CH_3), 24.7, 33.3 (CH_2), 106.4 ($=\text{C}-\text{I}$), 157.6 (br., $=\text{C}-\text{B}$) ppm.

trans-3-Diiodoboryl-4-iodo-3-hexene (1a'): Slow isomerization of **1a** (*cis*) at room temperature afforded **1a'** (not complete within 5 weeks as indicated by NMR in a CDCl_3 solution, with partial decomposition). ^1H NMR (CDCl_3 , 200 MHz): $\delta = 1.08$ (t, $^3J_{\text{H,H}} = 7.2$ Hz, 3 H, CH_3), 1.15 (t, $^3J_{\text{H,H}} = 6.7$ Hz, 3 H, CH_3), 2.2 (q, $^3J_{\text{H,H}} = 7.2$ Hz, 2 H, CH_2), 2.61 (q, $^3J_{\text{H,H}} = 6.7$ Hz, 2 H, CH_2) ppm. ^{11}B NMR (CDCl_3 , 64 MHz): $\delta = 43.5$ ppm. ^{13}C NMR (CDCl_3 , 50 MHz): $\delta = 12.8$, 14.0 (CH_3), 33.6, 39.1 (CH_2), 114.6 ($=\text{C}-\text{I}$), 158.1 (br., $=\text{C}-\text{B}$) ppm.

cis-3-Diiodoboryl-4-iodo-3-hexene-Pyridine Adduct (9): Pyridine (223 mg, 2.8 mmol) was added dropwise to a solution of **1a** (1.33 g, 2.8 mmol) in hexane (25 mL) at -25°C . The color immediately turned to deep red and a yellow precipitate then appeared. The mixture was warmed to room temperature, the solvent removed in vacuo, and an orange-yellow powder **9** was obtained quantitatively. The X-ray quality crystals were grown from a toluene solution at -28°C . M.p. 30°C . ^1H NMR (CDCl_3 , 200 MHz): $\delta = 1.05$ (t, $^3J_{\text{H,H}} = 7.4$ Hz, 3 H, CH_3), 1.29 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 3 H, CH_3),

2.77 (q, $^3J_{\text{H,H}} = 7.4$ Hz, 2 H, CH_2), 2.86 (q, $^3J_{\text{H,H}} = 7.4$ Hz, 2 H, CH_2), 7.70 (m), 8.19(m), 9.39 (m) (py-H) ppm. ^{11}B NMR (CDCl_3 , 64 MHz): $\delta = -13.9$ ppm. ^{13}C NMR (CDCl_3 , 50 MHz): $\delta = 14.4$, 14.9 (CH_3), 32.4, 39.5 (CH_2), 115.2 ($=\text{C}-\text{I}$), 126.6, 142.4, 147.6 ppm (py-C), the signal of the boron-bound carbon was not observed.

trans-3-Diiodoboryl-4-iodo-3-hexene-Pyridine Adduct (9'): Slow isomerization of **9** (*cis*) at room temperature afforded **9'** within one week as yellow crystals from a CH_2Cl_2 solution. M.p. $108-110^{\circ}\text{C}$, dec. ^1H NMR (CDCl_3 , 200 MHz): $\delta = 0.74$ (t, $^3J_{\text{H,H}} = 7.4$ Hz, 3 H, CH_3), 1.25 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 3 H, CH_3), 1.94 (q, $^3J_{\text{H,H}} = 7.2$ Hz, 2 H, CH_2), 2.98 (q, $^3J_{\text{H,H}} = 7.4$ Hz, 2 H, CH_2), 7.76 (m), 8.26(m), 9.47 (m) (py-H) ppm. ^{11}B NMR (CDCl_3 , 64 MHz): $\delta = -20.8$ ppm. $^{13}\text{C}\{^{11}\text{B}\}$ NMR (CDCl_3 , 50 MHz): $\delta = 12.9$, 13.7 (CH_3), 38.8, 45.3 (CH_2), 120.0 ($=\text{C}-\text{I}$), 126.4, 142.9, 146.9 (py-C), 147.9 ($=\text{C}-\text{B}$) ppm. The EI-MS failed to give definite information.

