Reactivity Studies on 2,3,4,5-Tetraethyl-1,6-diiodo-2,3,4,5-tetracarba-*nido*-hexaborane(6): Synthesis and Structures of New C_4B_2 *nido*-Carborane Derivatives

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Dedicated to Professor Manfred T. Reetz on the occasion of his 60th birthday

Keywords: Boron / Carboranes / Nucleophilic substitution / Iron / Cobalt

The reactivity of the title compound 2,3,4,5-tetraethyl-1,6-diiodo-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**1**) towards a variety of nucleophiles is reported. When **1** is treated with RC_2Li (R = Ph, *t*Bu, $SiMe_3$, *p*-tolyl) and Ph_2PLi, the corresponding new C_4B_2 *nido*-carborane derivatives **2a**–**d** and **3**, respectively, are obtained by selective substitution at the basal B–I group, whereas the apical B–I bond remains inert. The reaction of **1** with $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ affords the novel species **4**, which contains a $CpFe(CO)_2$ fragment σ-bonded to the basal boron atom of the C_4B_2 cluster. Attempts to isolate **4** by chromatography on silica gel led to cleavage of the Fe–B bond and formation of compound **5**, containing a basal BH vertex, which can be separately prepared by the reaction of **1** and $LiBEt_3H$. In the reactions of **1** with PhLi and Me_3SnLi, respectively, **6a** and **7a** are formed as the predominant B6-substituted carborane products. In addition, trace amounts of 1,6-disubstituted species **6b** and **7b** are also detected. The substitution at the apical B–I group in **2a** with an alkynyl group is effected by a Pd^0-catalyzed Negishi-type cross-coupling reaction to give compound **8**. The reaction of **1** and monolithio-*o*-carborane affords the C_4B_2–C_2B_{10} carborane **10**, while the reaction of **2a** and $Co_2(CO)_8$ furnishes the double cluster **9** (C_4B_2–C_2Co_2). In both **9** and **10** two different types of clusters are directly connected by a B–C bond. Compound **1** reacts with $ClZnC_6H_4C_6H_4ZnCl$ in the presence of the catalyst $Pd(PPh_3)_4$ to give **11**, in which two C_4B_2 clusters are linked by a $C_6H_4C_6H_4$ unit. The constitutions of the products follow from spectroscopic data, and X-ray diffraction analyses for **2a**, **2d**, **4**, **8**, **9**, and **10**.

Introduction

Although peralkylated 2,3,4,5-tetracarba-*nido*-hexaboranes(6)[1] are more stable than the parent compound $C_4B_2H_6$,[2] and are readily available by a variety of methods, their reactivity has only recently been studied.[3,4] To investigate substitution reactions in C_4B_2 *nido*-carboranes, functional groups at the boron atom(s) other than alkyl groups are needed. Wrackmeyer et al. were able to obtain 1,6-dibromo-2,3,4,5-tetracarba-*nido*-hexaboranes(6)[3a] 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 reaction between peralkylated 2,3,4,5-tetracarba-*nido*-hexaboranes(6) and an excess of BBr_3, whereby the corresponding B6-bromo-substituted carboranes were formed.[3b] Nucleophiles were found to replace the basal B6-bromo atom to give the corresponding carboranes with organyl,[3c]stannyl,[3d] diphenylphosphanyl[3e] as well as the *N*-bonded $(\mu\text{-NS})Fe_2(CO)_6$ [3f] group. In the 1,6-dibromo case, substitution with the *N*-bonded $(\mu\text{-NS})Fe_2(CO)_6$ cluster took place at the basal B−Br bond, an excess of the nucleophile did not induce additional substitution at the 1-position.[3f]

Berndt et al.[4] have reported that the reduction of *nido*-$(Me_3SiC)_2(CH)_2(BtBu)_2$ with Li in tetrahydrofuran affords a novel 1,3-diborabenzene anion, which could in turn be oxidized to give the starting carborane in refluxing 1,2-dibromoethane. As part of reactivity studies, we have reported transition metal derivatives of a benzo-C_4B_2 *nido*-carborane compound[5a] with metal complex fragments coordinated to the benzene ring.[5b] Very recently we have developed a convenient one-pot synthesis of 2,3,4,5-tetraalkyl-1,6-diiodo-2,3,4,5-tetracarba-*nido*-hexaborane(6) derivatives,[6] involving disubstituted alkynes, BI_3 and $NaK_{2.8}$. In this paper, we report the reactivity of the title compound **1** towards a variety of nucleophiles, and characterization of the resulting new carboranes.

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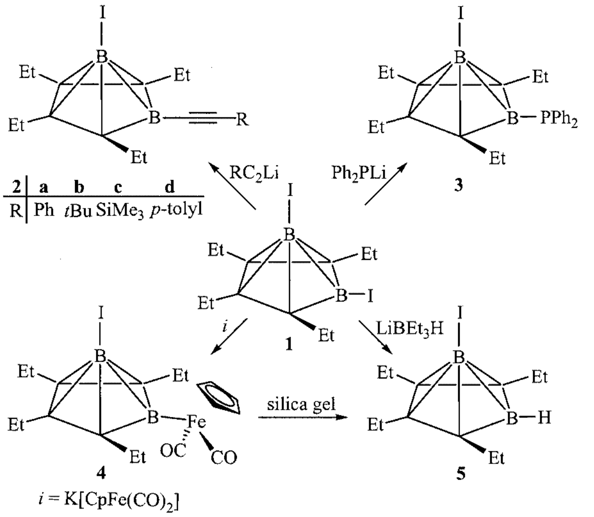
Results and Discussion

Regiospecific Substitution at the Basal Boron Atom

Nucleophilic substitution reactions of **1** with RC_2Li (R = Ph, *t*Bu, $SiMe_3$, *p*-tolyl) proceed smoothly, and the corresponding basal-boron-substituted carborane derivatives **2a−d** were produced in high yields (Scheme 1). The *nido*-C_4B_2 framework is retained, as little differences have been found in the ^1H and ^{13}C NMR spectra when compared with that of **1**. In the ^{11}B NMR spectra, the basal boron atoms give rise to signals at δ = 9.8−10.9 ppm, which are only slightly shifted downfield from that of **1** (δ = 5.5 ppm), while the shifts of the signals for the apical boron atoms are the same as that for **1** (δ = −52.5 ppm).



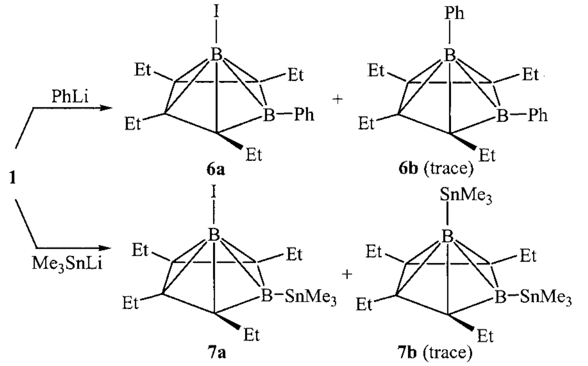
Scheme 1

X-ray structure analyses of **2a** and **2d** confirm the spectroscopic results. In agreement with Herberhold, Wrackmeyer et al.,[3f] an excess of lithium acetylide did not effect additional substitution at the apical boron atoms. Similar results are observed in the reactions of **1** with Ph_2PLi and $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ to give **3** and **4**, respectively, with regiospecific substitution at the basal position. In the ^{11}B NMR spectrum of **3**, the signal of the basal boron atom is shifted downfield by about 9 ppm, while the apical boron atom is unaffected. In the case of **4**, the basal boron atom of the C_4B_2 *nido*-cluster is significantly deshielded (δ = 28.6 ppm), and the signal of the apical boron is slightly shifted to δ = −49.6 ppm. This reveals that the $CpFe(CO)_2$ fragment is directly bonded to the basal boron atom by an Fe−B σ-bond, which is confirmed by an X-ray diffraction study (vide infra). Thus, **4** is the first transition metal derivative of the C_4B_2 *nido*-carborane with direct metal−boron bonding. A few iron derivatives[7] with other carborane or polyborane frameworks of this type have been reported with Fe−B or Fe−C bonding. Cooling of the solution of the crude product in hexane resulted in yellow crystals of **4**, along with an unknown paramagnetic impurity, which makes the NMR spectra not so satisfactory.

