ORGANOMETALLICS

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Preparation of Dihydroborole Derivatives by a Simple 1,1-Carboboration Route

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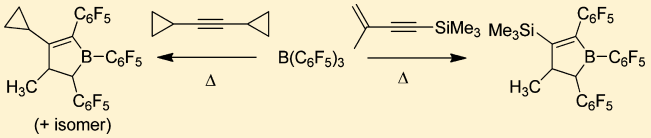
Supporting Information

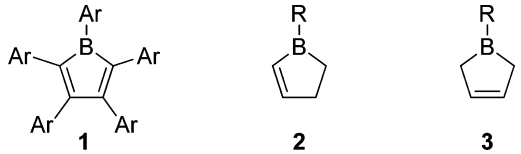
ABSTRACT: 2,3-Dihydroboroles are readily formed by treatment of dicyclopropylacetylene with the strongly electrophilic borane $B(C_6F_5)_3$. The reaction involves a sequence of 1,1-carboboration reactions and proceeds via dienylborane intermediates. Consistent with this, the reaction of the conjugated enyne **15c** with $B(C_6F_5)_3$ leads to the formation of a dihydroborole.



INTRODUCTION

There has been a recent revived interest in the chemistry of unsaturated five-membered boron heterocycles, the boroles (**1**), the 2,3-dihydroboroles (**2**), and the 2,5-dihydroboroles (**3**), respectively (see Chart 1). The potentially antiaromatic

Chart 1. Boron Heterocycles: Borole (1), 2,3-Dihydro- (2), and 2,5-Dihydroborole (3) Derivatives

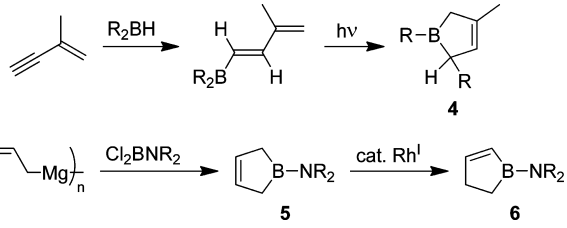


boroles can be synthesized and isolated by variants of the original route established by J. Eisch et al. if stabilized by sufficiently bulky aromatic substituents.[1] Eisch used the respective highly substituted 1,4-dilithio(tetraphenyl)butadiene reagent for the reaction with $RBCl_2$. Later variants employed, for example, the corresponding substituted zirconacyclopentadienes, as shown by Fagan et al.,[2] or the respective stannacyclopentadiene systems.[3−8]

2,5-Dihydroborole derivatives **4** were originally prepared by Zweifel from conjugated enynes in a two-step reaction sequence involving hydroboration and subsequent photolysis (see Chart 2).[9] Herberich synthesized the 2,5-dihydroborole system **5** by treatment of the Cl_2BNR_2 substrate with the oligomeric "butadiene-magnesium" reagent.[10] The Rh(I)-catalyzed isomerization of **5** represents one of the rare examples of a rather convenient 2,3-dihydroborole synthesis[11,12] (see Chart 2).

We have now found examples where 2,3-dihydroborole systems can be obtained in a very convenient way under mild reaction conditions by a 1,1-carboboration route[13,14] starting from simple substituted alkynes.

Chart 2. Syntheses of Dihydroborole Derivatives by Zweifel[9] (top) and Herberich[10] (bottom)



RESULTS AND DISCUSSION

In this study we reacted the strong boron Lewis acid $B(C_6F_5)_3$ (**7**)[15] with cyclopropylacetylene (**8a**) and dicyclopropylacetylene (**8b**),[16] respectively. The former reaction resulted in a clean 1,1-carboboration reaction of the acetylenic substrate; the latter reaction opened an easy pathway to 2,3-dihydroborole systems. Treatment of cyclopropylacetylene (**8a**) with $B(C_6F_5)_3$ (**7**) in [D_6]-benzene at ambient temperature gave a 2:1 mixture of the 1,1-carboboration products *Z*-**9a** and *E*-**9a** (characterized by NMR; for details see the Supporting Information). Subsequent photolysis (HPK 125, Pyrex filter) rapidly led to an almost complete isomerization of the *E*- to the *Z*-**9a** isomer. On a preparative scale a 1:1 mixture of **8a** and the borane **7** in pentane was stirred for 4 h at room temperature, followed by irradiation overnight and workup to give the pure *Z*-**9a** product in 63% yield as a colorless solid. The compound shows typical cyclopropyl ^{1}H NMR features at δ 0.42, 0.66 (2 H each) and 1.12 (1 H) and an olefinic =CH resonance at δ 6.36 (d, $^3J_{HH}$ = 11.0 Hz) (see Figure 1), a ^{11}B NMR signal at δ 61, and two sets of ^{19}F NMR signals in an overall 2:1 intensity ratio originating

Received: January 26, 2012
Published: March 14, 2012

   dx.doi.org/10.1021/om300065m | *Organometallics* 2012, 31, 2445−2451

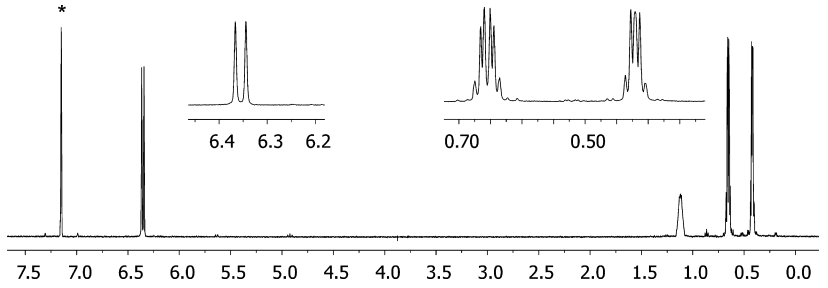
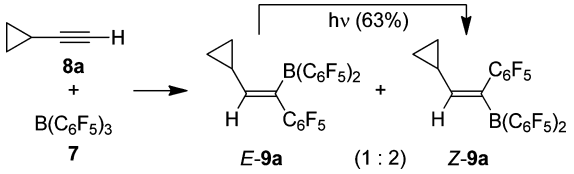


Figure 1. ^{1}H NMR spectrum (500 MHz, [D_6]-benzene*, 298 K) of the 1,1-carboboration product *Z*-**9a**.

from the $-B(C_6F_5)_2$ group and the adjacent (migrated) $-C_6F_5$ substituent.