cis-3-(1,3,2-Benzodioxaborol-2-yl)-4-iodo-3-hexene (10): A solution of **1a** (730 mg, 1.54 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of catechol (169 mg, 1.54 mmol) in CH_2Cl_2 (15 mL) at -45°C . The reaction mixture was warmed to ambient temperature and the solvent removed in vacuo to give 455 mg (90%) of **10** as a deep red liquid. ^1H NMR (CDCl_3 , 200 MHz): $\delta = 1.10$ (t, $^3J_{\text{H,H}} = 7.6$ Hz, 3 H, CH_3), 1.17 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 3 H, CH_3), 2.43 (q, $^3J_{\text{H,H}} = 7.6$ Hz, 2 H, CH_2), 2.73 (q, $^3J_{\text{H,H}} = 7.4$ Hz, 2 H, CH_2), 7.10- 7.33 (m, 4 H, C_6H_4) ppm. ^{11}B NMR (CDCl_3 , 64 MHz): $\delta = 31.1$ ppm. ^{13}C NMR (CDCl_3 , 50 MHz): $\delta = 12.9$, 14.4 (CH_3), 26.7, 35.7 (CH_2), 110.1 ($=\text{C}-\text{I}$), 112.7, 122.8, 147.9 ppm (C_6H_4), the boron-bound carbon n.o. ppm. EI-MS: m/z (%) = 328 (50.6) [M^+], 246 (100) [$\text{M}^+ - \text{C}_6\text{H}_{10}$], 201 (99.8) [$\text{M}^+ - \text{I}$]. HR-MS (EI): $m/z = 328.0116$ [M^+]; calcd. For $^{12}\text{C}_{12}^{1}\text{H}_{14}^{11}\text{B}^{127}\text{I}^{16}\text{O}_2$ 328.0131 ($\Delta m = -1.5$ mmu).

trans-3-(1,3,2-Benzodioxaborol-2-yl)-4-iodo-3-hexene (10'): The isomerization of **10** (*cis*) at room temperature afforded **10'** within ca. 3 weeks (as indicated by NMR in a CDCl_3 solution). ^1H NMR (CDCl_3 , 200 MHz): $\delta = 1.12$ (t, $^3J_{\text{H,H}} = 7.6$ Hz, 3 H, CH_3), 1.27 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 3 H, CH_3), 2.60 (q, $^3J_{\text{H,H}} = 7.4$ Hz, 2 H, CH_2), 3.22 (q, $^3J_{\text{H,H}} = 7.6$ Hz, 2 H, CH_2), 7.12- 7.33 (m, 4 H, C_6H_4) ppm. ^{11}B NMR (CDCl_3 , 64 MHz): $\delta = 29.1$ ppm. ^{13}C NMR (CDCl_3 , 50 MHz): $\delta = 13.3$, 15.6 (CH_3), 36.6, 39.9 (CH_2), 112.2 ($=\text{C}-\text{I}$), 112.6, 122.9, 147.9 ppm (C_6H_4), the boron-bound carbon n.o.

cis-3-(Diisopropylamino)iodoboryl-4-iodo-3-hexene (11): Diisopropylamine (1.07 g, 10.6 mmol) was added dropwise to a solution of **1a** (2.45 g, 5.2 mmol) in hexane (50 mL) at -40°C . The mixture was warmed to ambient temperature and filtered, the light yellow filtrate was dried in vacuo to give a red oil, which was distilled at $82^{\circ}\text{C}/5.9 \times 10^{-2}$ Torr to give yellow **11** (1.8 g, 76%). ^1H NMR (CDCl_3 , 200 MHz): $\delta = 1.04$ (t, $^3J_{\text{H,H}} = 7.3$ Hz, 3 H, Et CH_3), 1.14 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 3 H, Et CH_3), 1.24 (d, $^3J_{\text{H,H}} = 6.7$ Hz, 3 H, *i*Pr CH_3), 1.30 (d, $^3J_{\text{H,H}} = 6.7$ Hz, 3 H, *i*Pr CH_3), 1.49 (d, $^3J_{\text{H,H}} = 7.2$ Hz, 3 H, *i*Pr CH_3), 1.54 (d, $^3J_{\text{H,H}} = 7.2$ Hz, 3 H, *i*Pr CH_3), 2.10 (m, 1 H, Et CH_2), 2.31 (m, 1 H, Et CH_2), 2.53 (q, $^3J_{\text{H,H}} = 7.4$ Hz, 2 H, Et CH_2), 3.53 (sept, 1 H, *i*Pr CH), 3.95 (sept, 1 H, *i*Pr CH) ppm. ^{11}B NMR (CDCl_3 , 64 MHz): $\delta = 28.1$ ppm. ^{13}C NMR (CDCl_3 , 50 MHz): $\delta = 14.2$, 14.3, (Et CH_3), 21.0, 22.1, 23.0, 24.0 (*i*Pr CH_3), 25.5, 34.2 (Et CH_2), 47.8, 53.9 (*i*Pr CH), 110.1 ppm ($=\text{C}-\text{I}$), the boron-bound carbon n.o. EI-MS: m/z (%) = 447 (2.4) [M^+], 320 (100) [$\text{M}^+ - \text{I}$], 238 (39.8) [$\text{M}^+ - \text{I} - 2\text{C}_3\text{H}_5$]. HR-MS (EI): $m/z = 447.0079$ [M^+]; calcd. for $^{12}\text{C}_{12}^{1}\text{H}_{24}\text{N}^{11}\text{B}^{127}\text{I}_2$ 447.0091 ($\Delta m = -1.2$ mmu).

