Halogen exchange at boron in *nido*-C$_4$B$_2$ carboranes

Yong Nie, Hans Pritzkow, Hubert Wadepohl, Walter Siebert *

Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Dedicated to Prof. Sheldon G. Shore on the occasion of his 75th birthday

Abstract

The Pd(PPh$_3$)$_4$-catalyzed reaction of 1-iodo-6-phenylethynyl-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**1a**) with in situ generated arylzinc reagents (from arylbromides) leads to 1-bromo-6-phenylethynyl-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**2a**) and a trace amount of *nido*-(EtC)$_4$(BC≡CPh)$_2$ (**3a**). **3a** is separately synthesized by a Pd-catalyzed Negishi-type coupling reaction of **1a** with phenylethynyl-zincchloride. This is confirmed by the Pd-catalyzed reactions of 1-iodo-6-*tert*-butyl-ethynyl-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**1b**) with *n*-BuBr and PhZnCl, respectively, which produce the brominated carborane **2b** and *nido*-(EtC)$_4$(BC≡C*t*Bu)$_2$ (**3b**). With a dialkynylzinc reagent, a similar reaction of 1-iodo-6-*p*-tolylethynyl-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**1c**) gives the linked compound **4**, and a very small amount of ZnI$_2$(OPPh$_3$)$_2$ is formed. The selective basal halogen exchange of 1,6-diiodo-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**5**) with an excess of AgF leads to 1-iodo-6-fluoro-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-*nido*-hexa-borane(6) (**6**). The composition of the products follows from NMR and MS data and a single crystal X-ray analysis of **2a**. The X-ray structure of ZnI$_2$(OPPh$_3$)$_2$ is reported.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Boron; Carborane; Halogen exchange; Palladium catalysis

1. Introduction

B-halogenated polyhedral borane and carborane clusters are useful precursors for organyl-substituted products via direct or transition metal-catalyzed transformations, and for labeled derivatives via isotopic exchange in biomedical studies. Halogenated compounds can be obtained by (selective) halogenation of the B–H groups of boranes and carboranes. Although halogen exchange is a conventional way to functionalized organoboron compounds [1], it is rare in polyhedral borane and carborane chemistry [2].

Onak et al. [3] studied the halide exchange reactions involving B-halogenated *closo*-2,4-C$_2$B$_5$ carborane derivatives, leading to carborane products with lighter halogen atom(s) than the leaving halogen atom(s). Stanko et al. [4] described that 2-iodo-*p*-carborane was transformed to 2-chloro-*p*-carborane by treatment with CuCl; the exchange with Na^{131}I in 10-iodo-*o*-carborane, 9-iodo-*m*-carborane and 2-iodo-*p*-carborane, respectively, was observed [4b]. The Pd-catalyzed exchange reactions [5] afforded a series of ^{125}I-labelled *o,m,p*-carboranes. Recently, Grushin et al. [6] reported that, in the presence of *n*-Bu$_4$NBr, 9-I-*m*-carborane underwent halogen exchange to give 9-Br-*m*-carborane in the presence of a Pd catalyst. In the case of the *nido*-C$_4$B$_2$ cluster, it has been observed that a 6-bromo-peralkylated *nido*-C$_4$B$_2$ carborane reacts with AgF to give the 6-F-carborane derivative when a catalytic amount of Et$_3$N was present [7].

Recently, we have developed a one-pot synthesis of 1,6-diiodo-2,3,4,5-tetraalkyl-2,3,4,5-tetracarba-*nido*-hexaboranes(6) [8a], involving disubstituted alkynes, BI_3 and $NaK_{2.8}$. While the basal B–I bond is easily cleaved by a variety of nucleophiles, the apical B–I group remains largely inert, its substitution has been achieved by a Pd(0)-catalyzed Negishi-type cross-coupling reaction with an alkynylzinc reagent [8b] (Scheme 1). In order to study the scope and limitations of the apical functionalization, we have carried out similar reactions involving in situ generated arylzinc reagents (from arylbromides), however, the apical brominated species is observed instead of the expected products. Herein, we report on the apical halogen substitution as well as an example of selective basal halogen exchange.