The initial isolation of **4** by column chromatography on silica gel led to cleavage of the Fe−B bond to give **5** and paramagnetic impurities. The designed synthesis of **5** is achieved by the separate reaction of **1** with $LiBEt_3H$. No redox reaction between **1** and $(MeS)_2$ takes place, indicating the B−I bonds in **1** are dissimilar to the classical B−I bond of sp^2-hybridized boron atoms, which reacts to give the corresponding B−SMe products.[8]

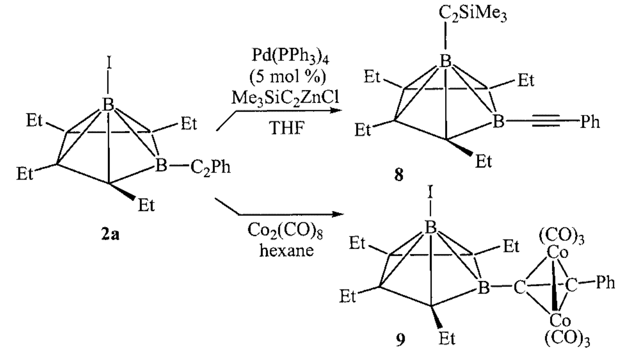
Reactions Involving Substitution at Both Boron Atoms

In the reactions of **1** with more than 2 equiv. of PhLi and Me_3SnLi, respectively (Scheme 2), the B6-substituted products **6a** and **7a** are formed, together with trace amounts of the disubstituted species **6b** and **7b**, as detected by mass spectrometry. For **6a** and **7a**, the ^{11}B NMR signals of the basal boron atoms are shifted downfield to δ = 17.9 and 16.1 ppm, respectively, while the signals of the apical boron atoms are unchanged.



Scheme 2

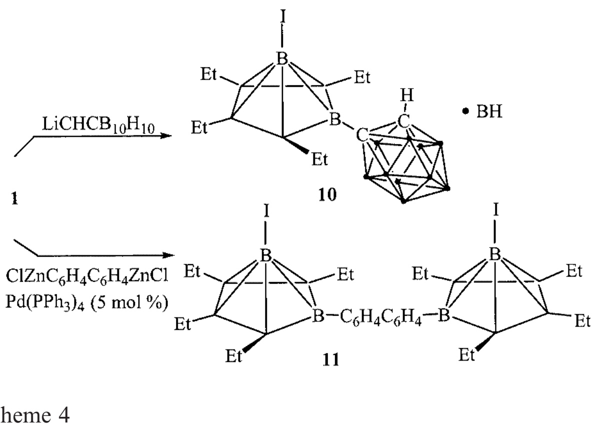
In most of the cases the apical B−I bonds are found to be inert, although its substitution by an alkynyl group has been realized by a Pd^0-catalyzed Negishi-type cross-coupling reaction of **2a** and Me_3SiC_2ZnCl in THF (Scheme 3). Heating of the reaction mixture for 10 d leads to yellow **8**. Interestingly, the ^{11}B NMR signal of the substituted apical boron atom is only slightly shifted downfield to δ = −50.7 ppm. Its structure was established by an X-ray diffraction analysis (see below). The mechanism of such Pd-catalyzed coupling reactions involving B−I bonds[9a] is expected to be similar to that of carbon−carbon cross coupling, however the very first step in the catalytic cycle — the oxidative addition of the B−I bond leading to a B−Pd−I species — has not yet been verified. Stirring of a mixture of **2a** and $Pd(PPh_3)_4$ in THF leads to a brown solution, whose ^{31}P NMR spectrum shows a signal at δ = 22.4 ppm, which is in the expected region $\{[PdIPh(PPh_3)_2]$: δ = 22.3 ppm$\}$.[9b] Its ^{11}B NMR spectrum shows a signal at δ = −36 ppm, which might be due to the formation of the (σ-carboranyl)palladium iodide complex. Shore et al.[10] have studied the reaction of $Pd(PPh_3)_4$ with the iodoborane cluster 9-I-1,7-$(SMe_2)_2B_{12}H_9$ and they observed similar results ($\delta^{31}P$ = 24.2/24.0 ppm).



Scheme 3

Cluster Linkages

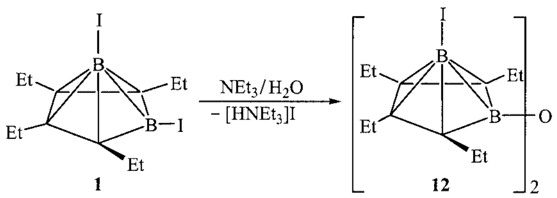
Nucleophilic substitution of *B*-functionalized C_4B_2 *nido*-carboranes by an anionic cluster $(\mu\text{-NS})Fe_2(CO)_6^-$ [3f] has been shown to be an effective way to linked clusters. The reaction of **2a** with $Co_2(CO)_8$, shown in Scheme 3, leads to the deep-brown product **9**, in which the *nido*-C_4B_2 and the C_2Co_2 tetrahedrane cluster are directly joined by a B−C bond at the basal position. In the ^{11}B NMR spectrum, the signal for the basal boron atom is shifted downfield by 6.5 ppm relative to that of **2a**, while the signal for the apical boron atom is only slightly shifted downfield by about 1.5 ppm. The molecular structure of **9** was confirmed by an X-ray diffraction analysis (see below). There are only a few acetylene−$Co_2(CO)_6$ complexes with boron groups attached to the acetylene unit,[11] and two[11b,11c] structurally characterized examples carry B−cat groups (cat = catechol). The C_4B_2−C_2B_{10} linked cluster **10** (Scheme 4) is produced by the reaction of **1** with monolithio-*o*-carborane, in which the C_4B_2 cluster is directly connected to the icosahedral *o*-carborane by a B6−C bond, as confirmed by X-ray diffraction analysis.



Scheme 4

Compound **11** with two C_4B_2 clusters connected by a $C_6H_4C_6H_4$ unit (Scheme 4) is obtained from the reaction of **1** with $ClZnC_6H_4C_6H_4ZnCl$ in the presence of a catalytic amount of $Pd(PPh_3)_4$. It should be noted that the reaction leading to **11** is performed in toluene because the basal B−I bond in **1** is sensitive to THF, resulting first in a yellow and then a deep-green solution. This is significantly different to the bromo derivatives of *nido*-C_4B_2, which have been studied in THF solution.[3d−3f] In compounds **10** and **11** the ^{11}B NMR signals of the basal boron atoms are shifted downfield to δ = 13.9 and 22.0 ppm, respectively, while the apical boron atom is essentially unaffected (δ = −53.4 ppm for **10** and δ = −52.4 ppm for **11**). The MS spectra exhibit the respective molecular ion peaks with the correct isotopic patterns.