Scheme 1. Synthesis of *Z*-9a in a 1,1-Carboboration Reaction



Compound *Z*-**9a** was characterized by X-ray diffraction (see Figure 2). The X-ray crystal structure analysis shows that the

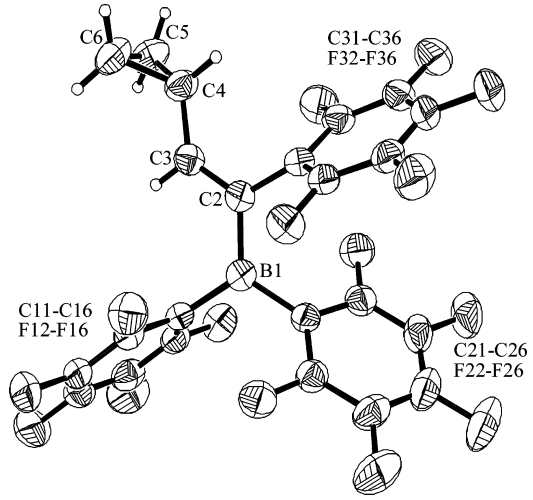
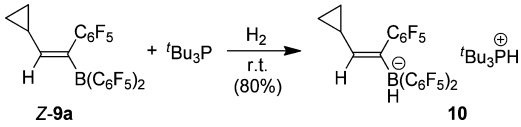


Figure 2. View of the molecular structure of the 1,1-carboboration product *Z*-**9a**.

boron Lewis acid **7** had added to a former acetylene carbon atom and shifted one of its C_6F_5 substituents to the same carbon center (B1−C2: 1.529(3) Å, C2−C31: 1.488(3) Å, angle B1−C2−C31 117.2(2)°). In order to allow the 1,1-carboboration sequence to take place, one of the former acetylene substituents (probably H) had to undergo a 1,2-migration along the acetylene $-C\equiv C-$ backbone. Consequently, we find both the H and the cyclopropyl substituent bonded to the other olefinic carbon atom (C3) of the product (C2−C3: 1.354(3) Å). The C_6F_5 and the cyclopropyl groups are found in a *Z*-1,2-arrangement at the central olefinic bond (angle C31−C2−C3: 121.8(2)°, C2−C3−C4: 127.4(2)°).

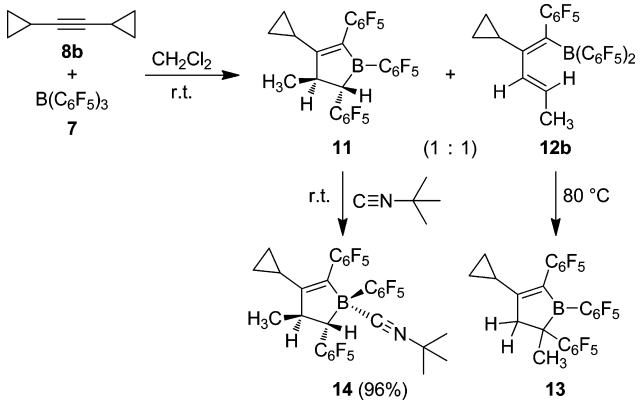
The product *Z*-**9a** could formally be regarded as a hydroboration product of 1-cyclopropyl-2-pentafluorophenylacetylene. Its straightforward formation from **8a** by the 1,1-carboboration/photochemical isomerization sequence underlines the emerging synthetic potential of these advanced 1,1-carboboration reactions.[14,17] The obtained alkenylborane *Z*-**9a** is a powerful Lewis acid itself. It forms a frustrated Lewis pair[18] with the bulky $^{t}Bu_3P$ phosphane Lewis base. This FLP rapidly activates dihydrogen under mild conditions to form the hydridoborate/phosphonium salt **10** (for details, including the X-ray crystal structure analysis of **10**, see the Supporting Information).

Scheme 2. Activation of Dihydrogen by the FLP *Z*-9a/P^{t}Bu$_3$



The reaction of dicyclopropylacetylene (**8b**) with $B(C_6F_5)_3$ (**7**) takes a slightly different course. The mixture of **8b** and **7** was dissolved in dichloromethane and stirred at room temperature overnight. This resulted in a 1:1 mixture of the products **11** and **12b** (see Scheme 3).[19] From the mixture we

Scheme 3. Preparation of 11, 13, and 14



identified the open product **12b** spectroscopically. It features the ^{1}H NMR signals of the terminal trans-propenyl group at δ 5.50/5.88 ($^{3}J_{HH}$ = 13.9 Hz) and δ 1.10 (CH_3) in addition to the typical cyclopropyl resonances. We find ^{19}F NMR signals of the single carbon-bound C_6F_5 group and of the $-B(C_6F_5)_2$ substituent. The ^{11}B NMR signal of **12b** occurs at ca. δ 66. The dihydroborole product **11** features a ^{11}B NMR signal at δ 70. It shows the ^{19}F NMR signals of three different C_6F_5 groups and ^{1}H NMR signals of the saturated endocyclic $-CH(CH_3)-CH(C_6F_5)-$ unit at δ 2.43/3.11 and 0.95 (CH_3). The 1,2-trans-arrangement of the CH_3/C_6F_5 substituents was secured by the X-ray crystal structure analysis of a derivative (**14**, see below).

dx.doi.org/10.1021/om300065m | *Organometallics* 2012, 31, 2445−2451

We found that heating of this mixture resulted in a clean rearrangement of the open product **12b** to a dihydroborole isomer **13**. Therefore, we carried out the reaction of **8b** with the borane **7** in toluene solution at 80 °C (20 h). After removal of the toluene solvent the pure dihydroborole product **11** was precipitated with pentane and isolated in 28% yield. The isomeric dihydroborole **13** was recovered from the pentane solution, admixed with a minor amount of **11** (~30%, **13**: **11** ≈ 3:1). Compound **13** was spectroscopically characterized (for details see the Experimental Section and the Supporting Information).

We treated the isolated pure dihydroborole **11** with a slight excess of *tert*-butylisocyanide (CH_2Cl_2, rt, overnight) to get the 1:1 adduct **14** in 96% yield. Single crystals of this compound suitable for X-ray crystal structure analysis (see Figure 3) were

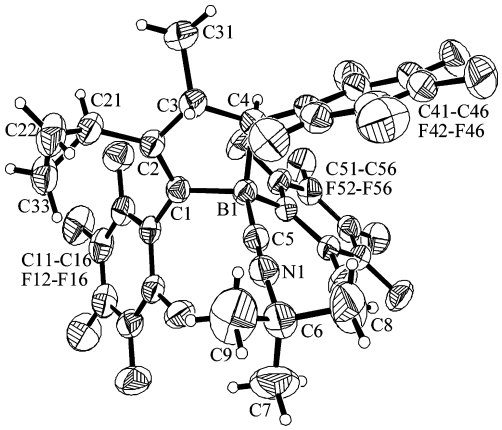


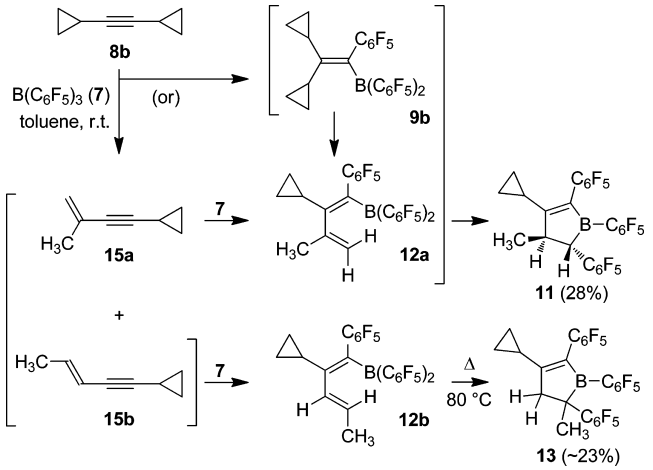
Figure 3. View of the molecular structure of the dihydroborole/isocyanide adduct **14**.