2. Results and discussion

As outlined in Scheme 2, the reactions of **1a** with aryl zinc reagents (generated in situ from 4,4′-dibromobiphenyl and 1,3,5-tribromobenzene, respectively, with the appropriate amounts of *n*-BuLi and $ZnCl_2$) in the presence of a catalytic amount of Pd(PPh$_3$)$_4$, did not give the apically linked clusters, but the brominated product **2a**.

The formation of **2a** was first deduced from its ^{11}B NMR spectrum ($\delta = 10.6$, -40.2 ppm), the signal for the basal boron (10.6 ppm) is unchanged compared to that of **1a** (10.3 ppm), but that of the apical boron is downfield shifted (-40.2 ppm) relative to that of **1a** (-52.6 ppm). The mass spectrum exhibits a base peak at $m/z = 366/368$ with the correct isotopic pattern for (EtC)$_4$(BC$_2$Ph)(BBr). In addition, a very weak peak at $m/z = 388$ in the mass spectrum is assigned to be *nido*-(EtC)$_4$(BC$_2$Ph)$_2$ (**3a**). It is available from the separate reaction of **1a** with PhC≡CZnCl in the presence of the catalyst Pd(PPh$_3$)$_4$, similar to the formation of (EtC)$_4$(BC$_2$Ph)(BC$_2$SiMe$_3$) (Scheme 1) [8b]. The yellow product **3a** was obtained by heating the reaction mixtures for 7 days. Interestingly, the ^{11}B NMR signal of the substituted apical boron is only slightly downfield shifted ($\delta = -49.8$ ppm) compared to that of **1a**.

The structure of **2a** (Fig. 1) has been established by a single crystal X-ray diffraction analysis, which is very similar to that of **1a** [8b]. The alkynyl B2–C1–C2 moiety is almost linear, the corresponding B–C–C angle is
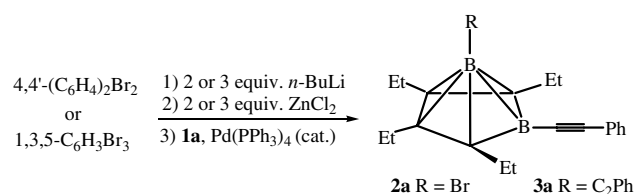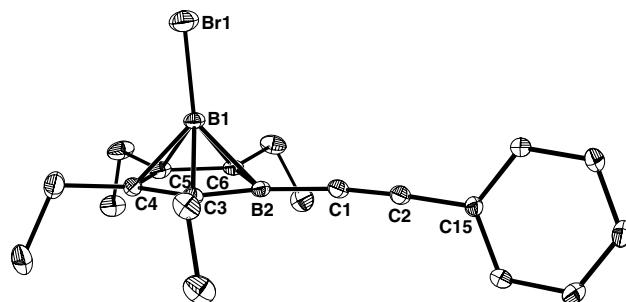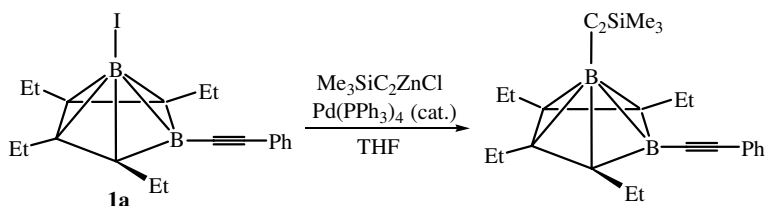
Scheme 2.

Fig. 1. Molecular structure of **2a**. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Br(1)–B(1) 1.906(3), B(1)–C(3) 1.712(3), B(1)–C(4) 1.720(4), B(1)–C(5) 1.717(3), B(1)–C(6) 1.711(4), B(1)–B(2) 1.820(4), B(2)–C(3) 1.523(3), B(2)–C(6) 1.529(3), B(2)–C(1) 1.531(3), C(3)–C(4) 1.456(3), C(4)–C(5) 1.442(4), C(5)–C(6) 1.451(3), C(1)–C(2) 1.208(3), C(2)–C(15) 1.434(3); B(2)–B(1)–Br(1) 138.76(17), C(1)–B(2)–B(1) 132.12(19), C(2)–C(1)–B(2) 174.0(2), C(1)–C(2)–C(15) 174.9(3).