The reaction of **1** with $LiC_6H_4C_6H_4Li$ did not yield the expected product **11**, instead the oxygen-bridged species **12** was detected, formed by the hydrolysis of **1**. In the Et_3N/H_2O reaction (Scheme 5), the formed by-product ammonium salt $[Et_3NH]I$, was identified by FAB-MS. Compound **12** was characterized by ^{11}B NMR spectroscopy (δ = 22.1 and −51.9 ppm) and HR-MS which exhibits the molecular ion peak with the correct isotopic pattern.



Scheme 5

X-ray Structure Analyses of 2a, 2d, 4, 8, 9 and 10

The molecular structures of **2a**, **4**, **8**, **9** and **10** are shown in Figures 1, 2, 3, 4, and 5, respectively. As the structure of **2d** (at room temperature) is very similar to that of **2a**, it will not be shown here. In the structures, the C_4B_2 *nido*-carborane frameworks are essentially the same as that of the start-

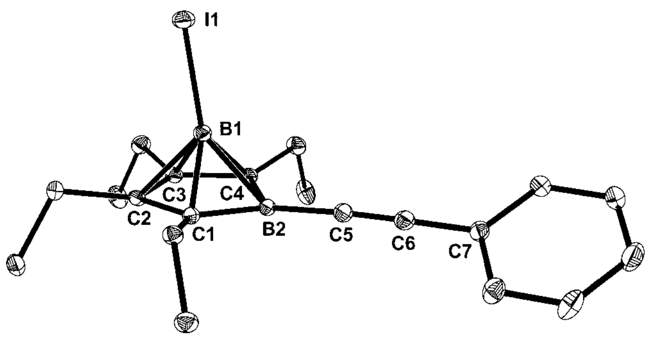


Figure 1. Molecular structure of **2a**; hydrogen atoms omitted for clarity; thermal ellipsoids are shown at 40% probability; selected bond lengths [Å] and angles [°]: I(1)−B(1) 2.139(2), B(1)−C(1) 1.714(3), B(1)−C(2) 1.722(3), B(1)−C(3) 1.714(3), B(1)−C(4) 1.706(3), B(1)−B(2) 1.825(3), B(2)−C(1) 1.537(3), B(2)−C(4) 1.532(3), C(1)−C(2) 1.453(3), C(2)−C(3) 1.446(2), C(3)−C(4) 1.459(3), B(2)−C(5) 1.529(3), C(5)−C(6) 1.211(3), C(6)−C(7) 1.435(3); B(2)−B(1)−I(1) 143.3(1), C(5)−B(2)−B(1) 131.2(2), C(6)−C(5)−B(2) 177.0(2), C(5)−C(6)−C(7) 178.3(2)

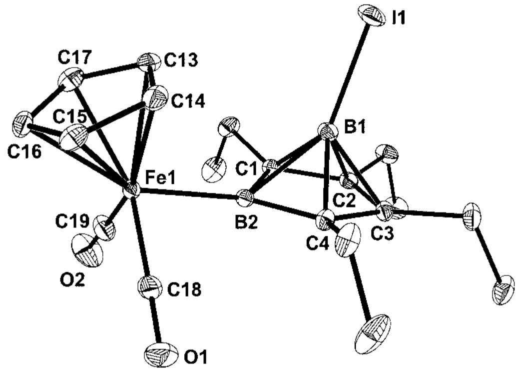


Figure 2. Molecular structure of **4**; hydrogen atoms omitted for clarity; thermal ellipsoids are shown at 40% probability; selected bond lengths [Å] and angles [°]: I(1)−B(1) 2.135(2), B(1)−C(1) 1.692(2), B(1)−C(2) 1.711(2), B(1)−C(3) 1.709(2), B(1)−C(4) 1.689(3), B(1)−B(2) 1.841(3), B(2)−C(1) 1.547(2), B(2)−C(4) 1.547(2), C(1)−C(2) 1.460(2), C(2)−C(3) 1.431(2), C(3)−C(4) 1.468(2), Fe(1)−B(2) 2.069(2), Fe(1)−C(19) 1.739(2), Fe(1)−C(18) 1.742(2), Fe(1)−C_{Cp} 2.094−2.116(2), O(1)−C(18) 1.150(2), O(2)−C(19) 1.151(2); B(2)−B(1)−I(1) 142.91(11), B(1)−B(2)−Fe(1) 133.48(11), C(19)−Fe(1)−C(18) 92.59(10), C(19)−Fe(1)−B(2) 86.26(8), C(18)−Fe(1)−B(2) 85.03(8), O(1)−C(18)−Fe(1) 178.7(2), O(2)−C(19)−Fe(1) 178.6(2)

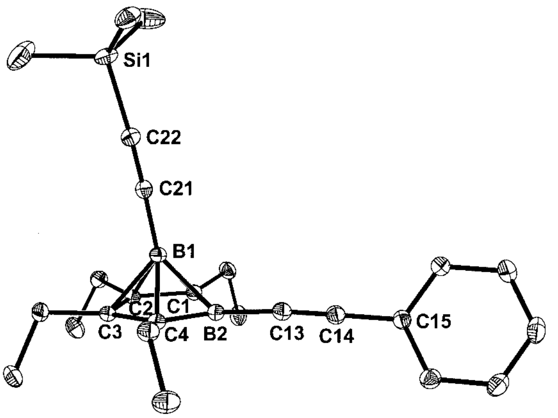


Figure 3. Molecular structure of **8**; hydrogen atoms omitted for clarity; thermal ellipsoids are shown at 40% probability; selected bond lengths [Å] and angles [°]: B(1)−C(1) 1.723(2), B(1)−C(2) 1.735(2), B(1)−C(3) 1.734(2), B(1)−C(4) 1.731(2), B(1)−B(2) 1.833(2), B(2)−C(1) 1.532(2), B(2)−C(4) 1.532(2), C(1)−C(2) 1.455(2), C(2)−C(3) 1.440(2), C(3)−C(4) 1.452(2), B(2)−C(13) 1.536(2), C(13)−C(14) 1.207(2), C(14)−C(15) 1.438(2), B(1)−C(21) 1.522(2), C(21)−C(22) 1.205(2); C(21)−B(1)−B(2) 142.49(10), C(13)−B(2)−B(1) 132.30(10), C(14)−C(13)−B(2) 175.39(13), C(13)−C(14)−C(15) 178.79(13), C(22)−C(21)−B(1) 177.62(12) C(21)−C(22)−Si(1) 175.45(12)

ing carborane **1**.[6] The B−I bond lengths in **2a** (2.139 Å), **2d** (2.119 Å), **4** (2.135 Å), **9** (2.121 Å) and **10** (2.125 Å) are very similar to the corresponding value (2.126 Å) in **1** despite the B6-substitution. In the alkynyl-substituted compounds **2a**, **2d** and **8**, the B−C−C moieties are almost linear, and the corresponding B−C−C bond angles are 177.0° for **2a**, 173.2° for **2d**, and 177.6° (apical)/175.4° (basal) for **8**. The B−C and C≡C bond lengths in **2a** (1.529, 1.211 Å), **2d** (1.530, 1.197 Å), and **8** (1.522, 1.205 Å) are similar to each other, and are also in agreement with the reported values for borylacetylenes.[11c,12] In **2a**, **2d**, **4**, **8**, **9** and **10**, the apical substituents are bent away from the B_{basal} group, the B2−B1−X angle being 143.3(3)°, 141.3(3)°, 141.9(1)°, 142.5(1)°, 140.7(2)° and 141.5(1)°, respectively (in **1** the corresponding angle is 140.06°).