obtained from CD_2Cl_2/cyclopentane by the diffusion method. Compound **14** features a single diastereomer of the ^{t}BuNC adduct of the dihydroborole **11** in the crystal. It exhibits a slightly envelope-shaped unsaturated five-membered heterocyclic framework with bond lengths B1−C1 = 1.621(3) Å and C1−C2 = 1.335(3) Å, a C1−B1−C4 angle of 98.2(1)°, and dihedral angles B1−C1−C2−C3 = 1.4(2)° and C1−C2−C3−C4 = 16.9(2)°. The 3-CH_3, 4-C_6F_5, and B-C_6F_5 substituents are each oriented 1,2-trans to each other. The C1−C2 carbon−carbon double bond bears a C_6F_5 substituent (at C1 adjacent to boron) and an intact cyclopropyl group (at C2). The linear ^{t}BuNC ligand is attached at the endocyclic dihydroborole boron atom (B1−C5: 1.611(3) Å, C5−N1: 1.137(2) Å, angles B1−C5−N1: 177.3(2)°, C5−N1−C6: 172.7(2)°).

The observation of the formation of the dienylborane product **12b** indicates that one of the cyclopropyl substituents of the substrate **8b** was opened during the reaction (see Scheme 4).[19] The isomer **12a** was not observed; it apparently reacted further to the eventually isolated dihydroborole product **11**. This reaction represents a rare example of a 1,1-carboboration reaction of an alkene substrate.[9,20] The open product **12b** eventually undergoes the analogous cyclization reaction by thermally induced intramolecular alkene 1,1-carboboration upon heating.

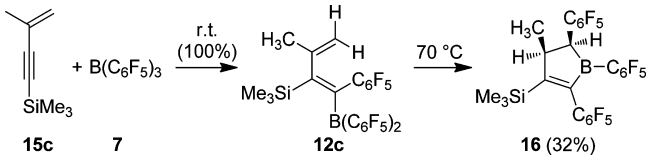
These results suggested that it should be possible to prepare 2,3-dihydroboroles by reacting a conjugated enyne with, for example, $B(C_6F_5)_3$. This is indeed the case. The reaction of the substituted enyne starting material **15c** with one molar equivalent of $B(C_6F_5)_3$ (**7**) was carried out at 70 °C overnight

Scheme 4. Possible Pathways for the Formation of 11 and 13



in toluene to give the 2,3-dihydroborole product **16**. Single crystals of **16** were obtained from pentane. The X-ray crystal structure analysis confirmed the formation of the five-membered boron-heterocycle by a consecutive 2-fold C_6F_5 migration from boron to carbon. Consequently, the −$SiMe_3$ has undergone a 1,2-shift along the C1−C2 vector (1.362(3) Å). The boron atom is planar tricoordinate (sum of the C−B−C bond angles: 359.8°). In contrast to the related compound **14**, the 2,3-dihydroborole **16** features the pair of vicinal CH_3 and C_6F_5 substituents at the C3−C4 single bond in cis positions (see Scheme 5 and Figure 4).

Scheme 5. Synthesis of 2,3-Dihydroborole 16 Starting from Enyne 15c



In solution compound **16** features the ^{19}F NMR signals of three different C_6F_5 groups as well as ^{1}H NMR signals of the methyl (δ 0.99, 3 H) and −$SiMe_3$ substituents (δ 0.10, 9 H, $^2J_{SiH}$ = 6.7 Hz). We obtained some information about the

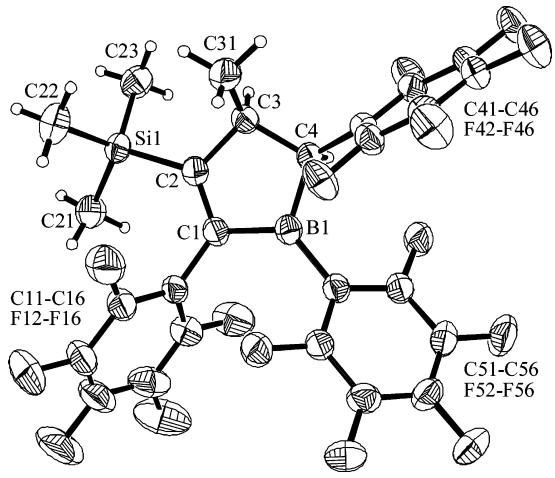


Figure 4. Molecular structure of 2,3-dihydroborole **16**.

dx.doi.org/10.1021/om300065m | *Organometallics* 2012, 31, 2445−2451

alleged intermediate **12c** by carrying out the reaction of **15c** with $B(C_6F_5)_3$ (**7**) in [D_6]-benzene at ambient temperature in an NMR experiment. **12c** is characterized by ^{1}H NMR signals of the olefinic $=CH_2$ group at δ 4.62, the methyl group (δ 1.50), and the $-SiMe_3$ moiety (δ −0.04). It features a ^{11}B NMR signal at δ 61 and the ^{19}F NMR signals for two different C_6F_5 groups in the ratio of 2:1. Eventually heating of the solution containing **12c** to 70 °C resulted in the formation of **16**.