174.0(2)° [cf. those in **1a** 177.0°, and in (EtC)$_4$(BC$_2$Ph)-(BC$_2$SiMe$_3$) 173.2°]. The apical B–Br group [bond length: 1.906(3) Å] is bent away from the B$_{basal}$ [B2–B1–Br1 138.76(17)°], comparable to those in **1a** and (EtC)$_4$(BC$_2$Ph)(BC$_2$SiMe$_3$) [143.3(3)° and 141.3(3)°, respectively].

The formation of **2a** implies that the apically brominated *nido*-C$_4$B$_2$ carborane derivative is not suitable for the Pd-catalyzed Negishi-type cross coupling with zinc reagents. Obviously the bromine sources for the formation of **2a** are 4,4′-dibromodiphenyl and 1,3,5-tribromobenzene. They react with *n*-BuLi to generate *n*-BuBr along with the aryllithium reagents, which in turn yield with $ZnCl_2$ the corresponding zinc reagents.

Two control reactions were therefore carried out (Scheme 3). The reaction of **1b** with *n*-BuBr and a catalytic amount of Pd(PPh$_3$)$_4$ produced the brominated **2b**, whereas the similar reaction of **1b** with PhZnCl did not
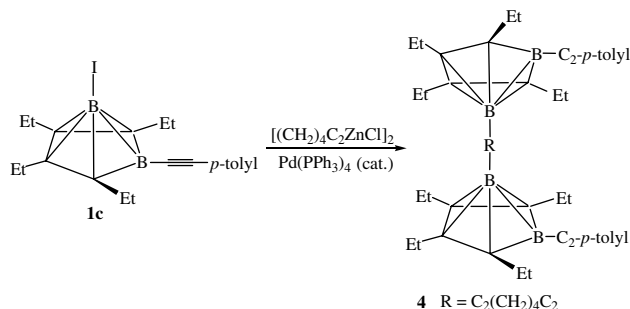
Scheme 1.
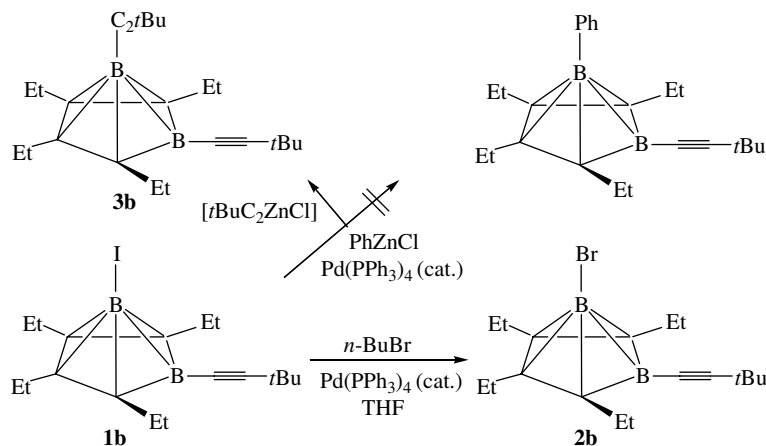
Scheme 3.

give any apically phenylated product, but the apically alkynylated species **3b**, as indicated by its ^{11}B NMR spectrum (δ = 8.9, −52.6 ppm, comparable to that of **3a**) and mass spectrum (m/z = 348). The formation of **3b** may originate from an intermolecular reaction: the basal B–$C_{alkynyl}$ group of **1b** is cleaved thereby forming the alkynylzinc reagent $tBuC{\equiv}CZnCl$, which reacts with the apical B–I group of another molecule of **1b** to form **3b** under Pd catalysis.

While **1c** did not react with $LiC{\equiv}C(CH_2)_4C{\equiv}CLi$, its reaction with the corresponding zinc reagent $ClZnC{\equiv}C(CH_2)_4C{\equiv}CZnCl$ produced the apically linked cluster **4** (Scheme 4) in the presence of a Pd catalyst. The yellow oil exhibits in the ^{11}B NMR spectrum two signals at δ = 10.2 and −49.4 ppm. The mass spectrum of **4** shows the molecule ion peak with the correct isotopic pattern. After workup colorless crystals (a very small amount) were unexpectedly obtained and found to be $ZnI_2(OPPh_3)_2$ by an X-ray structure analysis. The zinc center (Fig. 2) adopts a slightly distorted tetrahedral geometry. The formation of the long known $ZnI_2(OPPh_3)_2$ [9] results obviously from ZnI_2 and $OPPh_3$ (formed by contact of air with PPh_3 from $Pd(PPh_3)_4$).

