Synthesis and Reactivity of Monoborylacetylene Derivatives

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Dedicated to Prof. Ulrich Müller on the occasion of his 60th birthday

Keywords: Alkynes / Boranes / Boron / Hydroboration / Phenols

The catechol-substituted monoborylacetylenes **1a**–**d** are obtained from the reaction of bis(diisopropylamino)borylacetylene with catechol derivatives and 2,2′-biphenol. The catalytic trimerization of **1a**–**d** with $[(\eta^5\text{-}C_5H_5)Co(CO)_2]$ yields isomeric mixtures of the triborylbenzene derivatives **2a,2a′**, **2b,2b′**, and **2c,2c′**. The reaction of **2a,2a′** with mesitylllithium provides the hexamesityl-substituted 1,3,5-triborylbenzene **2e**. Hydroboration of **1a** with catecholborane affords a mixture of 1,1-bis(1,3,2-benzodioxaborol-2-yl)ethene (**3a**) and *trans*-1,2-bis(1,3,2-benzodioxaborol-2-yl)ethene (**4a**). Hydroboration of **1a** and **3a** with one or two mol of $HBCl_2$ and subsequent substitution of the chlorine atoms of the product with catechol leads in each case to the 1,1,1-trisborylmethane derivative **5a** in 83 and 78% yield, respectively, which forms the tris(THF) adduct **5a**$(thf)_3$. Treatment of **5a** with *t*BuLi yields 1,1,1-tris[di(*tert*-butyl)boryl]ethane **6a**. $[Co_2(CO)_8]$ reacts with **1a** to give 3-(1,3,2-benzodioxaborol-2-yl)-1,2-bis(tricarbonylcobalta)tetrahedrane **(9a)**. The new compounds have been characterized by NMR spectroscopy and mass spectrometry as well as by X-ray structure analyses for **1a**, **3a**, **5a**, **5a**$(thf)_3$, and **9a**.

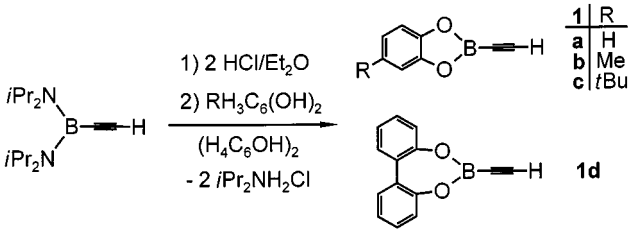
Introduction

Alkynylboranes are interesting synthons for a variety of compounds. Köster et al.[1] prepared monoborylacetylenes by reacting amine-stabilized dialkylchloroboranes with metal acetylides. The addition of diethyl ether-trifluoroborane to the formed adducts leads to donor-free borylacetylenes. Thermally stable monoborylacetylenes[2,3] are obtained with electron-donating groups such as dialkylamino or alkoxy, which reduce the Lewis acidity at the boron center. Dialkoxyborylacetylenes[4,5] may be formed from the corresponding aminoacetylenes. In the reaction of metal acetylides with dialkoxyhaloboranes the halogen atom as well as the alkoxy substituents are replaced. In contrast, the reaction of diaminohaloboranes with metal acetylides leads to the expected compounds in good yields. Here we report on the synthesis and properties of the catechol-substituted monoborylacetylene derivatives **1a−c**.

Results and Discussion

Synthesis and Properties of Monoborylacetylenes (1)

For the preparation of catechol-substituted monoborylacetylenes bis(diisopropylamino)borylacetylene[6] is reacted in THF with two equivalents of HCl and one equivalent of catechol or biphenol, leading to the monoborylacetylenes **1a−d** in 46 to 68% yield (Scheme 1). The colorless solids may be sublimed in vacuo (**1a−c**) or recrystallized (**1d**); the melting points of the products are between 45 °C (**1c**) and 115 °C (**1d**). Compounds **1a−c** are soluble in common organic solvents whereas **1d** dissolves only in toluene and THF and forms a stable THF adduct.