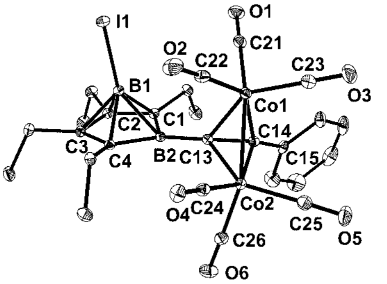


Figure 4. Molecular structure of **9**; hydrogen atoms omitted for clarity; thermal ellipsoids are shown at 40% probability; selected bond lengths [Å] and angles [°]: I(1)−B(1) 2.121(2), B(1)−C(1) 1.712(3), B(1)−C(2) 1.712(3), B(1)−C(3) 1.718(3), B(1)−C(4) 1.705(3), B(1)−B(2) 1.826(3), B(2)−C(1) 1.537(3), B(2)−C(4) 1.537(3), C(1)−C(2) 1.458(3), C(2)−C(3) 1.443(3), C(3)−C(4) 1.456(3), B(2)−C(13) 1.554(3), C(13)−C(14) 1.348(3), C(14)−C(15) 1.465(3), Co(1)−Co(2) 2.483(4), Co(1)−C(13) 1.999(2), Co(1)−C(14) 1.952(2), Co(2)−C(13) 1.990(2), Co(2)−C(14) 1.976(2); B(2)−B(1)−I(1) 140.7(2), C(13)−B(2)−B(1) 130.5(2), C(14)−C(13)−B(2) 141.1(2), C(13)−C(14)−C(15) 140.1(2)

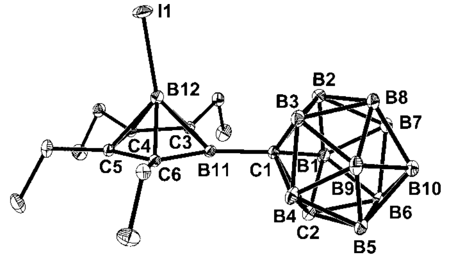


Figure 5. Molecular structure of **10**; hydrogen atoms omitted for clarity; thermal ellipsoids are shown at 40% probability; selected bond lengths [Å] and angles [°]: I(1)−B(12) 2.125(2), B(12)−C(3) 1.708(2), B(12)−C(4) 1.731(2), B(12)−C(5) 1.731(2), B(12)−C(6) 1.710(2), B(11)−B(12) 1.817(2), B(11)−C(3) 1.543(2), B(11)−C(6) 1.541(2), B(11)−C(1) 1.595(2), C(1)−C(2) 1.687(2), B(11)−B(12)−I(1) 141.46(10), C(1)−B(11)−B(12) 132.04(12)

In **4**, a $CpFe(CO)_2$ fragment is directly σ-bonded to the basal boron atom, the Fe−B bond length is 2.069 Å, which is significantly longer than the corresponding values for iron−boryl complexes, [1.959(6)−2.034(3) Å,[13a,13b] 1.964(8)−2.027(5) Å[13c,13d]] and iron−borylene complexes [2.010(3) Å[13e]], but in the range of the reported values for ferracarboranes (1.968−2.161 Å[13f]). This long Fe−B distance is also consistent with the easy decomposition of **4** with the cleavage of the Fe−B bond on silica gel. The iron center achieves an 18-electron configuration through coordination to two CO ligands (2e donor), the cyclopentadienyl group (5e donor), and the Fe−B interaction (1e donor).

In the structure of **9** (Figure 4), the almost linear B−C≡C−Cmoiety in **2a** has been altered by the complexation of the $Co_2(CO)_6$ fragment, with the angles decreasing to 141.07° (B2−C13−C14) and 140.1° (C13−C14−C15). The Co1−Co2 and C13−C14 bond lengths of 2.483 and 1.348 Å, respectively, are similar to the corresponding values in similar complexes carrying B−cat groups.[11b,11c]

The structure of **10** (Figure 5) contains the small C_4B_2 *nido*-cluster connected to the large *closo*-*o*-carboranyl cluster. Interestingly, in the asymmetric unit two cocrystallized free *o*-carborane molecules have been found, and surprisingly there is no significant intermolecular interaction among the three molecules. The B11−C1 bond length of 1.595 Å is typical of a C−B single bond. In the *o*-carboranyl fragment the C1−C2 bond length is 1.687 Å, which is significantly longer than that in *o*-carborane [1.630(6) Å].[14] The B−B bond lengths [av. distance 1.776(2) Å, ranging from 1.744(2) to 1.793(2) Å] and the C−B bond lengths [av. distance 1.720(2) Å, ranging from 1.703(2) to 1.731(2) Å] are close to the expected values.

Conclusion

The reactivity of compound **1** towards various nucleophiles has been investigated. In most of the cases, the substitution with hydride, alkynyl, diphenylphosphanyl, trimethylstannyl, $CpFe(CO)_2$, and even the bulky *o*-carboranyl group, takes place regiospecifically at the basal boron atom of the *nido*-C_4B_2 frameworks, while the "inert" apical B−I bond can be substituted by a Pd^0-catalyzed Negishi-type cross-coupling reaction, as demonstrated in the synthesis of compound **8**. A new strategy for cluster linkages has been developed, and compounds with different types of cluster linkages have been prepared, either by direct B−C bonding ($C_4B_2-C_2B_{10}$ and $C_4B_2-C_2Co_2$), or by a linking $C_6H_4C_6H_4$ unit, at the basal boron atom of the *nido*-C_4B_2 skeletons. The reactivity of the basal B−I bond of **1** is further shown by its sensitivity to THF as solvent and by the formation of the oxygen-bridged species **12**.

Experimental Section

General: 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 spectra were recorded with a Bruker DRX 200 spectrometer (^{1}H: 200.13 MHz, ^{11}B: 64.21 MHz, ^{13}C: 50.32 MHz) in $CDCl_3$ as the solvent. $Et_2O\cdot BF_3$ was used as the external standard for ^{11}B NMR spectroscopy, and as internal references for ^{1}H and ^{13}C NMR spectroscopy the signals of the deuterated solvents 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 or FAB ionization techniques. Melting points (uncorrected) were measured with a Büchi apparatus, using capillaries which were filled under nitrogen and sealed. $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$[15] and Me_3SnLi[16] were prepared according to literature procedures.