The reactions of **5** [8a] with an excess of AgF and SbF_3, respectively, were carried out (Scheme 5) to obtain

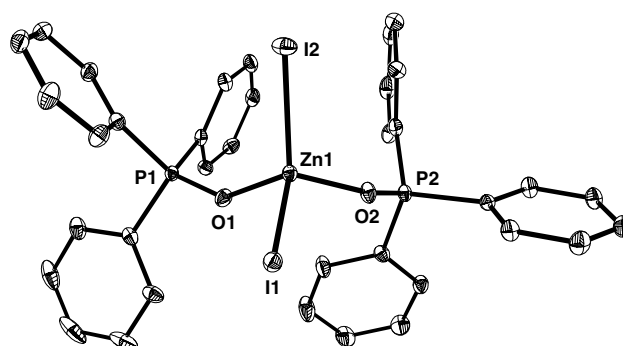Fig. 2. Molecular structure of $ZnI_2(OPPh_3)_2$. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): I(1)–Zn(1) 2.5550(4), I(2)–Zn(1) 2.5439(4), Zn(1)–O(1) 1.977(2), Zn(1)–O(2) 1.967(2), O(1)–P(1) 1.506(2), O(2)–P(2) 1.503(2); O(2)–Zn(1)–O(1) 101.06(9), O(2)–Zn(1)–I(2) 110.59(6), O(1)–Zn(1)–I(2) 112.11(6), O(2)–Zn(1)–I(1) 111.32(6), O(1)–Zn(1)–I(1) 104.29(6), I(2)–Zn(1)–I(1) 116.275(12).

the difluoro-*nido*-C_4B_2 intermediate **7**, which, as has been demonstrated by Timms [10], would rearrange to give the classic structure **8**. While no reaction was observed between **5** and SbF_3 in hexane at room temperature, the reaction with AgF (without catalyst) led only to the basal-substituted monofluoro derivative **6**, characterized by its ^{11}B NMR spectrum [δ = 21.8, −53.1 ppm, cf. that of **5**: δ = 5.5 (B_{basal}) and −52.5 (B_{apical}) ppm]. The mass spectrum exhibits the molecule ion peak at m/z = 332 with the correct isotopic distribution.

3. Conclusion

We have shown that the halogen exchange occurs at both the basal and the apical boron atoms of the *nido*-C_4B_2 carboranes. In accord with Onak [3], such halogen exchange reactions depend on the strength of the B–X (X = F, Cl, Br, I) bonds, which is possible only with heavier halogens as leaving atoms.
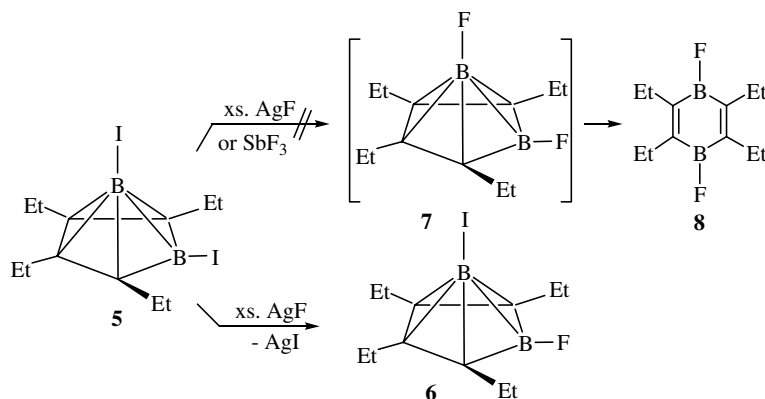
Scheme 4.

Scheme 5.

4. Experimental

4.1. 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 on a Bruker DRX 200 spectrometer (^{1}H: 200.13 MHz, ^{11}B: 64.21 MHz, ^{13}C: 50.32 MHz) in CDCl$_3$, CD$_2$Cl$_2$ and C$_6$D$_6$ as solvents. Et$_2$OBF$_3$ was used as external standard for ^{11}B NMR. As internal references for ^{1}H and ^{13}C NMR, the signals of the deuterated solvents were used, the shifts were calculated relative to TMS and given in ppm. MS: ZAB-2F VH Micromass CTD spectrometer, and a JEOL MS Station JMS 700 spectrometer.