Scheme 1

The ^1H NMR spectra of **1a−d** exhibit a singlet for the acetylenic proton between δ = 2.77 (**1a**) and 2.37 (**1d**). In the ^{13}C NMR spectra the signals of the α carbon atoms (bound to boron) were not observed; the signals for the β carbon atoms (δ = 94−86) are shifted to lower field relative to alkylacetylenes (δ = 70−80),[7] which may indicate an interaction of the empty orbital at boron with the π system of the triple bond. Also, the oxygen atoms in **1a−c** may compete for the empty orbital at boron. In **1d** the boron atom is in bonding contact with the oxygen atom of one THF molecule. The ^{11}B NMR signal for **1d** is shifted to higher field (δ = 15.9) relative to the values for **1a** (δ = 24.1), **1b**, and **1c** (both δ = 24.3). The X-ray structure analysis of **1a** (Figure 1) reveals an almost linear B−C−C−H moiety. The boron atom is trigonal coordinated, and the heterocycle is almost planar. Compound **1a** has approximately C_{2v} symmetry, the C≡C distance [1.195(3) Å] is slightly widened relative to other R−C≡C−R compounds[8] (1.183 Å) and the B−C bond [1.520(4) Å] is short

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for a B−C single bond. This is in agreement with structural data for oxygen-substituted diborylacetylenes.[6,9]

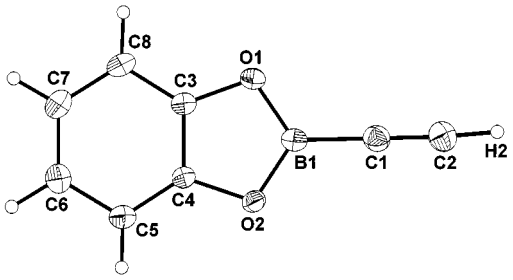
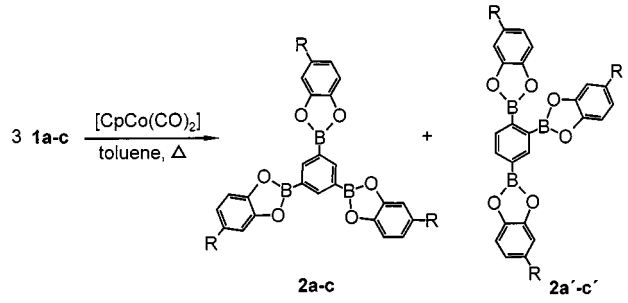


Figure 1. Molecular structure of **1a** in the crystal; selected bond length [Å] and angles [°]: B1−O1 1.387(3), B1−O2 1.372(3), B1−C1 1.520(4), C1−C2 1.195(3), C2−H2 1.00(3); O1−B1−O2 112.3(2), O1−B1−C1 123.2(2), O2−B1−C1 124.4(2), B1−C1−C2 178.7(2), C1−C2−H2 176(1)

Trimerization of 1 to Triborylbenzene Derivatives (2)

Only a few triborylbenzene derivatives are known;[10,11] these have been prepared in low yields by Grignard reactions. The synthesis of substituted arenes by cobalt-catalyzed trimerization of alkynes is well established and has led to a broad application in organic synthesis.[12] Very recently we obtained hexaborylbenzene derivatives by cyclotrimerization of diborylacetylenes in the presence of catalytic amounts of (η^5-cyclopentadienyl)dicarbonylcobalt.[13,14] Analogously, in refluxing toluene the monoborylacetylenes **1a−c** form isomeric mixtures of the triborylbenzene derivatives **2a,2a′**, **2b,2b′**, and **2c,2c′** in good yields (>50%; Scheme 2). The 1,3,5- and 1,2,4-isomers could not be separated.

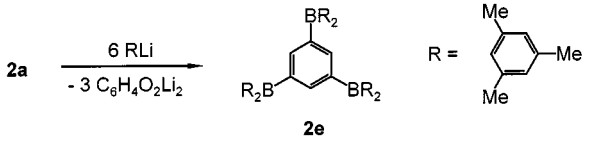


Scheme 2

The mixtures of **2a−c,2a′−c′** are light brown, air-stable solids. The product **2a,2a′** is not soluble in most organic solvents; it partially dissolves in methanol, however, with slow decomposition and formation of catBOMe ($\delta^{11}B$ = 18). In contrast, **2b,2b′** and **2c,2c′** easily dissolve in THF and CH_2Cl_2.