2,3,4,5-Tetraethyl-1-iodo-6-(phenylethynyl)-2,3,4,5-tetracarba-*nido*-hexaborane(6) (2a): *n*BuLi (2.5 M in hexanes, 2 mL) was added at −50 °C to a solution of phenylacetylene (507 mg, 5 mmol) in hexane (30 mL), the mixture was stirred for 30 min, and then warmed up to room temp. The resulting white suspension was cooled to −60 °C, and added with a syringe to a solution of **1** (900 mg, 2.05 mmol) in hexane (30 mL). The mixture was warmed to room temperature and stirred for 2 d. Filtration (G4 frit) gave a light-yellow filtrate, which was dried in vacuo to give **2a** as a yellow powder (746 mg, 88%), m.p. 74 °C. Crystals suitable for X-ray diffraction analysis were grown from a toluene/hexane solution at −28 °C. ^{1}H NMR: δ = 1.25 (t, $^{3}J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.33 (t, $^{3}J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 2.0 (m), 2.38 (m) (8 H, CH_2), 7.27−7.48 (m, Ph) ppm. ^{11}B NMR: δ = 10.3 (s, B_{basal}), −52.6 (s, B_{apical}) ppm. ^{13}C NMR: δ = 13.4, 14.3 (CH_3), 18.4, 19.8 (CH_2), 104.4 (br., *B*-bound basal C atoms), 113.0 (skeletal C atoms non-adjacent to the basal B atom), 124.6, 127.6, 128.1, 131.7 (Ph) ppm; signals of alkynyl C atoms not observed. EI-MS: *m*/*z* (%) = 414 (100) [M^+], 287 (14.6) [M^+ − I]. HR-MS (EI): *m*/*z* = 414.1224 [M^+]; calcd. for $^{12}C_{20}{}^{1}H_{25}{}^{11}B_2{}^{127}I$ 414.1187 (Δm = 3.7 mmu).

6-(*tert*-Butylethynyl)-2,3,4,5-tetraethyl-1-iodo-2,3,4,5-tetracarba-*nido*-hexaborane(6) (2b): Prepared in a similar manner to **2a** from *t*BuC=CLi (750 mg, 8.5 mmol) and **1** (528 mg, 1.2 mmol) in hexane (50 mL). Compound **2b** (450 mg, 95%) was obtained as a yellow oil. ^{1}H NMR: δ = 1.2 (br., 6 H, CH_3), 1.25 (br., 6 H, CH_3), 1.25 (s, 9 H, *t*Bu-H), 1.91 (m), 2.28 (m) (8 H, CH_2) ppm. ^{11}B NMR: δ = 10.8 (s, B_{basal}), −52.6 (s, B_{apical}) ppm. ^{13}C NMR: δ = 13.4, 14.0 (CH_3), 18.3, 19.6 (CH_2), 30.8 [$C(CH_3)_3$], 31.2 [$C(CH_3)_3$], signals of *B*-bound basal C atoms not observed, 112.3 (skeletal C atoms non-adjacent to the basal B atom) ppm; signals of alkynyl C atoms not observed. EI-MS: *m*/*z* (%) = 394 (100) [M^+], 267 (10.8) [M^+ − I]. HR-MS (EI): *m*/*z* = 394.1517 [M^+]; calcd. for $^{12}C_{18}{}^{1}H_{29}{}^{11}B_2{}^{127}I$ 394.1500 (Δm = 1.7 mmu).

2,3,4,5-Tetraethyl-1-iodo-6-(trimethylsilylethynyl)-2,3,4,5-tetracarba-*nido*-hexaborane(6) (2c): Prepared in a similar manner to **2a** from Me_3SiC=CH (310 mg, 3.16 mmol), *n*BuLi (2.5 M in hexanes, 3 mmol) and **1** (634 mg, 1.44 mmol) in hexane (50 mL). Compound **2c** (536 mg, 91%) was obtained as a yellow oil. ^{1}H NMR: δ = 0.18 (s, $SiMe_3$), 1.21 (t, $^{3}J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.26 (t, $^{3}J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.94 (m), 2.29 (m) (8 H, CH_2) ppm. ^{11}B NMR: δ = 9.8 (s, B_{basal}), −52.8 (s, B_{apical}) ppm. ^{13}C NMR: δ = 0.18 ($SiMe_3$), 13.3, 14.1 (CH_3), 18.3, 19.7 (CH_2), 105.2 (*B*-bound basal C atoms), 112.8 (skeletal C atoms non-adjacent to the basal B atom) ppm; signals of alkynyl C atoms not observed. ^{29}Si NMR ($CDCl_3$, 39.7 MHz): δ = −19.8 ppm. EI-MS: *m*/*z* (%) = 410 (100) [M^+], 283 (13.5) [M^+ − I]. HR-MS (EI): *m*/*z* = 410.1265 [M^+]; calcd. for $^{12}C_{17}{}^{1}H_{29}{}^{11}B_2{}^{127}I$ 410.1269 (Δm = −0.4 mmu).

2,3,4,5-Tetraethyl-1-iodo-6-(*p*-tolylethynyl)-2,3,4,5-tetracarba-*nido*-hexaborane(6) (2d): Prepared in a similar manner to **2a** from *p*-tolylacetylene (431 mg, 3.72 mmol) and **1** (264 mg, 0.6 mmol) in hexane (50 mL). Compound **2d** (247 mg, 96%) was obtained as a yellow solid, m.p. 81 °C. Crystals suitable for X-ray analysis were grown from a toluene solution at −28 °C. ^{1}H NMR: δ = 1.24 (t, $^{3}J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.31 (t, $^{3}J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.97 (m), 2.29 (m) (8 H, CH_2), 2.32 (s, 3 H, *p*-tolyl-CH_3), 7.08 (d, $^{3}J_{H,H}$ = 7.94 Hz, C_6H_4), 7.38 (d, $^{3}J_{H,H}$ = 7.94 Hz, C_6H_4) ppm. ^{11}B NMR: δ = 10.9 (B_{basal}), −52.6 (s, B_{apical}) ppm. ^{13}C NMR: δ = 13.3, 14.2 (CH_3), 18.4, 19.7 (CH_2), 21.4 (*p*-tolyl-CH_3), signals of *B*-bound basal C atoms not observed, 112.9 (skeletal C atoms non-adjacent to the basal B atom), 121.6, 128.8, 131.6, 137.6 (C_6H_4) ppm; signals of alkynyl C atoms not observed. EI-MS: *m*/*z* (%) = 428 (100) [M^+], 301 (13.6) [M^+ − I]. HR-MS (EI): *m*/*z* = 428.1360 [M^+]; calcd. for $^{12}C_{21}{}^{1}H_{27}{}^{11}B_2{}^{127}I$ 428.1344 (Δm = 1.6 mmu).

2,3,4,5-Tetraethyl-1-iodo-6-(diphenylphosphanyl)-2,3,4,5-tetracarba-*nido*-hexaborane(6) (3): A suspension of Ph_2PLi (170 mg, 0.88 mmol, prepared in situ from $HPPh_2$ and *n*BuLi in hexane) in hexane (5 mL) was cooled to −60 °C and added to a solution of **1** (194 mg, 0.44 mmol) in hexane (10 mL). The mixture was allowed to warm to room temp., stirred overnight and filtered. The yellow filtrate was dried in vacuo to give **3** (158 mg, 72%) as a yellow oil. ^{1}H NMR: δ = 0.99 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.37 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.94 (m), 2.36 (m) (8 H, CH_2), 7.37−7.56 (m, 10 H, aromatic H) ppm. ^{11}B NMR: δ = 14.8 (br., B_{basal}), −52.8 (s, B_{apical}) ppm. ^{13}C NMR: δ = 13.7, 15.1 (CH_3), 18.8, 19.2 (CH_2), signals of *B*-bound basal C atoms not observed, 116.1 (skeletal C atoms non-adjacent to the basal B atom), 127.2, 128.5, 134.4, 138.2 (aromatic C) ppm; signals of alkynyl C atoms not observed. ^{31}P{^{1}H} NMR ($CDCl_3$, 80.92 MHz): δ = −40.1 ppm. EI-MS: *m*/*z* (%) = 498 (59.1) [M$^+$], 371 (9.8) [M$^+$ − I], 186 (100) [$HPPh_2$]. HR-MS (EI): *m*/*z* = 498.1307 [M$^+$]; calcd. for $^{12}C_{24}{}^1H_{30}{}^{11}B_2{}^{127}I^{31}P$ 498.1316 (Δ*m* = −0.9 mmu).