4.2. 1-Bromo-6-phenylethynyl-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-nido-hex-borane(6) (2a)

A portion of *n*BuLi (2.5 M in hexanes, 1.2 ml, 3 mmol) was added into a solution of 1,3,5-tribromo-benzene (254 mg, 0.8 mmol) in THF (15 mL) at −60 °C, and slowly warmed to r.t.. To this solution ZnCl$_2$ (340 mg, 2.5 mmol) was added and stirred for 3 h. The resulting light yellow solution was then added to a mixture of **1a** (240 mg, 0.56 mmol) and Pd(PPh$_3$)$_4$ (80 mg, 0.07 mmol), and the mixture was heated at reflux for 7 days. All volatiles were removed, the black oily residue was extracted with hexane (30 mL) and filtered. The light yellow filtrate was dried in vacuo to give **2a** (201 mg, 94%) as a yellow oil. **3a** was identified only by MS. Suitable crystals for X-ray analysis were obtained by cooling a neat sample at 4 °C. ^{1}H NMR (C$_6$D$_6$): 0.92 (t, 6H, $^3J_{H,H}$ = 7.6 Hz, CH$_3$), 1.37 (t, 6H, $^3J_{H,H}$ = 7.6 Hz, CH$_3$), 2.2–2.5 (m, 8H, CH$_2$), 7.50 (m, 5H, Ph). ^{11}B NMR (C$_6$D$_6$): δ = 10.8 (s, B$_{basal}$), −39.9 (s, B$_{apical}$). ^{13}C NMR (C$_6$D$_6$): δ = 13.8, 14.2 (CH$_3$), 17.6, 19.4 (CH$_2$), 105 (br, CB$_{basal}$), 112.8 (CEt), 124.9,

125.7, 131.7 (Ph), alkynyl carbon atoms n.o. EI-MS: *m/z* (%) = 366 (100) [M$^+$], 388 (3) [**3a**$^+$]. HR-MS (EI): *m/z* = 366.1330 [M$^+$]; Calc. for ^{12}C$_{20}$^{1}H$_{25}$^{11}B$_2$ ^{79}Br 366.1326 (Δ*m* = 0.4 mmu); *m/z* = 388.2556 [**3a**$^+$]; Calcd. for ^{12}C$_{28}$^{1}H$_{30}$ ^{11}B$_2$ 388.2533 (Δ*m* = 2.3 mmu).

4.3. 1-Bromo-6-tert-butylethynyl-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-nido-hexaborane(6) (2b)

A portion of *n*BuBr (130 mg, 0.95 mmol) was added to a mixture of **1b** (180 mg, 0.46 mmol) and Pd(PPh$_3$)$_4$ (30 mg, 0.026 mmol) in THF (15 mL) at r.t. The yellow mixture was stirred overnight and heated at reflux for 5 days. After removing the solvent the yellow brown residue was extracted with hexane (2 × 20 mL) and filtered. The filtrate was dried in vacuo to give **2b** (136 mg, 85%) as a red-orange oil. ^{1}H NMR (C$_6$D$_6$): δ = 1.0 (br, 6H, CH$_3$), 1.27 (s, 9H, *t*Bu-H), 1.3 (br, 6H, CH$_3$), 2.0–2.3 (m, 8H, CH$_2$). ^{11}B NMR (C$_6$D$_6$): δ = 11.1 (s, B$_{basal}$), −40.0 (s, B$_{apical}$). ^{13}C NMR (C$_6$D$_6$): δ = 13.0, 14.0 (CH$_3$), 17.6, 19.3 (CH$_2$), 29.8 (C(CH$_3$)$_3$), 31.1 (*C*(CH$_3$)$_3$), 103 (br, CB$_{basal}$), 112.7 (CEt), alkynyl carbon atoms n.o. EI-MS: *m/z* (%) = 348 (100) [M$^+$]. HR-MS (EI): *m/z* = 348.1644 [M$^+$]; Calcd. for ^{12}C$_{18}$^{1}H$_{29}$^{11}B$_2$^{79}Br 348.1638 (Δ*m* = 0.6 mmu).