The ^{11}B NMR spectra exhibit broad signals at δ = 30.1 for **2a,2a′** (in [D_4]MeOH), δ = 29.6 for **2b,2b′**, and δ = 33.9 for **2c,2c′** (in CD_2Cl_2). In the ^1H NMR spectrum of **2a,2a′** several signals appear in the arene region. The pattern for *ortho* substitution of the catechol group is found between δ = 6.60 and 6.76. A multiplet between δ = 8.1 and 7.5 is assigned to the central rings of **2a,a′**. In the ^{13}C NMR spectrum, three signals at δ = 146.2, 120.9, and 116.3 are found for the carbon atoms of the catechol groups. A signal at δ = 131.6 is assigned to the hydrogen-substituted carbon atoms of the central aromatic ring of the symmetrical isomer **2a**. Resonances at δ = 141.6, 137.9, and 134.7 are due to the central aromatic carbon atoms (CH) of the unsymmetrical derivative **2a′**. The ^1H NMR spectra of **2b,2b′** and **2c,2c′** indicate that the unsymmetrical derivatives are the main products. In the aromatic region, these compounds exhibit multiplets for the substituted catechol groups at δ = 6.44−6.66 for **2b,2b′** (in [D_4]MeOH) and δ = 7.17−7.43 for **2c,2c′** (in CD_2Cl_2). A second multiplet at δ = 7.50−7.77 in the spectrum of **2b,b′** is generated by the three unsymmetrical protons of the central arene ring. The corresponding signals for **2c′** can be fully assigned: the two adjacent protons give rise to two doublets of doublets at δ = 8.31 ($^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz) and δ = 8.14 ($^3J_{HH}$ = 7.5 Hz, $^5J_{HH}$ = 0.8 Hz), the resonance for the remaining proton appears as a pseudo triplet at δ = 8.74 (averaged $J_{HH} \approx 1$ Hz). In addition, the nine methyl groups of the three *tert*-butyl substituents of **2c′** result in two signals at δ = 1.37 and 1.35, integrating for nine and eighteen protons respectively, which belong to the groups in the 2- and 1,4-positions. The ^{13}C NMR spectra also indicate the predominant formation of the unsymmetrical structures **2b′** and **2c′**. In the aromatic region of the ^{13}C NMR spectra of **2c,2c′** 19 of the expected 21 signals for the nonboron-bound carbon atoms can be distinguished. A signal for the central C(H) carbon atoms in the symmetrical structure is not found, which means either that **2c** is not present or that its concentration is very low. In the spectra of the products **2a,2a′** and **2b,2b′**, however, the presence of small amounts of the isomers **2a** and **2b** is clearly seen. Beside the aromatic ^{13}C resonances for **2a′/2b′**, signals at δ = 131.6 and 130.7 are assigned to the central C(H) atoms in **2a** and **2b**, respectively.

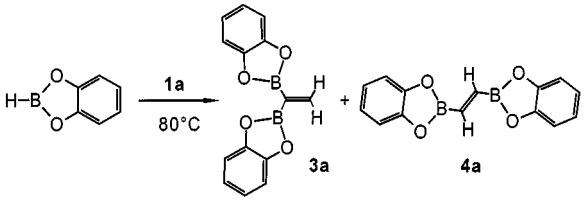
The reaction of **2a,2a′** with mesityllithium provides the hexamesityl-substituted triborylbenzene derivative **2e** in 49% yield (Scheme 3). Its spectroscopic data and the X-ray structure analysis confirm that the symmetric isomer 1,3,5-tris(dimesitylboryl)benzene (**2e**) has been formed. This compound was first prepared in 2% yield from 1,3,5-tribromobenzene Grignard reagent and fluorodimesitylborane.[11]



Scheme 3

Hydroboration of 1a to Yield 1,1-Bis(1,3,2-benzodioxaborol-2-yl)ethene (3a), *trans*-1,2-Bis(1,3,2-benzodioxa-borol-2-yl)ethene (4a), and 1,1,1-Tris(1,3,2-benzodioxaborol-2-yl)ethane (5a)

Alkynes and alkenes are hydroborated regioselectively by 1,3,2-benzodioxaborole (catecholborane).[15] The reaction of the monoborylacetylene **1a** with catecholborane at 80 °C leads to a mixture of 1,1-bis(1,3,2-benzodioxa-borol-2-yl)ethene (**3a**) and a small amount of *trans*-1,2-bis(1,3,2-benzo-