X-ray Structural Determinations: Crystal data and details of the structural determinations are listed in Table 1. The intensity data

Table 1. Crystal data and structure refinement for **2a**, **3**, **9** and **9'**

	2a	3	9	9'
Empirical formula	C ₁₂ H ₂₀ B ₂ I ₂	C ₆ H ₁₀ B ₂ I ₄	C ₁₁ H ₁₅ BI ₃ N	C ₁₁ H ₁₅ BI ₃ N
Molecular weight	439.70	611.36	552.75	552.75
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	Pna2 ₁	P2 ₁ /n	P2 ₁ /n	Pbca
<i>a</i> (Å)	12.1078(7)	11.9871(7)	11.0923(9)	8.6602(4)
<i>b</i> (Å)	14.3226(8)	7.7401(4)	12.0214(10)	14.2028(7)
<i>c</i> (Å)	9.2587(5)	14.8450(9)	11.8779(10)	24.8358(13)
α [°]	90	90	90	90
β [°]	90	102.841(1)	92.848(2)	90
γ [°]	90	90	90	90
<i>V</i> (Å ³)	1605.6(2)	1342.9(2)	1581.9(2)	3054.8(3)
<i>Z</i>	4	4	4	8
<i>d</i> _{calcd.} [g cm ⁻³]	1.819	3.024	2.321	2.404
μ (Mo-K α) [mm ⁻¹]	3.89	9.236	5.905	6.116
<i>F</i> (000)	832	1072	1008	2016
Crystal size [mm]	0.45 × 0.15 × 0.08	0.37 × 0.25 × 0.16	0.45 × 0.36 × 0.25	0.25 × 0.15 × 0.12
Θ_{max} [°]	32.0	32.0	32.0	32.0
Index ranges <i>h</i> , <i>k</i> , <i>l</i>	0/17, 0/21, -13/13	-17/17, 0/11, 0/21	-16/16, 0/17, 0/17	0/12, 0/21, 0/36
Reflections collected	14404	412363	14891	29275
Independent (<i>R</i> int)	5198 (0.0274)	4559(0.0279)	5345(0.0270)	5281(0.0374)
No. of parameters	226	145	205	205
GooF	1.050	1.106	1.117	1.095
<i>R</i> 1(<i>I</i> > 2 σ <i>I</i>)	0.0219	0.0289	0.0273	0.0245
<i>wR</i> 2 (all reflections)	0.0526	0.0734	0.0714	0.0592
Resid. electron density [e·Å ⁻³]	1.240/ -0.518	2.265/ -2.149	1.476/ -2.388	1.695/ -0.694

for **2a**, **3**, **9**, **9'** were collected with a Bruker AXS Smart CCD diffractometer at 103(2) K (graphite-monochromated Mo-K α radiation, λ = 0.71073 Å, ω -scans). Data were corrected for Lorentz polarization and absorption effects (semiempirical, SADABS^[31]). The structures were solved by direct methods (SHELXS-86)^[32] and refined by least-squares methods based on *F*² with all measured reflections (SHELXL-97).^[32] All non-hydrogen atoms were refined anisotropically. CCDC-219079 (for **2a**), -219080 (for **3**), -219081 (for **9**) and -219082 (for **9'**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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