6-[Dicarbonyl(η^5-cyclopentadienyl)iron]-2,3,4,5-tetraethyl-1-iodo-2,3,4,5-tetracarba-*nido*-hexaborane(6) (4): A solution of **1** (317 mg, 0.72 mmol) in hexane (10 mL) was added to a suspension of K[(η^5-C_5H_5)Fe(CO)$_2$] (395 mg, 1.8 mmol) in toluene (30 mL) at room temp. The mixture was stirred for 4 d and then filtered. The deep-red filtrate was concentrated and cooled to −28 °C; yellow crystals were formed after one week (258 mg, 73%), m.p. 132 °C. ^{1}H NMR: δ = 1.2 (br., 6 H, CH_3) , 1.3 (br., 6 H, CH_3), 1.93 (m), 2.22 (m) (8 H, CH_2), 4.8 (s, Cp) ppm. ^{11}B NMR: δ = 28.6 (br., B_{basal}), −49.6 (s, B_{apical}) ppm. ^{13}C NMR: δ = 13.6, 14.1 (CH_3), 19.3, 21.7 (CH_2), 88.1 (Cp), 106.5 (*B*-bound basal C atoms), 117.9 (skeletal C atoms non-adjacent to the basal B atom), 217.2 (CO) ppm; signals of alkynyl C atoms not observed. IR (hexane): ν_{co}: 1998.1 (s), 1942.4 (s) cm^{-1}. EI-MS: *m*/*z* (%) = 490 (4.2) [M$^+$], 462 (24.1) [M$^+$ − CO], 434 (100) [M$^+$ − 2 CO], 405 (7.3) [M$^+$ − 2 CO − Et], 307 (22.9) [M$^+$ − 2 CO − I]. HR-MS (EI): *m*/*z* = 490.0431 [M$^+$]; calcd. for $^{12}C_{19}{}^1H_{25}O_2{}^{11}B_2Fe^{127}I$ 490.0435 (Δ*m* = −0.4 mmu).

2,3,4,5-Tetraethyl-6-hydrido-1-iodo-2,3,4,5-tetracarba-*nido*-hexaborane(6) (5). a) By Decomposition of 4: In an attempt to separate **4** by column chromatography on silica gel, the crude product was eluted with hexane; only decomposition was observed. Compound **5** and paramagnetic impurities were formed, as indicated by the NMR spectroscopy. **b) By Reaction of 1 with LiBEt$_3$H:** A solution of $LiBEt_3H$ (1.0 M in THF, 0.4 mmol) was added dropwise at −65 °C to a solution of **1** (194 mg, 0.44 mmol) in hexane (5 mL). A white precipitate was formed, the mixture was allowed to warm to room temp. and filtered. The colorless filtrate was dried in vacuo to give **5** (123 mg, 89%) as a colorless oil. ^{1}H NMR: δ = 1.2 (br., 6 H, CH_3), 1.2 (br., 6 H, CH_3), 2.04 (m), 2.21 (m) (8 H, CH_2) ppm. ^{11}B NMR: δ = 11.5 (d, $J_{B,H}$ = 148.3 Hz, B_{basal}), −53.8 (s, B_{apical}) ppm. ^{13}C NMR: δ = 13.1, 14.3 (CH_3), 18.5, 20.1 (CH_2), 106.3 (*B*-bound basal C atoms), 114.8 (skeletal C atoms non-adjacent to the basal B atom) ppm. EI-MS: *m*/*z* (%) = 314 (100) [M$^+$], 187 (10) [M$^+$ − I]. HR-MS (EI): *m*/*z* = 314.0893 [M$^+$]; calcd. for $^{12}C_{12}{}^1H_{21}{}^{11}B_2{}^{127}I$ 314.0874 (Δ*m* = 1.9 mmu).

2,3,4,5-Tetraethyl-1-iodo-6-phenyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (6a): A suspension of PhLi [obtained upon solvent removal from a solution (1.6 M) in diethyl ether/cyclohexane, 1 mmol] in hexane (5 mL) was cooled to −60 °C and added to a solution of **1** (194 mg, 0.44 mmol) in hexane (10 mL). The mixture was allowed to warm to room temp., stirred overnight and filtered. The light-yellow filtrate was dried in vacuo to give **6a** (150 mg, 87%) as a colorless oil, and trace amount of **6b**. ^{1}H NMR: δ = 1.19 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.4 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 2.08 (m), 2.36 (m) (8 H, CH_2), 7.40−7.55 (m, Ph) ppm. ^{11}B NMR: δ = 17.9 (s, B_{basal}), −52.4 (s, B_{apical}) ppm. ^{13}C NMR: δ = 13.7, 14.2 (CH_3), 18.5, 19.0 (CH_2), 103.4 (br., *B*-bound basal C atoms), 112.9 (skeletal C atoms non-adjacent to the basal B atom), 126.8, 127.2, 128.8, 133.2, 141.3 (Ph) ppm. EI-MS: *m*/*z* (%) = 390 (100) [M$^+$], 361 (10.8) [M$^+$ − Et], 263 (5.9) [M$^+$ − I]. HR-MS (EI): *m*/*z* = 390.1188 [M$^+$]; calcd. for $^{12}C_{18}{}^1H_{25}{}^{11}B_2{}^{127}I$ 390.1187 (Δ*m* = 0.1 mmu); *m*/*z* = 340.2532 (**6b**)$^+$; calcd. for $^{12}C_{24}{}^1H_{30}{}^{11}B_2$ 340.2534 (Δ*m* = −0.2 mmu).

2,3,4,5-Tetraethyl-1-iodo-6-(trimethylstannyl)-2,3,4,5-tetracarba-*nido*-hexaborane(6) (7a): A solution of **1** (194 mg, 0.44 mmol) in hexane (10 mL) was added to a suspension of Me_3SnLi (1 mmol) in hexane (20 mL) at −60 °C. The mixture was allowed to warm to room temp., stirred for 3 d and then filtered. The light-yellow filtrate was dried in vacuo to give **7a** (170 mg, 81%) as a yellow oil, and a trace amount of **7b**. ^{1}H NMR: δ = 0.3 (s, 9 H, $SnMe_3$), 1.2 (br., 6 H, CH_3), 1.3 (br., 6 H, CH_3), 2.11 (m), 2.24 (m) (8 H, CH_2) ppm. ^{11}B NMR: δ = 16.1 (br., B_{basal}), −52.6 (s, B_{apical}) ppm. ^{13}C NMR: δ = −6.0 ($SnMe_3$), 13.5, 14.1 (CH_3), 19.2, 22.2 (CH_2), signals of *B*-bound basal C atoms not observed, 118.6 (skeletal C atoms non-adjacent to the basal B atom) ppm. ^{119}Sn NMR ($CDCl_3$, 74.5 MHz): δ = −97.9 ppm. EI-MS: *m*/*z* (%) = 463 (100) [M$^+$ − CH_3], 499 (68.5) [**7b**$^+$− CH_3]. HR-MS (EI): *m*/*z* = 463.0254 [M$^+$ − CH_3]; calcd. for $^{12}C_{14}{}^1H_{26}{}^{11}B_2{}^{127}I^{120}Sn$ 463.0288 (Δ*m* = −3.4 mmu); *m*/*z* = 501.0996 [**7b**$^+$ − CH_3]; calcd. for $^{12}C_{17}{}^1H_{35}{}^{11}B_2{}^{120}Sn_2$ 501.0968 (Δ*m* = 2.8 mmu).