Scheme 4

dioxaborol-2-yl)ethene (**4a**) in 86% yield (Scheme 4).[16] The *cis*-addition of catecholborane proceeds regioselectively favoring the formation of the 1,1-isomer **3a**. Only a minor amount of the 1,2-isomer **4a** is obtained. Related 1,2-derivatives with a *cis*-arrangement have been reported by Marder and Norman,[17] and isomeric 1,1-diborylethene derivatives have been synthesized by Matteson.[18] Colorless **3a** melts at 105 °C with decomposition, it is soluble in toluene, benzene, and THF.

In the NMR spectra only signals for **3a** were found, indicating that the amount of the 1,2-derivative **4a** is rather small. However, its formation was unambiguously proven by X-ray structure analysis (see below). The ^{1}H NMR spectrum of **3a** exhibits a multiplet signal between δ = 6.60−6.93 for the aromatic protons and for the alkene hydrogen atoms. In the ^{13}C NMR spectrum one finds three signals at δ = 148.8, 123.1, and 112.9 for the aromatic carbon atoms. One sharp signal for the CH_2 carbon atom of the ethene unit at δ = 154.9 proves the presence of the 1,1-isomer, its chemical shift is similar to that of comparable compounds.[19,20] In the ^{11}B NMR spectrum one signal appears at δ = 32.2.

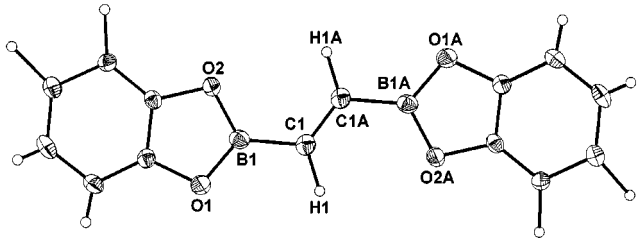
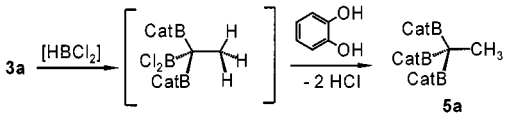


Figure 2. Molecular structure of **4a** in the crystal; selected bond lengths [Å] and angles [°]: C1−C1a 1.348(10), C1−B1 1.554(8), B1−O1 1.386(7), B1−O2 1.386(7), C1−H1 1.12(5); C1a−C1−B1 122.3(6), C1−B1−O1 125.8(5), C1−B1−O2 122.8(5), O1−B1−O2 111.4(5)

In the solid state the molecule **4a** (Figure 2) has a crystallographic inversion center at the midpoint of the C=C double bond and is almost planar (max. dev. 0.04 Å) resulting in C_{2h} symmetry. Both the B and C atoms of the ethene unit are planar coordinated. The heterocycles are almost planar and they are in a coplanar arrangement (dihedral angle: 0°). The length of the C1−C1a bond [1.348(10) Å] is that of a double bond and the B−C bonds [1.554(8) Å] are a bit shorter than single bonds.

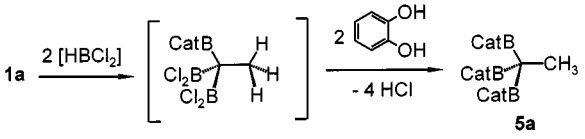
As indicated above, the hydroboration of **1a** with catecholborane stops after the first *cis*-addition. However, **3a** reacts with $HBCl_2$,[21,22] and subsequent substitution of the Cl atoms by catechol leads to 1,1,1-triborylethane **(5a)** in



Scheme 5

78% yield (Scheme 5). It is a colorless solid, which is soluble in toluene, THF, and dichloromethane. The spectroscopic data of **5a** are discussed below.