4.4. 1,6-Bis(phenylethynyl)-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-nido-hexaborane(6) (3a)

To a solution of phenylacetylene (146 mg, 1.43 mmol) in THF (10 mL) was added *n*BuLi (2.5 M in hexanes, 0.6 mL, 1.6 mmol) at −40 °C. The mixture was stirred for 30 min, ZnCl$_2$ (218 mg, 1.6 mmol) in a solution of THF (5 mL) was then added and the resulting yellow solution was warmed up and stirred for 2 h. The solution was transferred to a mixture of **1a** (436 mg, 1.1 mmol) and Pd(PPh$_3$)$_4$ (61 mg, 0.05 mmol) and the resulting yellow mixture was heated at reflux for 7 days. The solvent was removed, the yellow brown oily residue was extracted with hexane (2 × 20 mL) and filtered. The

yellow filtrate was dried in vacuo to give **3a** (350 mg, 86%) as a yellow oil. ^{1}H NMR (CDCl$_3$): δ = 1.28 (t, 6H, $^3J_{H,H}$ = 7.5 Hz, CH$_3$), 1.38 (t, 6H, $^3J_{H,H}$ = 7.5 Hz, CH$_3$), 2.3–2.5 (m, 8H, CH$_2$), 7.2–7.6 (m, 5H, Ph). ^{11}B NMR (CDCl$_3$): δ = 9.9 (s, B$_{basal}$), −49.8 (s, B$_{apical}$). ^{13}C NMR (CDCl$_3$): δ = 13.8, 14.9 (CH$_3$), 17.5, 19.3 (CH$_2$), 104 (CB$_{basal}$), 112.7 (CEt), 127.5, 128.0, 131.8, 132.1 (Ph), alkynyl carbon atoms n.o. EI-MS: m/z (%) = 388 (100) [M$^+$]. HR-MS (EI): m/z = 388.2519 [M$^+$]; Calcd. for ^{12}C$_{28}$^{1}H$_{30}$^{11}B$_2$ 388.2534 (Δm = −1.5 mmu).

4.5. 1,6-Bis(tert-butylethynyl)-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-nido-hexaborane(6) (3b)

The solvents of a solution of PhLi (1.8 M in cyclohexane/ether, v/v = 70/30, 1.62 mmol) were removed. THF (10 mL) and ZnCl$_2$ (235 mg, 1.72 mmol) were added at 0 °C and stirred for 3 h. To the resulting light yellow solution **1b** (180 mg, 0.46 mmol) and Pd(PPh$_3$)$_4$ (28 mg, 0.024 mmol) were added, and the yellow mixture was heated at reflux for 7 days. The solvent was removed, and the dark brown residue was extracted with hexane (2 × 20 mL) and filtered. The filtrate was dried in vacuo to give **3b** (60 mg, 37.5% based on **1b**) as a yellow oil. ^{1}H NMR (CD$_2$Cl$_2$): 1.2 (br, 6H, CH$_3$), 1.3 (br, 6H, CH$_3$), 1.36 (s, 9H, tBu-H), 1.37 (s, 9H, tBu-H), 2.2–2.4 (m, 8H, CH$_2$). ^{11}B NMR (CD$_2$Cl$_2$): δ = 8.9 (s, B$_{basal}$), −52.7 (s, B$_{apical}$). ^{13}C NMR (CD$_2$Cl$_2$): δ = 13.9, 14.4 (CH$_3$), 17.3, 19.0 (CH$_2$), 29.8 (C(CH$_3$)$_3$), 30.8, 31.1 (C(CH$_3$)$_3$), 103 (br, CB$_{basal}$), 111.9 (CEt). EI-MS: m/z (%) = 348 (100) [M$^+$]. HR-MS (EI): m/z = 348.3153 [M$^+$]; Calc. for ^{12}C$_{24}$^{1}H$_{38}$^{11}B$_2$ 348.3160 (Δm = −0.7 mmu).