CONCLUSIONS

Our study shows that 2,3-dihydroboroles can rather easily become available by the advanced variants of the 1,1-carboboration reaction. The use of strongly electrophilic $RB(C_6F_5)_2$-type boranes has made this reaction type very attractive for carrying out reaction sequences that require specific C−C bond formation. In addition, our example shows that carbon−carbon σ-bond activation,[14a] like that in the reaction sequence leading to **12a**,**b**, is observed more often in these advanced 1,1-carboboration reactions. This indicates that 1,1-carboboration may be of increasing importance in achieving progress in the selective rupture of nonactivated C−C single bonds and their utilization as "reactive groups" in synthesis, like that taking place in the described dihydroborole synthesis.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under an argon atmosphere with Schlenk-type glassware or in a glovebox. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use (for more information see the Supporting Information). The following instruments were used for physical characterization of the compounds. Elemental analyses: Foss-Heraeus CHNO-Rapid. NMR: Bruker AC 200P (^{11}B: 64 MHz), Bruker AV300 (^{1}H: 300 MHz, ^{19}F: 282 MHz), Varian 500 MHz INOVA (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{11}B: 160 MHz, ^{19}F: 470 MHz, ^{29}Si: 99 MHz), Varian UNITY plus NMR spectrometer (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{11}B: 193 MHz, ^{19}F: 564 MHz, ^{31}P: 243 MHz). Assignments of the resonances are supported by 2D experiments. All NMR spectra were recorded at room temperature unless otherwise noted. Melting points: DSC 2010 (TA-Instruments) apparatus, determined by the baseline method. Infrared spectroscopy: Varian 3100 FT-infrared spectroscopy (Excalibur Series) spectrometer. X-ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307−326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228−234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112−122), graphics XP (BrukerAXS, 2000). Graphics show thermal ellipsoids with 50% probability, *R* values are given for the observed reflections, and wR_2 values for all independent ones.

Materials. All reagents were obtained commercially and used without further purification unless otherwise noted. Cyclopropylacetylene (**8a**) was obtained from Aldrich and dried over 4 Å molecular sieves. $B(C_6F_5)_3$ (**7**) was prepared according to procedures reported in the literature (caution: the LiC_6F_5 intermediate involved is explosive).[15] Following a modified literature procedure, dicyclopropylacetylene (**8b**) was prepared using commercially available 5-chloro-1-pentyne.[16] Also, trimethyl-(3-methylbut-3-en-1-ynyl)silane (**15c**) was obtained from commercially available 2-methyl-1-buten-3-yne following a literature procedure.[21]

Preparation of Vinylborane *Z*-9a. Tris(pentafluorophenyl)-borane (**7**, 300 mg, 0.59 mmol, 1.0 equiv) was dissolved in *n*-pentane (25 mL). After the addition of cyclopropylacetylene (**8a**, 50 μL, 39 mg, 0.59 mmol, 1.0 equiv) the yellow reaction mixture was stirred at ambient temperature for 4 h. Subsequently, the mixture was irradiated overnight (UV light; HPK 125, Pyrex filter). When concentrating the reaction mixture (ca. 10 mL), the borane *Z*-**9a** precipitated as a white solid. The product was isolated after 10 min at −78 °C via cannula filtration. Finally the product was washed with cold *n*-pentane (5 mL) and dried under vacuum. (246 mg, 0.43 mmol, 63%, colorless solid). Colorless crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of a solution of compound *Z*-**9a** in *n*-pentane. Anal. Calcd for $C_{23}H_6BF_{15}$ (M = 578.08 g/mol): C, 47.79; H, 1.05. Found: C, 47.28; H, 0.21. Mp: 137 °C. ^{1}H NMR (500 MHz, [D_6]-benzene, 298 K): δ 6.36 (d, $^3J_{HH}$ = 11.0 Hz, 1H, =CH), 1.12 (br, 1H, CH), 0.66 (m, 2H, $CH_{2(trans)}$), 0.42 (m, 2H, $CH_{2(cis)}$). ^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 298 K): δ 178.2 (=CH), 146.2 (dm, $^1J_{FC} \approx$ 246 Hz, *m*-^{B}C_6F_5), 144.0 (dm, $^1J_{FC} \approx$ 245 Hz, *m*-^{C}C_6F_5), 143.3 (dm, $^1J_{FC} \approx$ 258 Hz, *p*-^{B}C_6F_5), 140.7 (dm, $^1J_{FC} \approx$ 255 Hz, *p*-^{C}C_6F_5), 137.8 (dm, $^1J_{FC} \approx$ 251 Hz, *o*-^{C}C_6F_5), 137.6 (dm, $^1J_{FC} \approx$ 254 Hz, *o*-^{B}C_6F_5), 130.8 (br, =C^B), 114.9 (tm, $^2J_{FC}$ = 19.4 Hz, *i*-^{C}C_6F_5), 113.5 (br, *i*-^{B}C_6F_5), 17.9 (CH), 12.4 (CH_2). ^{11}B{^{1}H} NMR (160 MHz, [D_6]-benzene, 298 K): δ 61 ($\nu_{1/2} \approx$ 1000 Hz). ^{19}F NMR (470 MHz, [D_6]-benzene, 298 K): δ −130.5 (m, 4F, *o*-^{B}C_6F_5), −139.2 (m, 2F, *o*-^{C}C_6F_5), −147.2 (t, $^3J_{FF}$ = 20.7 Hz, 2F, *p*-^{B}C_6F_5), −154.4 (t, $^3J_{FF}$ = 21.4 Hz, 1F, *p*-^{C}C_6F_5), −160.4 (m, 4F, *m*-^{B}C_6F_5), −161.6 (m, 2F, *m*-^{C}C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 13.2].

X-ray crystal structure of *Z*-9a: formula $C_{23}H_6BF_{15}$, M = 578.09, colorless crystal 0.45 × 0.20 × 0.15 mm, a = 8.8154(3) Å, b = 12.9050(6) Å, c = 19.3331(5) Å, V = 2199.39(14) Å^3, ρ_{calc} = 1.746 g cm^{-3}, μ = 1.743 mm^{-1}, empirical absorption correction ($0.508 \le T \le 0.780$), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 11 561 reflections collected ($\pm h, \pm k, \pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 3764 independent (R_{int} = 0.036) and 3604 observed reflections [$I \ge 2\sigma(I)$], 352 refined parameters, R = 0.032, wR_2 = 0.087, Flack parameter 0.00(10), max. (min.) residual electron density 0.12 (−0.17) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Characterization of Vinylborane *E*-9a. *NMR Scale.* The *E*-isomer *E*-**9a** was characterized by NMR spectroscopy of a mixture of isomers *Z*-**9a** and *E*-**9a**. Therefore tris-(pentafluorophenyl)borane (**7**, 26 mg, 0.050 mmol, 1.0 equiv) was dissolved in [D_6]-benzene (0.7 mL), and cyclopropylacetylene (**8a**, 3.8 μL, 3.0 mg, 0.050 mmol, 1.0 equiv) was added in the dark. The reaction mixture was transferred into an NMR tube, which was sealed immediately in an argon atmosphere. *Z*-**9a** and *E*-**9a** were obtained in a ratio of *Z*-**9a**:*E*-**9a** = 2:1 (determined from the ^{1}H NMR spectrum; admixed with a compound not identified yet). ^{1}H NMR (500 MHz, [D_6]-benzene, 299 K): δ 5.83 (d, $^3J_{HH}$ = 11.2 Hz, 1H, =CH), 1.16 (br, 1H, CH), 0.38 (m, 2H, $CH_{2(trans)}$), 0.31 (m, 2H, $CH_{2(cis)}$). ^{13}C{^{1}H} NMR (126 MHz, [D_6]-benzene, 299 K): δ 168.3 (=CH), 127.5 (=C^B)[1], 16.8 (CH), 11.0 (CH_2), [C_6F_5 not listed; [1]from the GHMBC experiment]. ^{19}F NMR (470 MHz, [D_6]-benzene, 299 K): δ −129.3 (m, 4F, *o*-^{B}C_6F_5), −142.9 (m, 2F, *o*-^{C}C_6F_5), −145.1 (m, 2F, *p*-^{B}C_6F_5), −156.0 (t, $^3J_{FF}$ = 21.4 Hz, 1F, *p*-^{C}C_6F_5), −160.5 (m, 4F, *m*-^{B}C_6F_5), −162.2 (m, 2F, *m*-^{C}C_6F_5), [$\Delta\delta$ $^{19}F_{m,p}$ = 15.4].