2,3,4,5-Tetraethyl-6-(phenylethynyl)-1-(trimethylsilylethynyl)-2,3,4,5-tetracarba-*nido*-hexaborane(6) (8): A portion of lithium trimethylsilylacetlylide (138 mg, 1.33 mmol) was dissolved in THF (15 mL) at room temp. and $ZnCl_2$ (180 mg, 1.33 mmol) was added. The mixture was stirred for 3 h and was then added to a mixture of **2a** (146 mg, 0.35 mmol) and Pd(PPh$_3$)$_4$ (20 mg, 0.017 mmol). The resulting yellow mixture was stirred for 3 d and then heated at reflux for 10 d. The solvent was removed, the black residue was extracted with hexane (2 × 20 mL) and filtered. The yellow filtrate was dried in vacuo to give a yellow viscous oil. A minimum amount of hexane was added and, on cooling to −28 °C, yellow crystals of **8** (115 mg, 85%) grew, m.p. 72 °C. ^{1}H NMR: δ = 0.08 ($SiMe_3$), 1.22 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.30 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 2.22 (m), 2.35 (m) (8 H, CH_2), 7.27−7.50 (m, 5 H, Ph) ppm. ^{11}B NMR: δ = 9.8 (s, B_{basal}), −50.7 (s, B_{apical}) ppm. ^{13}C NMR: δ = 0.01 ($SiMe_3$), 13.6, 14.7 (CH_3), 17.4, 19.1 (CH_2), 104.4 (*B*-bound basal C atoms), 112.4 (skeletal C atoms non-adjacent to the basal B atom), 125.0, 127.4, 128.0, 131.7 (Ph) ppm; signals of alkynyl C atoms not observed. ^{29}Si NMR ($CDCl_3$, 39.7 MHz): δ = −19.4 ppm. EI-MS: *m*/*z* (%) = 384 (100) [M$^+$]. HR-MS (EI): *m*/*z* = 384.2621 [M$^+$]; calcd. for $^{12}C_{25}{}^1H_{34}{}^{11}B_2{}^{28}Si$ 384.2616 (Δ*m* = 0.5 mmu).

3-Carboranyl-4-phenyl-1,2-bis(tricarbonylcobalta)tetrahedrane (9): A solution of **2a** (193 mg, 0.47 mmol) in hexane (15 mL) was added to a solution of $Co_2(CO)_8$ (178 mg, 0.52 mmol) in hexane (15 mL) at −40 °C. The mixture was allowed to warm to room temp. and stirred for 4 d until the reaction was complete. The solvent was removed in vacuo and the black residue was extracted with dichloromethane (2 mL) and separated by column chromatography (Florisil®) with hexane as eluent. After a small amount of unchanged $Co_2(CO)_8$, a deep-brown band was eluted. The solution was concentrated and cooled to −28 °C to give black crystals of **9** (170 mg, 52%), m.p. 140−141 °C (decomp.). ^{1}H NMR: δ = 1.09 (br., 6 H, CH_3), 1.35 (br., 6 H, CH_3), 1.84 (br.), 2.28 (br.) (8 H, CH_2), 7.26−7.51 (m, 5 H, Ph) ppm. ^{11}B NMR: δ = 16.3 (br., B_{basal}), −51.1 (s, B_{apical}) ppm. ^{13}C NMR: δ = 13.6, 14.1 (CH_3), 18.6, 19.0 (CH_2), 102.6 (*B*-bound basal C atoms), 114.0 (skeletal C atoms non-adjacent to the basal B atom), 127.2, 128.4, 129.7 (Ph), 200.4 (CO) ppm. EI-MS: *m*/*z* (%) = 672 (13.0) [M$^+$ − CO], 644 (12.1) [M$^+$ − 2 CO], 616 (19.0) [M$^+$ − 3 CO], 588 (28.2) [M$^+$ − 4 CO], 560 (11.7) [M$^+$ − 5 CO], 532 (100) [M$^+$ − 6 CO], 473 (20.6) [M$^+$ − 6 CO − 2 Et]. HR-MS (EI): *m*/*z* = 671.9595 [M$^+$ − CO];

calcd. for $^{12}C_{25}{}^{1}H_{25}O_5{}^{11}B_2Co_2{}^{127}I$ 671.9596 ($\Delta m = -0.1$ mmu). $C_{26}H_{25}B_2Co_2IO_6$ (699.9): calcd. C 44.62, H 3.60; found C 44.08, H 3.98.

6-(*o*-Carboranyl)-2,3,4,5-tetraethyl-1-iodo-2,3,4,5-tetracarba-*nido*-hexaborane(6) (10): *n*BuLi (2.5 M in hexanes, 0.4 mL, 1 mmol) was added at −65 °C to a solution of *o*-carborane (126 mg, 0.875 mmol) in toluene (15 mL). The colorless mixture was allowed to warm to room temp. and stirred overnight. The resulting white suspension was cooled to −65 °C and a solution of **1** (264 mg, 0.58 mmol) in hexane (7 mL) was added. The mixture was warmed to room temp., heated at reflux overnight, and filtered. The colorless filtrate was dried in vacuo to give a solid. A minimum amount of $CDCl_3$ was added and, on cooling to −28 °C, colorless crystals of **10** (200 mg, 76%) were obtained, m.p. 108 °C. ^1H NMR: δ = 1.20 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.28 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 1.93 (m), 2.25 (m) (8 H, CH_2), 3.3−3.8 (m, *o*-carborane) ppm. $^{11}B\{^1H\}$ NMR: δ = 13.9 (s, B_{basal}), −2.4 (2 B), −9.2 (2 B), −13.6 (4 B), −14.8 (2 B), −53.4 (s, B_{apical}) ppm. ^{13}C NMR: δ = 13.6, 14.7 (CH_3), 17.4, 19.1 (CH_2), 59.6 (C_{cage}), 102.3 (br., *B*-bound basal C atoms), 114.5 (skeletal C atoms non-adjacent to the basal B atom) ppm. EI-MS: *m/z* (%) = 456 (100) [M$^+$]. HR-MS (EI): *m/z* = 458.2604 [M$^+$]; calcd. for $^{12}C_{14}{}^{1}H_{31}{}^{11}B_{12}{}^{127}I$ 458.2587 (Δm = 1.7 mmu).