4.6. Apically C$_2$(CH$_2$)$_4$C$_2$-linked clusters 4

n-BuLi (2.5 M in hexanes, 0.32 mL, 0.8 mmol) was added to a solution of 1,7-octadiyne (43 mg, 0.40 mmol) in THF (15 mL) at −60 °C, and stirred for 2 h. To the resulting white suspension ZnCl$_2$ (110 mg, 0.8 mmol) was added in one portion. The mixture was stirred for 2 h and half of the white suspension added to a mixture of **1c** (231 mg, 0.54 mmol) and Pd(PPh$_3$)$_4$ (30 mg, 0.026 mmol) in 10 mL of THF. The resulting mixture was heated at reflux for 7 days. After removing the solvent, the dark brown residue was extracted with hexane (2 × 25 mL) and filtered. The light yellow filtrate was dried in vacuo to give **4** (95 mg, 67%) as a yellow oil. On standing at r.t., a few colorless crystals were obtained and found to be ZnI$_2$(OPPh$_3$)$_2$. ^{1}H NMR (C$_6$D$_6$): δ = 1.0 (br, 12H, CH$_3$), 1.2 (br, 12H, C$_{cage}$-CH$_2$), 1.4 (br, 4H, CH$_2$CH$_2$), 2.0 (br, 4H, ≡CCH$_2$), 2.2–2.5 (m, 16H, CH$_2$). ^{11}B NMR (C$_6$D$_6$): δ = 10.4 (s, 2B, B$_{basal}$), −50.0 (s, 2B, B$_{apical}$). ^{13}C NMR (C$_6$D$_6$): δ = 13.6, 14.0 (CH$_3$), 17.4, 19.5 (cage-bound CH$_2$), 20.9 (≡CCH$_2$), 27.3 (CH$_2$CH$_2$), 105 (br, CB$_{basal}$), 111.9 (CEt), alkynyl carbon atoms n.o. EI-MS: m/z

(%) = 706 (46) [M$^+$]. HR-MS (EI): m/z = 706.5247 [M$^+$]; Calcd. for ^{12}C$_{50}$^{1}H$_{62}$^{11}B$_4$ 706.5224 (Δm = 2.3 mmu).

4.7. 1-Iodo-6-fluoro-2,3,4,5-tetraethyl-2,3,4,5-tetracarba-nido-hexaborane(6) (6)

(a) Reaction of **5** with SbF$_3$: A solution of **5** (145 mg, 0.33 mmol) in hexane (3 mL) was added dropwise to a suspension of SbF$_3$ (600 mg, 3.4 mmol) in hexane (2 mL) at r.t. The mixture was stirred for one week. The starting compound **5** remained unreacted as checked by ^{11}B NMR (δ = 6.5, −52.3 ppm).

(b) Reaction of **5** with AgF: A solution of **5** (145 mg, 0.33 mmol) in hexane (3 mL) was added dropwise to a suspension of AgF (180 mg, 1.4 mmol) in hexane (7 mL) at r.t. with exclusion of light. The mixture was stirred overnight and a colorless solution was obtained after filtration, which was dried to give **6** (60 mg, 56%) as a colorless oil. ^{1}H NMR (CDCl$_3$): δ = 1.18 (br, 6H, CH$_3$), 1.26 (br, 6H, CH$_3$), 2.08 (m), 2.33 (m) (8H, CH$_2$). ^{11}B NMR: δ = 21.9 (br, B$_{basal}$), −53.1 (s, B$_{apical}$). ^{13}C NMR: δ = 13.3, 14.1 (CH$_3$), 18.5, 20.1 (CH$_2$), 106 (br, CB$_{basal}$), signals for the other skeletal carbon atoms n.o. EI-MS: m/z (%) = 332 (100) [M$^+$], 205 (67) [M$^+$ − I]. HR-MS (EI): m/z = 332.0782 [M$^+$]; Calcd. for ^{12}C$_{12}$^{1}H$_{20}$^{19}F^{11}B$_2$ ^{127}I 332.0780 (Δm = 0.2 mmu).

4.8. Crystal structure determination for 2a and ZnI$_2$(OPPh$_3$)$_2$

Diffraction data were collected on a Bruker-AXS Smart 1000 CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å, graphite monochromator, ω-scans). Crystal data and details of the measurements are summarized in Table 1. Data were corrected for Lorentz polarization and absorption effects (semi-empirical, SADABS [11]). The structures were solved by direct methods (SHELXS86 [12]) and refined by full-matrix least-squares methods (SHELXL97 [12]) based on F^2 with all reflections. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were located in difference Fourier syntheses and refined isotropically (compound **2a**) or input in calculated positions [ZnI$_2$(OPPh$_3$)$_2$].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center: CCDC No. 268967 for ZnI$_2$(OPPh$_3$)$_2$, No. 268968 for **2a**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +44 (1223)336 033; e-mail deposit@ccde.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Table 1
Crystal data and details of data collection and structure solution of **2a** and ZnI$_2$(OPPh$_3$)$_2$