Preparation of Compound 10. Both *Z*-**9a** (28.9 mg, 50.0 μmol, 1.00 equiv) and tri(*tert*-butyl)phosphane (10.1 mg, 50.0 μmol, 1.00 equiv) were dissolved in *n*-pentane (each 2 mL) separately and then mixed together. The turbid reaction mixture was stirred for 30 min at ambient temperature until the mixture became clear again. Subsequently, the flask was evacuated, flushed with dihydrogen ($p(H_2)$ = 2.5 bar), and stirred for 24 h. The colorless precipitate was isolated via cannula filtration and washed with *n*-pentane (2 × 2 mL). After drying under high vacuum, compound **10** was isolated as a colorless solid (31 mg, 40 μmol, 80%). Single crystals suitable for an X-ray diffraction analysis were obtained by slow diffusion of *n*-pentane into a solution of **10** in dichloromethane at −35 °C. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 5.32 (d, $^1J_{PH}$ = 433.8 Hz, 1H, PH), 4.77 (d, $^3J_{HH}$ = 9.3 Hz, 1H, =CH), 3.20 (br 1:1:1:1 q, $^1J_{BH} \approx$ 94 Hz, 1H, BH), 1.64 (d, $^3J_{PH}$ = 15.7 Hz, 27H, CH_3), 0.98 (m, 1H, CH), 0.50 (m, 2H, $CH_{2(trans)}$), 0.22 (m, 2H, $CH_{2(cis)}$). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2,

298 K): δ 211.8 (=C^B), 138.1 (=CH), 38.0 (d, $^1J_{PC}$ = 27.0 Hz, C^{tBu}), 30.3 (CH_3), 13.1 (CH), 6.4 (CH_2), [C_6F_5 not listed]. ^{11}B NMR (192 MHz, CD_2Cl_2, 298 K): δ −40.0 (br d, $^1J_{BH} \approx 92$ Hz). $^{11}B\{^1H\}$ NMR (192 MHz, CD_2Cl_2, 298 K): δ −40.0 ($\nu_{1/2} \approx 50$ Hz). ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ −131.3 (m, 4F, *o*-$^BC_6F_5$), −140.8 (m, 2F, *o*-$^CC_6F_5$), −164.2 (t, $^3J_{FF}$ = 20.9 Hz, 1F, *p*-$^CC_6F_5$), −164.9 (t, $^3J_{FF}$ = 20.4 Hz, 2F, *p*-$^BC_6F_5$), −166.6 (m, 2F, *m*-$^CC_6F_5$), −167.7 (m, 4F, *m*-$^BC_6F_5$), [$\Delta\delta$ $^{19}F_{m,p}$ = 2.8]. ^{31}P NMR (243 MHz, CD_2Cl_2, 298 K): δ 58.7 (d28tet, $^1J_{PH}$ = 433.8 Hz, $^3J_{PH}$ = 15.7 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, CD_2Cl_2, 298 K): δ 58.7 ($\nu_{1/2} \approx 5$ Hz).

X-ray crystal structure analysis of 10: formula $C_{35}H_{35}BF_{15}P$, M = 782.41, colorless crystal 0.25 × 0.20 × 0.17 mm, a = 9.9747(8) Å, b = 12.2460(13) Å, c = 16.1369(17) Å, α = 87.714(12)°, β = 75.686(9)°, γ = 72.078(8)°, V = 1815.9(3) Å^3, ρ_{calc} = 1.431 g cm^{-3}, μ = 1.604 mm^{-1}, empirical absorption correction (0.690 ≤ T ≤ 0.772), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 19 519 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 6210 independent (R_{int} = 0.039) and 5596 observed reflections [$I \geq 2\sigma(I)$], 484 refined parameters, R = 0.076, wR_2 = 0.229, max. (min.) residual electron density 1.31 (−0.46) e Å^{-3}, cation disordered and refined with thermal restraints, hydrogen atoms at P and B from difference Fourier calculations, others calculated and refined as riding atoms.

Preparation of 2,3-Dihydroborole 11. Both tris(pentafluorophenyl)borane (**7**, 512 mg, 1.00 mmol, 1.00 equiv) and dicyclopropylacetylene (**8b**, 106 mg, 1.00 mmol, 1.00 equiv) were dissolved in toluene (each 3 mL) separately and then mixed together. Subsequently, the orange solution was heated at 80 °C for 20 h. After removal of the solvent *in vacuo*, the residue was dissolved in *n*-pentane (5 mL) and the mixture was dried again. This procedure was repeated four times. Thereupon, *n*-pentane (5 mL) was added and a colorless precipitate was formed, which was isolated via cannula filtration at −10 °C and thoroughly washed with *n*-pentane (5 × 3−5 mL). Finally, the obtained product **11** was dried under vacuum (173 mg, 0.280 mmol, 28%, colorless solid). Single crystals suitable for an X-ray diffraction analysis were obtained by slow evaporation of a mixture of **11** and **13** in *n*-pentane (for details see the Supporting Information). Anal. Calcd for $C_{26}H_{10}BF_{15}$ (M = 618.14 g/mol): C, 50.52; H, 1.63. Found: C, 50.00; H, 1.98. Mp: 151 °C. ^{1}H NMR (500 MHz, [D_6]-benzene, 298 K): δ 3.11 (br, 1H, CH^{C6F5}), 2.43 (qd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.0 Hz, 1H, CH^{Me}), 1.27 (m, 1H, CH), 0.95 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3), 0.65 (trans), 0.44 (cis) (each m, each 1H, CH_2), 0.56 (trans), 0.47 (cis) (each m, each 1H, $CH_{2'}$). $^{13}C\{^1H\}$ NMR (126 MHz, [D_6]-benzene, 298 K): δ 200.1 (=C^C), 132.9 (br, =C^B), 116.0 (tm, $^2J_{FC} \approx 19$ Hz, *i*-$^CC_6F_5$[a]), 114.3 (tm, $^2J_{FC} \approx 20$ Hz, *i*-$^CC_6F_5$[b]), 109.5 (br, *i*-$^BC_6F_5$), 52.5 (CH^{Me}), 41.7 (br, CH^{C6F5}), 19.9 (CH_3), 15.9 (CH), 10.7 (CH_2), 8.7 ($CH_{2'}$), [C_6F_5 not listed]. $^{11}B\{^1H\}$ NMR (160 MHz, [D_6]-benzene, 298 K): δ 70 ($\nu_{1/2} \approx 1000$ Hz). ^{19}F NMR (470 MHz, [D_6]-benzene, 298 K): δ −130.2 (m, 2F, *o*-$^BC_6F_5$), −138.4 (m, 1F, *o*-$^CC_6F_5$[b]), −142.5 (m, 1F, *o'*-$^CC_6F_5$[b]), −143.2 (m, 2F, *o*-$^CC_6F_5$[a]), −146.5 (m, 1F, *p*-$^BC_6F_5$), −155.6 (t, $^3J_{FF}$ = 21.6 Hz, 1F, *p*-$^CC_6F_5$[b]), −156.8 (t, $^3J_{FF}$ = 21.4 Hz, 1F, *p*-$^CC_6F_5$[a]), −160.0 (m, 2F, *m*-$^BC_6F_5$), −161.8 (m, 2F, *m*-$^CC_6F_5$[a]), −162.3 (m, 1F, *m*-$^CC_6F_5$[b]), −162.6 (m, 1F, *m'*-$^CC_6F_5$[b]), [$\Delta\delta^{19}F_{m,p}$ = 13.5].