The hydroboration of **1a** with $[HBCl_2]$ and subsequent substitution of the chlorine atoms by catechol groups leads to 1,1,1-triborylethane **(5a)** in 83% yield (Scheme 6). The solid is recrystallized from THF to yield the THF adduct **5a**$(thf)_3$; in toluene it loses THF and forms crystalline **5a**. Both compounds have been studied by X-ray structure analyses (see below). The related compound $[(MeO)_2B]_3CCH_3$ has been reported previously.[18]



Scheme 6

The ^{1}H NMR spectrum of **5a** indicates a C_3 symmetry with three boryl substituents bonded to one carbon atom. The *ortho* substitution pattern for the aromatic region is observed between δ = 6.67−6.97, and a singlet appears at δ = 2.04 for the methyl group. The ^{13}C NMR spectroscopic data confirm the assignments from the ^{1}H NMR spectrum. The ^{11}B NMR spectrum shows one broad signal at δ = 35.

The X-ray diffraction study reveals that **5a**$(thf)_3$ has approximately C_{3v} symmetry (Figure 3 and 4). The heterocycles are almost planar. The boron-bound carbon atom is almost tetrahedral, and the C1−C2 bond is 1.556(5) Å. All B−C and B−O bond lengths in **5a**$(thf)_3$ are normal. The distances from the boron to the oxygen atoms of the THF molecules (2.72−2.91 Å) are relatively short. This, and the geometrical arrangement of the THF molecules, suggests a very weak interaction between these atoms. A similar arrangement was found in 1,1,2,2-tetrakis(1,3,2-benzodioxaborol-2-yl)ethane·2THF.[9] The THF-free solid-state structure of **5a** is almost identical to that of **5a**$(thf)_3$. No significant changes in bond lengths and angles are observed, which means that the influence of the THF molecules in **5a**$(thf)_3$ on its structural parameters is negligible.

1,1,1-Tris[di(*tert*-butyl)boryl]ethane (6a)

Treatment of **5a** with *t*BuLi results in the formation of 1,1,1-tris[di(*tert*-butyl)boryl]ethane (**6a**) in 12% yield (Scheme 7). Compound **6a** is a colorless, thermally stable liquid, which does not form any *closo*-C_2B_3 carborane by elimination of trisorganoboranes. In the mass spectrum of **6a** the molecular ion M^+ is absent; however, M^+ patterns for the C_2B_3 carborane derivative **7a** (m/z = 258) and for the C_2B_4 carborane derivative **8a** [m/z = 325, $(M - H)^+$] appear. These carboranes are most likely formed in the mass spectrometer. The ^{11}B NMR spectrum does not show

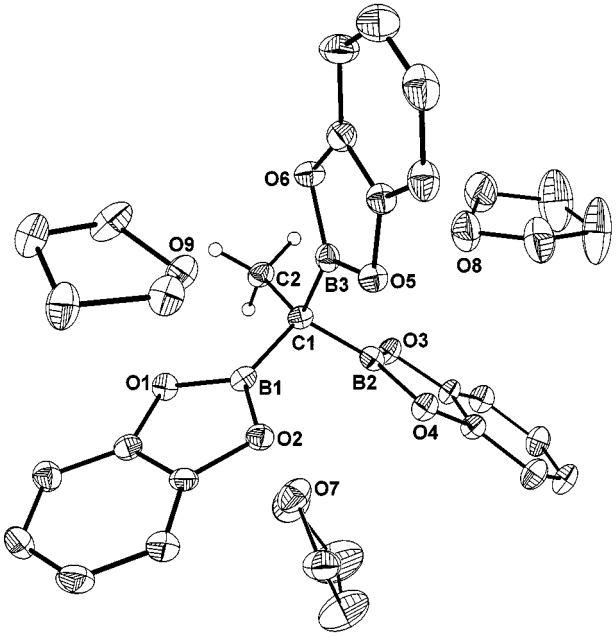


Figure 3. Molecular structure of **5a(thf)$_3$** in the crystal; selected bond lengths [Å] and angles [°]: C1−C2 1.556(5), C1−B1 1.544(6), C1−B2 1.564(6), C1−B3 1.569(6), B1−O1 1.407(5), B1−O2 1.395(5), B2−O3 1.397(5), B2−O4 1.385(5), B3−O5 1.387(6), B3−O6 1.395(6); B1−C1−C2 110.8(3), B1−C1−B2 110.2(3), B1−C1−B3 105.9(3), B2−C1−B3 108.5(3), C2−C1−B2 110.5(3), C2−C1−B3 110.9(3). Selected bond lengths [Å] and angles [°] for **5a**: C−C 1.556 [1.554−1.557(3)], C−B 1.568 [1.560−1.581(3)], B−O 1.385 [1.380−1.398(3)], B−C−C 110.4−113.1(2), B−C−B 103.3−113.1(2)