Identification Code	**2a**	ZnI$_2$(OPPh$_3$)$_2$
Empirical formula	C$_{20}$H$_{25}$B$_2$Br	C$_{36}$H$_{30}$I$_2$O$_2$P$_2$Zn
Formula weight	366.93	875.71
Temperature (K)	103(2)	100(2)
Crystal system	Monoclinic	Triclinic
Space group	*P*2(1)/*c*	*P*1
Unit cell dimensions		
a (Å)	7.6106(4)	10.0138(5)
b (Å)	16.0975(9)	10.2701(5)
c (Å)	16.1470(9)	10.6702(5)
α (°)	90	65.5770(10)
β (°)	101.127(1)	62.7660(10)
γ (°)	90	89.9560(10)
V (Å^3)	1941.0(2)	863.99(7)
Z	4	1
Calculated density (g/cm^3)	1.256	1.683
Absorption coefficient (mm^{-1})	2.114	2.620
F(0 0 0)	760	428
Crystal size (mm)	0.37 × 0.24 × 0.03	0.30 × 0.13 × 0.08
Maximum (°)	30.51	32.01.
Index ranges	−10/10, 0/22, 0/23	−14/14, −14/15, −15/15
Reflections collected	24,618	15,004
Independent reflections	5932 [R_{int} = 0.0427]	9363 [R^{int} = 0.0238]
Data/restraints/parameters	5932/0/308	9363/3/388
Flack x-parameter	–	0.011(8)
Goodness-of-fit on F^2	1.080	0.997
Final R indices		
R_1 [$I > 2\sigma(I)$]	0.0487	0.0253
wR_2 (all data)	0.1497	0.0572
Largest difference peak/hole (e Å^{-3})	0.689/−0.760	0.910/−0.479

References

[1] Houben-Weyl, Methoden der Organischen Chemie, Band 13/3a; R. Köster (Eds.), 1982; and 13/3b, 1982.
[2] (a) R.N. Grimes, Carborane, Academic Press, New York, 1970;
(b) T. Onak, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 1, Pergamon Press, Oxford, 1982, p. 411;
(c) T. Onak, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive organometallic chemistry, vol. 1, Pergamon Press, Oxford, 1995, p. 217.
[3] (a) K. Fuller, T. Onak, J. Organomet. Chem. 249 (1983) C6;
(b) B. Ng, T. Onak, J. Fluorine Chem. 27 (1985) 119;
(c) B. Ng, T. Onak, K. Fuller, Inorg. Chem. 24 (1985) 4371;

(d) F.A. Gomez, T. Onak, J. Arias, C. Alfonso, Main Group Metal Chem. 13 (1990) 237.
[4] (a) V.I. Stanko, Y.V. Gol'tyanin, Zhu. Obsh. Khim. 40 (1970) 127 [translated from Russ. J. Gen. Chem., 40 (1970) 115];
(b) V.I. Stanko, N.G. Iroshnikova, Zhu. Obsh. Khim. 40 (1970) 311 [translated from Russ. J. Gen. Chem., 40 (1970) 281].
[5] K.J. Winberg, G. Barbera, L. Eriksson, F. Texidor, V. Tolmachev, C. Vinas, S. Sjöberg, J. Organomet. Chem. 680 (2003) 188.
[6] W.J. Marshall, R.J. Young, Jr., V.V. Grushin, Organometallics 20 (2001) 523.
[7] A.D. Glöckle, Ph. D. Thesis, University of Bayreuth, 1998.
[8] (a) Y. Nie, S. Schwiegk, H. Pritzkow, W. Siebert, Eur. J. Inorg. Chem. (2004) 1630;
(b) Y. Nie, H. Pritzkow, W. Siebert, Eur. J. Inorg. Chem. (2004) 2425.
[9] G.B. Deacon, J.H.S. Green, Chemistry & Industry (London, United Kingdom) (1965) 1031.
[10] P.L. Timms, Acc. Chem. Res. 6 (1973) 118, and refs. therein.
[11] G.M. Sheldrick, SADABS, University of Göttingen, Germany, 1999.
[12] G.M. Sheldrick, SHELXS86, University of Göttingen, Germany, 1986;
G.M. Sheldrick, SHELXL97, University of Göttingen, Germany, 1997.