Characterization of Butadienylborane 12b. Both tris(pentafluorophenyl)borane (**7**, 512 mg, 1.00 mmol, 1.00 equiv) and dicyclopropylacetylene (**8a**, 106 mg, 1.00 mmol, 1.00 equiv) were dissolved in dichloromethane (each 3 mL) separately and then mixed together. Subsequently, the orange solution was stirred overnight at ambient temperature. After removal of the solvent *in vacuo* a 1:1 mixture (determined in ^{1}H NMR) of **12b** and **11** was obtained. ^{1}H NMR (500 MHz, [D_6]-benzene, 298 K): δ 5.88 (dq, $^3J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, =CH^{Me}), 5.50 (dm, $^3J_{HH}$ = 13.9 Hz, 1H, =CH), 1.24 (m, 1H, CH), 1.10 (dd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.5 Hz, 3H, CH_3), 0.55 (m, 2H, $CH_{2(trans)}$), 0.48 (m, 2H, $CH_{2(cis)}$). $^{13}C\{^1H\}$ NMR (126 MHz, [D_6]-benzene, 298 K): δ 174.1 (=C), 143.3 (=C^{Me}), 133.6 (=CH), 130.6 (=C^B)[1], 17.9 (CH_3), 17.6 (CH), 9.7 (CH_2), [C_6F_5 not listed; [1]from the GHMBC experiment]. $^{11}B\{^1H\}$ NMR (64 MHz, [D_6]-benzene, 298 K) [mixture]: δ ∼66 ($\nu_{1/2} \approx 2000$ Hz). ^{19}F NMR (470 MHz, [D_6]-benzene, 298 K): δ −131.4 (m, 4F, *o*-$^BC_6F_5$), −139.3 (m, 2F, *o*-$^CC_6F_5$), −149.0 (t, $^3J_{FF}$ = 19.2 Hz, 2F, *p*-$^BC_6F_5$), −155.2 (t, $^3J_{FF}$ = 21.5 Hz, 1F, *p*-$^CC_6F_5$), −162.4 (m, 4F, *m*-$^BC_6F_5$), −163.1 (m, 2F, *m*-$^CC_6F_5$), [$\Delta\delta^{19}F_{m,p}$ = 13.4].

Characterization of 2,3-Dihydroborole 13. Both tris(pentafluorophenyl)borane (**7**, 512 mg, 1.00 mmol, 1.00 equiv) and dicyclopropylacetylene (**8b**, 106 mg, 1.00 mmol, 1.00 equiv) were dissolved in toluene (each 3 mL) separately and then mixed together. Subsequently, the orange solution was heated at 80 °C for 20 h. After removal of the solvent *in vacuo*, the residue was dissolved in *n*-pentane (5 mL) and the mixture was dried again. This procedure was repeated four times. Thereupon, *n*-pentane (5 mL) was added and a colorless precipitate was formed. At −10 °C the solution was filtered off and the reddish residue was washed with cold *n*-pentane (4 × 5 mL). After evaporation of the solvent, a mixture of **13** and **11** in a ratio of 3:1 was obtained as an orange, highly viscous oil (192 mg, 0.311 mmol, 31%). NMR scale: 2,3-Dihydroborole **13** was characterized by NMR spectroscopy of a mixture of the 2,3-dihydroboroles **11** and **13**. Therefore tris(pentafluorophenyl)borane (**7**, 51.2 mg, 0.100 mmol, 1.00 equiv) was dissolved in [D_6]-benzene (0.7 mL) and dicyclopropylacetylene (**8b**, 10.6 mg, 0.100 mmol, 1.00 equiv) was added. The reaction mixture was transferred into an NMR tube, which was sealed immediately in an argon atmosphere. **11** and **13** were obtained in a ratio of **11**:**13** = 1:1 (determined in ^{1}H NMR). ^{1}H NMR (500 MHz, [D_6]-benzene, 298 K): δ 2.36, 2.12 (AB, each d, each $^2J_{HH}$ = 18.5 Hz, each 1H, $^CCH_2$), 1.44 (t, J = 2.3 Hz, 3H, CH_3), 1.42 (m, 1H, CH), 0.64, 0.58 (each m, Σ 4H, CH_2). $^{13}C\{^1H\}$ NMR (126 MHz, [D_6]-benzene, 298 K): δ 192.9 (=C), 131.3 (=C^B), 51.1 ($^CCH_2$), 37.6 (br, ^{Me}CB), 20.7 (m, CH_3), 16.7 (CH), 10.7, 10.5 (CH_2), [C_6F_5 not listed]. ^{19}F NMR (470 MHz, [D_6]-benzene, 298 K): δ −128.9 (m, 2F, *o*-$^BC_6F_5$), −139.4 (m, 2F, *o*-$^CC_6F_5$[a]), −141.0 (m, 1F, *o*-$^CC_6F_5$[b]), −141.1 (m, 1F, *o'*-$^CC_6F_5$[b]), −148.3 (m, 1F, *p*-$^BC_6F_5$), −156.9 (t, $^3J_{FF}$ = 21.4 Hz, 1F, *p*-$^CC_6F_5$[b]), −158.2 (t, $^3J_{FF}$ = 21.6 Hz, 1F, *p*-$^CC_6F_5$[a]), −161.4 (m, 2F, *m*-$^BC_6F_5$), −163.3 (m, 2F, *m*-$^CC_6F_5$[a]), −163.3 (m, 1F, *m*-$^CC_6F_5$[b]), −163.6 (m, 1F, *m'*-$^CC_6F_5$[b]), [$\Delta\delta^{19}F_{m,p}$ = 13.1].