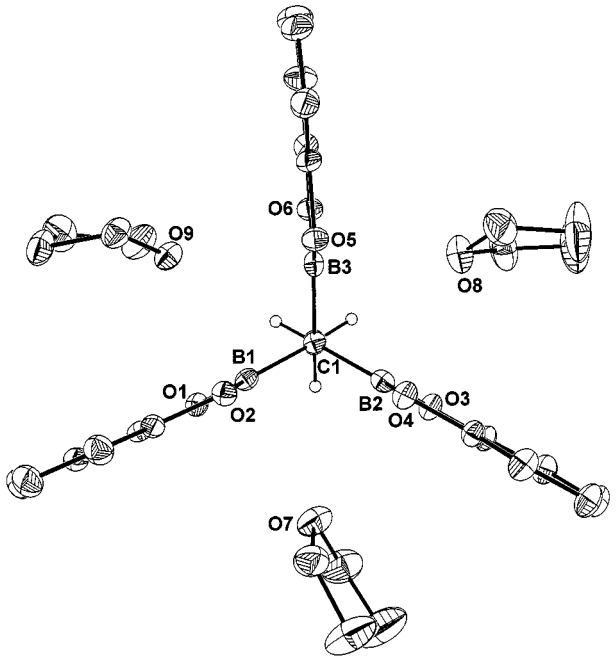
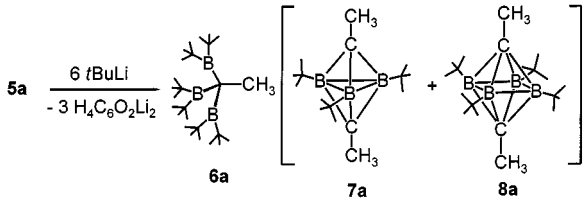


Figure 4. Molecular structure of **5a(thf)$_3$** as viewed along the C1−C2 vector

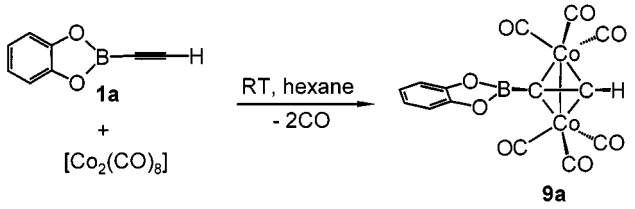
any signal for the carboranes, it contains only the signal for **6a** at δ = 83.4. The ^{1}H NMR spectrum exhibits two singlets at δ = 1.92 and 1.11 in the ratio 1:18, the ^{13}C NMR spectrum shows two signals at δ = 14.1 and 30.3, the carbon atoms adjacent to boron are not detected.



Scheme 7

3-(1,3,2-Benzodioxaborol-2-yl)-1,2-bis(tricarbonylcobalta)-tetrahedrane (9a)

Dicobaltahexacarbonyl-η^2-alkyne complexes are obtained by reacting alkynes with $Co_2(CO)_8$.[23] Analogously, the monoborylacetylene **1a** reacts with [$Co_2(CO)_8$] in hexane with elimination of CO to give complex **9a** (Scheme 8).



Scheme 8

Chromatographic workup of the dark brown solution and crystallization from toluene gives dark crystals of **9a** in 42 % yield. It is soluble in hexane, toluene, THF, or CH_2Cl_2, although it decomposes when exposed to light or heat. In the ^{1}H NMR spectrum the aromatic protons appear as an *ortho* pattern between δ = 6.70−6.94, the aliphatic proton gives a singlet at δ = 5.83 and is thus shifted downfield by more than 3 ppm relative to **1a** (δ = 2.77). This has been explained in related compounds by the electronegativity of the Co_2C_2 unit and the anisotropy effect of the C≡O groups. In the ^{13}C NMR spectrum three signals appear at δ = 149.0, 123.2, and 112.8 for the aromatic carbon atoms. The signal for CO at δ = 200 is broadened by intramolecular CO exchange. A broad signal at δ = 71 is found for the boron-bonded carbon, whereas the signal for the other carbon atoms appears at δ = 81.9. The ^{11}B NMR signal at δ = 32.6 is shifted downfield by 8 ppm with respect to that of **1a** (δ = 24.1).