The $C_6H_4C_6H_4$-Connected Carborane 11: *n*BuLi (2.5 M in hexanes, 0.6 mL, 1.5 mmol) was added to a solution of 4,4′-dibromobiphenyl (164 mg, 0.53 mmol) in THF (15 mL) at −65 °C, and stirred at that temp. for 2 h. $ZnCl_2$ (150 mg, 1.1 mmol) was added in one portion to the resulting white suspension. The mixture was allowed to warm to room temp. to form a cloudy mixture, which was dried, and dry toluene (25 mL), **1** (200 mg, 0.45 mmol, in 5 mL of hexane) and $Pd(PPh_3)_4$ (60 mg, 0.052 mmol) were added to the solid. The resulting yellow mixture was stirred at room temp. for 3 d and filtered. The light-yellow filtrate was dried in vacuo, the residue was extracted with hexane (2 × 20 mL) and filtered. The colorless filtrate was dried in vacuo to give **11** as an oil (90 mg, 50%). ^1H NMR: δ = 1.2 (br., 6 H, CH_3), 1.3 (br., 6 H, CH_3), 2.10 (m), 2.32 (m) (8 H, CH_2), 7.41 (d, *J* = 8 Hz, 4 H), 7.48 (d, *J* = 8 Hz, 4 H, $C_6H_4C_6H_4$) ppm. ^{11}B NMR: δ = 22.0 (br., 2 B, B_{basal}), −52.4 (s, 2 B, B_{apical}) ppm. ^{13}C NMR: δ = 13.4, 14.3 (CH_3), 18.4, 19.8 (CH_2), 104.4 (*B*-bound basal C atoms), 113.0 (skeletal C atoms non-adjacent to the basal B atom), 124.6, 127.6, 128.1, 131.7 ($C_6H_4C_6H_4$) ppm. FAB-MS: *m/z* (%) = 778 (100) [M$^+$]. HR-MS (FAB): *m/z* = 778.2294 [M$^+$]; calcd. for $^{12}C_{36}{}^{1}H_{48}{}^{11}B_4{}^{127}I_2$ 778.2217 (Δm = 7.7 mmu).

The Oxygen-Bridged Carborane 12: Wet Et_3N (92 mg) was added to a solution of **1** (198 mg, 0.45 mmol) in hexane (5 mL) at − 60 °C. The mixture was allowed to warm to room temp. and stirred overnight. The colorless filtrate and the white precipitate were then separated by filtration. The filtrate was dried in vacuo to give **12** as an oil (100 mg, 69%). ^{11}B NMR: δ = 22.1 (br., 2 B, B_{basal}), −51.9 (s, 2 B, B_{apical}) ppm. EI-MS: *m/z* (%) = 642 (100) [M$^+$], 613 (61.2) [M$^+$ − Et], 515 (48.6) [M$^+$ − I]. HR-MS (EI): *m/z* = 642.1533 (100) [M$^+$]; calcd. for $^{12}C_{24}{}^{1}H_{40}{}^{11}B_4{}^{127}I_2{}^{16}O$ 642.1541 (Δm = −0.8 mmu). Negative FAB-MS of the white precipitate exhibited peaks at *m/z* = 356 $[Et_3NH]I_2^-$, 483 $[Et_3NH]I_3^-$, 584.9 $[Et_3NH]_2I_3^-$, indicating its identity as $[Et_3NH]I$.

X-ray Structure Determinations: Crystal data and details of the structure determinations are listed in Tables 1 and 2. The intensity data for **2a**, **4**, **8**, **9**, and **10** were collected with a Bruker AXS Smart CCD diffractometer at 103(2) K, and for **2d** at 298 K (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, ω-scans). Data were corrected for Lorentz polarization and absorption effects (semiempirical, SADABS[17]). The structures were solved by direct methods (SHELXS-86)[18] and refined by least-squares methods

Table 1. Crystal data and structure refinement for **2a**, **2d**, **4**

	2a	**2d**	**4**
Empirical formula	$C_{20}H_{25}B_2I$	$C_{21}H_{27}B_2I$	$C_{19}H_{25}B_2FeIO_2$
Formula mass	413.92	427.95	489.76
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a [Å]	7.3783(6)	7.8362(4)	9.5495(5)
b [Å]	10.4260(8)	8.3469(4)	24.2877(11)
c [Å]	12.5718(9)	18.2876(10)	8.9340(4)
α [°]	86.083(1)	80.286 (1)	90
β [°]	86.301(1)	85.038(1)	99.480(1)
γ [°]	85.441(2)	64.989(1)	90
V [Å^3]	960.09(13)	1068.29(9)	2043.8(2)
Z	2	2	4
$D_{calcd.}$ [g cm^{-3}]	1.432	1.330	1.592
μ(Mo-K_α) [mm^{-1}]	1.664	1.498	2.257
F(000)	416	432	976
Crystal size [mm]	0.35 × 0.09 × 0.04	0.45 × 0.32 × 0.27	0.32 × 0.25 × 0.20
Θ_{max} [°]	32.0	26.3	32.0
Index ranges	−10/10, −15/15, −0/18	−9/9, −10/10, 0/22	−14/14, 0/36, 0/13
Reflections collected	16837	13336	27347
Independent (R_{int})	6504 (0.0387)	4370(0.0210)	7027(0.0239)
No. of parameters	308	319	326
GooF	1.071	1.064	1.215
*R*1 ($I > 2\sigma I$)	0.0304	0.0404	0.0290
*wR*2 (all reflections)	0.077	0.1092	0.0670
Resid. electron dens. [e·Å^{-3}]	1.322/−1.248	0.973/−0.623	1.292/−0.713

Table 2. Crystal data and structure refinement for **8**, **9** and **10**

	8	**9**	**10**
Empirical formula	$C_{25}H_{34}B_2Si$	$C_{26}H_{25}B_2Co_2IO_6$	$C_{14}H_{31}B_{12}I\cdot 2(C_2H_{12}B_{10})$
Formula mass	384.23	699.84	744.44
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/c$	$P2/c$
a [Å]	7.3346(4)	16.7233(9)	26.1136(12)
b [Å]	8.9453(4)	12.4541(7)	6.8725(3)
c [Å]	19.1092(10)	13.5390(8)	24.6178(12)
α [°]	90	90	90
β [°9	91.254(1)	93.599(1)	115.469(1)
γ [°]	90	90	90
V [Å^3]	1253.46(11)	2814.3(3)	3988.7(3)
Z	2	4	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.018	1.652	1.240
μ(Mo-K_α) [mm^{-1}]	0.101	2.313	0.821
F(000)	416	1384	1504
Crystal size [mm]	0.15 × 0.24 × 0.36	0.33 × 0.10 × 0.06	0.55 × 0.30 × 0.23
$\Theta_{\max}$ [°]	32.01	32.0	32.0
Index ranges	−10/10, −10/13, −0/28	−24/24, 0/18, 0/20	−38/35, 0/10, 0/36
Reflections collected	11997	37985	53142
Independent (R_{int})	6728 (0.0247)	9662(0.0429)	13706(0.0342)
No. of parameters	389	434	680
GooF	1.066	1.050	1.114
$R1$ ($I > 2\sigma I$)	0.0385	0.0318	0.0348
$wR2$ (all reflections)	0.1018	0.0780	0.0819
Resid. electron dens. (e·Å^{-3})	0.393/−0.180	1.002/−0.522	1.197/−1.009

based on F^2 with all measured reflections (SHELXL-97).[18] All non-hydrogen atoms were refined anisotropically. CCDC-221474 (**2a**), -221475 (**2d**), -221476 (**4**), -221477 (**8**), -221478 (**9**) and -221479 (**10**) 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 Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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