Preparation of Dihydroborole/Isocyanide Adduct 14. Both the 2,3-dihydroborole **11** (68.5 mg, 0.110 mmol, 1.00 equiv) and *tert*-butyl isocyanide (11 mg, 0.13 mmol, 1.2 equiv) were dissolved in dichloromethane (each 2 mL) separately and then mixed together. Subsequently, the colorless solution was stirred overnight at ambient temperature. After removal of the solvent *in vacuo*, the colorless residue was washed with *n*-pentane (3 mL). Finally, product **14** was dried under vacuum (74.0 mg, 0.106 mmol, 96%, colorless solid). Colorless crystals suitable for an X-ray crystal structure analysis were obtained by slow diffusion of cyclopentane into a solution of compound **14** in deuterated dichloromethane. Mp: 171 °C. ^{1}H NMR (600 MHz, [D_6]-benzene, 298 K): δ 3.43 (br m, 1H, CH^{Me}), 3.24 (d, $^3J_{HH}$ = 9.5 Hz, 1H, CH^{C6F5}), 1.44 (m, 1H, CH), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 0.80 (s, 9H, CH_3^{tBu}), 0.46 (trans), 0.13 (cis) (each m, each 1H, CH_2), 0.33 (trans), −0.03 (cis) (each m, each 1H, $CH_{2'}$). $^{13}C\{^1H\}$ NMR (151 MHz, [D_6]-benzene, 298 K): δ 162.5 (=C), 129.3 (=C^B)[1], 127.3 (C≡N)[1], 119.7 (tm, $^2J_{FC} \approx 17$ Hz, *i*-$^CC_6F_5$[a]), 117.6 (tm, $^2J_{FC} \approx 20$ Hz, *i*-$^CC_6F_5$[b]), 116.2 (br, *i*-$^BC_6F_5$), 59.3 (C^{tBu}), 46.7 (br, CH^{Me}), 41.5 (br, CH^{C6F5}), 28.1 (m, CH_3^{tBu}), 20.0 (m, CH_3), 12.7 (CH), 6.1 ($CH_{2'}$), 5.1 (CH_2), [not listed: *o*-, *m*-, *p*-C_6F_5; [1]from the GHMBC experiment]. $^{11}B\{^1H\}$ NMR (192 MHz, [D_6]-benzene, 298 K): δ −13.4 ($\nu_{1/2} \approx 150$ Hz). ^{19}F NMR (564 MHz, [D_6]-benzene, 298 K): δ −133.9 (m, 2F, *o*-$^BC_6F_5$), −136.9 (m, 1F, *o*-$^CC_6F_5$[b]), −140.9 (br, 2F, *o*-$^CC_6F_5$[a]), −142.0 (m, 1F, *o'*-$^CC_6F_5$[b]), −156.2 (t, $^3J_{FF}$ = 20.9 Hz, 1F, *p*-$^BC_6F_5$), −158.2 (t, $^3J_{FF}$ = 21.5 Hz, 1F, *p*-$^CC_6F_5$[b]), −159.9 (t, $^3J_{FF}$ = 21.5 Hz, 1F, *p*-$^CC_6F_5$[a]), −162.7 (m, 1F, *m*-$^CC_6F_5$[b]), −162.9 (m, 2F, *m*-$^BC_6F_5$), −163.4 (br, 2F, *m*-$^CC_6F_5$[a]), −165.1 (m, 1F, *m'*-$^CC_6F_5$[b]), [$\Delta\delta^{19}F_{m,p}$ = 6.7].

X-ray crystal structure analysis of 14: formula $C_{31}H_{19}BF_{15}N$, M = 701.28, colorless crystal 0.30 × 0.30 × 0.27 mm, a = 13.1586(5) Å, b = 10.5956(3) Å, c = 21.6978(9) Å, β = 94.760(4)°, V = 3014.74(19) Å^3, ρ_{calc} = 1.545 g cm^{-3}, μ = 1.391 mm^{-1}, empirical absorption correction (0.680 ≤ T ≤ 0.705), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 25 924 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.60 Å^{-1}, 5240 independent (R_{int} = 0.042) and 4615 observed reflections [$I \geq 2\sigma(I)$],

dx.doi.org/10.1021/om300065m | *Organometallics* 2012, 31, 2445−2451

437 refined parameters, R = 0.044, wR_2 = 0.121, max. (min.) residual electron density 0.20 (−0.23) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Characterization of Vinylborane 12c. *NMR Scale.* Both the enyne **15c** (13.8 mg, 0.100 mmol, 1.00 equiv) and tris(pentafluorophenyl)borane (**7**, 51.2 mg, 0.100 mmol, 1.00 equiv) were dissolved in [D$_6$]-benzene (each ca. 0.4 mL) separately and then mixed together. The yellow reaction mixture was transferred into an NMR tube, which was sealed in an argon atmosphere immediately. **12c** was obtained in 100% conversion of the starting materials. ^{1}H NMR (500 MHz, [D$_6$]-benzene, 299 K): δ 4.62 (m, 2H, =CH$_2$), 1.50 (s, 3H, CH$_3$), −0.04 (s, $^2J_{SiH}$ = 2.5 Hz, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (126 MHz, [D$_6$]-benzene, 299 K): δ 173.4 (=C^{Si}), 148.5 (dm, $^1J_{FC}$ ≈ 250 Hz, C$_6$F$_5$), 147.1 (=C^{Me}), 144.6 (dm, $^1J_{FC}$ ≈ 260 Hz, C$_6$F$_5$), 144.0 (dm, $^1J_{FC}$ ≈ 245 Hz, C$_6$F$_5$), 140.7 (dm, $^1J_{FC}$ ≈ 255 Hz, C$_6$F$_5$), 138.6 (=C^B), 137.8 (dm, $^1J_{FC}$ ≈ 255 Hz, C$_6$F$_5$), 137.7 (dm, $^1J_{FC}$ ≈ 255 Hz, C$_6$F$_5$), 116.0 (m,$^2J_{FC}$ ≈ 22 Hz, i-^{C}C$_6$F$_5$), 114.1 (br m, i-^{B}C$_6$F$_5$), 112.4 (=CH$_2$), 22.8 (CH$_3$), 0.4 ($^1J_{SiC}$ = 53.2 Hz, SiMe$_3$). ^{11}B{^{1}H} NMR (160 MHz, [D$_6$]-benzene, 299 K): δ ∼61 ($\nu_{1/2}$ ≈ 1400 Hz). ^{19}F NMR (470 MHz, [D$_6$]-benzene, 299 K): δ −126.7 (m, 4F, o-^{B}C$_6$F$_5$), −136.8 (m, 2F, o-^{C}C$_6$F$_5$), −143.6 (tm, $^3J_{FF}$ = 20.9 Hz, 2F, p-^{B}C$_6$F$_5$), −153.5 (t, $^3J_{FF}$ = 21.4 Hz, 1F, p-^{C}C$_6$F$_5$), −160.5 (m, 4F, m-^{B}C$_6$F$_5$), −162.0 (m, 2F, m-^{C}C$_6$F$_5$), [$\Delta\delta$ ^{19}F$_{m,p}$ = 16.9]. ^{29}Si{^{1}H} DEPT (99 MHz, [D$_6$]-benzene, 299 K): δ −4.8 (SiMe$_3$).

Preparation of 2,3-Dihydroborole 16. Both enyne **15c** (138 mg, 1.00 mmol, 1.00 equiv) and tris(pentafluorophenyl)borane (**7**, 512 mg, 1.00 mmol, 1.00 equiv) were dissolved in toluene (each 5 mL) separately and then mixed together. Subsequently, the yellow solution was stirred overnight at 70 °C before the orange reaction mixture was evaporated. After removal of the solvent *in vacuo*, the residue was dissolved in *n*-pentane (5 mL) and the mixture was dried again. This procedure was repeated four times. Finally, *n*-pentane (5 mL) was added, and the solution was cooled to −78 °C and kept for 30 min. During this time the product precipitated and the solution was removed via cannula. The product was washed with *n*-pentane (3 × 3 mL) at −78 °C and eventually dried under vacuum (211 mg, 0.320 mmol, 32%, colorless solid). Colorless crystals suitable for X-ray crystal structure analysis were obtained by slow evaporation of a solution of compound **16** in *n*-pentane at ambient temperature. Anal. Calcd for C$_{26}$H$_{14}$BF$_{15}$Si (M = 650.26 g/mol): C, 48.02; H, 2.17. Found: C, 48.14; H, 2.45. Mp: 95 °C. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): δ 3.83 (br m, 1H, CH^{Me}), 3.66 (br m, 1H, CH^{C6F5}), 0.99 (d, $^3J_{HH}$ = 7.3 Hz, 3H, CH$_3$), 0.10 (d, $^2J_{SiH}$ = 6.7 Hz, 9H, SiMe$_3$). ^{19}F NMR (470 MHz, CD$_2$Cl$_2$, 298 K): δ −130.6 (m, 2F, o-^{B}C$_6$F$_5$), −138.4, −143.0 (each br, each 1F, o-^{C}C$_6$F$_5^a$), −140.5, −142.0 (each m, each 1F, o-^{C}C$_6$F$_5^b$), −149.2 (m, 1F, p-^{B}C$_6$F$_5$), −157.0 (t, $^3J_{FF}$ = 20.7 Hz, 1F, p-^{C}C$_6$F$_5^b$), −157.4 (t, $^3J_{FF}$ = 20.7 Hz, 1F, p-^{C}C$_6$F$_5^a$), −161.3 (m, 2F, m-^{B}C$_6$F$_5$), −162.9 (br, 2F, m-^{C}C$_6$F$_5^a$), −163.0, −163.5 (each m, each 1F, m-^{C}C$_6$F$_5^b$), [$\Delta\delta$ ^{19}F$_{m,p}$ = 12.1]. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, 253 K): δ 3.79 (br m, 1H, CH^{Me}), 3.63 (br m, 1H, CH^{C6F5}), 0.95 (d, $^3J_{HH}$ = 7.2 Hz, 3H, CH$_3$), 0.06 (s, $^2J_{SiH}$ = 6.8 Hz, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (126 MHz, CD$_2$Cl$_2$, 253 K): δ 208.7 (=C^{Si}), 145.5 (=C^B), 115.7 (tm, $^2J_{FC}$ ≈ 20 Hz, i-^{C}C$_6$F$_5^b$), 114.9 (tm, $^2J_{FC}$ ≈ 20 Hz, i-^{C}C$_6$F$_5^a$), 109.4 (br m, i-^{B}C$_6$F$_5$), 52.9 (CH^{Me}), 40.5 (br, CH^{C6F5}), 19.2 (CH$_3$), −1.6 ($^1J_{SiC}$ = 52.8 Hz, SiMe$_3$), [not listed o-, p-, m-C$_6$F$_5$]. ^{19}F NMR (470 MHz, CD$_2$Cl$_2$, 253 K): δ −130.5 (m, 2F, o-^{B}C$_6$F$_5$), −138.4, −142.9 (each m, each 1F, o-^{C}C$_6$F$_5^a$), −140.7, −142.0 (each m, each 1F, o-^{C}C$_6$F$_5^b$), −149.0 (m, 1F, p-^{B}C$_6$F$_5$), −156.7 (t, $^3J_{FF}$ = 21.0 Hz, 1F, p-^{C}C$_6$F$_5^b$), −157.3 (t, $^3J_{FF}$ = 21.0 Hz, 1F, p-^{C}C$_6$F$_5^a$), −161.0 (m, 2F, m-^{B}C$_6$F$_5$), −162.5, −162.9 (each m, each 1F, m-^{C}C$_6$F$_5^a$), −162.7, −163.2 (each m, each 1F, m-^{C}C$_6$F$_5^b$), [$\Delta\delta$ ^{19}F$_{m,p}$ = 12.0]. ^{29}Si{^{1}H} DEPT (99 MHz, CD$_2$Cl$_2$, 253 K): δ −5.6 (SiMe$_3$).

X-ray crystal structure analysis of 16: formula C$_{26}$H$_{14}$BF$_{15}$Si·1/2C$_5$H$_{12}$, M = 686.35, colorless crystal 0.35 × 0.28 × 0.27 mm, a = 7.4428(2) Å, b = 12.5739(10) Å, c = 16.1379(5) Å, α = 92.161(3)°, β = 102.917(2)°, γ = 100.476(4)°, V = 1442.67(13) Å^3, ρ_{calc} = 1.580 g cm^{-3}, μ = 1.810 mm^{-1}, empirical absorption correction (0.570 ≤ T ≤ 0.641), Z = 2, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 21 478 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.60 Å^{-1}, 4930 independent (R_{int} = 0.036) and 4763 observed reflections [$I \geq 2\sigma(I)$], 439 refined parameters, R = 0.041, wR_2 = 0.114, max. (min.) residual electron density 0.29 (−0.32) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving further experimental and spectroscopic details and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

§X-ray crystal structure analyses.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank Boulder Scientific Company for a donation of B(C$_6$F$_5$)$_3$.

■ DEDICATION

Dedicated to Professor Friedrich Bickelhaupt on the occasion of his 80th birthday.

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