The X-ray diffraction study confirms the structure of **9a** as that of a tetrahedrane (Figure 5). The almost linear B−C−C−H moiety in **1a** has been altered by the complexation, the angles are decreased to 151.0(2)° (B1−C2−C1) and 141(1)° (C2−C1−H1). The atoms C1−C2−Co1−Co2 form a distorted tetrahedrane, the dihedral angle O1−B1−C2−C1 is 11.9°. The Co−Co bond length of 2.48 Å is comparable with other data,[24] the distance between the carbon atoms of the tetrahedrane [1.334(3) Å] is 0.14 Å longer than the C−C bond in **1a**, and is of the same magnitude as a double bond.[24b,24c]

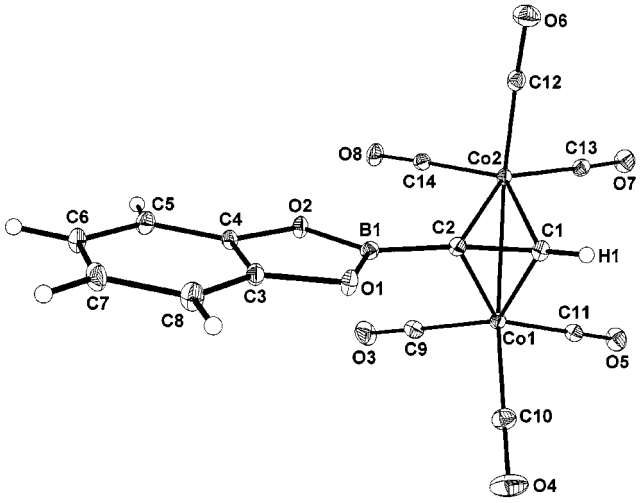


Figure 5. Molecular structure of **9a** in the crystal; selected bond lengths [A] and angles [°]: C1−C2 1.334(3), C1−Co1 1.956(2), C1−Co2 1.957(2), C2−Co1 1.991(2), C2−Co2 1.976(2), Co1−Co2 2.480(1), C2−B1 1.528(3); H1−C1−C2 141(1), C1−C2−B1 151.0(2), Co1−C1−Co2 78.67(7), Co1−C2−Co2 77.41(7), C1−C2−Co1 68.9(1), C1−C2−Co2 69.4(1), C2−C1−Co1 71.7(1), C2−C1−Co2 70.9(1), C1−Co1−C2 39.51(8), C1−Co2−C2 39.66(8), C1−Co1−Co2 50.68(6), C2−Co1−Co2 51.03(5)

Experimental Section

General: All reactions were carried out under a purified nitrogen atmosphere. The solvents were dried according to published procedures. − NMR: Bruker AC 200 or DRX 200 and Jeol FX-90 Q (^{11}B, external standard, $BF_3{\cdot}OEt_2$; ^{1}H, ^{13}C, standards were the signals of the residual protons in the deuterated solvents, calculated relative to TMS). − MS: Finnigan MAT 8230, ZAB-2F VG-Micromass and Jeol MS station JMS 700. − The following compounds were prepared according to literature procedures: bis(diisopropylamino)borylacetylene,[6] catecholborane.[15] * Boron carbide formation often reduces the found values.

1,3,2-Benzodioxaborol-2-yl-acetylene (1a), 1,3,2-(5-Methylbenzo)-dioxaborol-2-yl-acetylene (1b), 1,3,2-(5-*tert*-Butyl-benzo)dioxaborol-2-yl-acetylene (1c), and 2-Ethinyldibenzo[d.f]-1,3,2-dioxaborepine·THF (1d·thf): To a stirred solution of bis(diisopropylamino)borylacetylene (3.307 g, 14.0 mmol) in 50 mL of THF at −78 °C was added $HCl{\cdot}OEt_2$ (3.12 M; 10 mL, 31.2 mmol) within 30 min. Stirring was continued for 30 min., and NH_2iPr_2Cl formed as a white solid. Then, 14.0 mmol of the corresponding aromatic diol (**1a:** 1.540 g of catechol; **1b:** 1.744 g of 4-methylcatechol; **1c:** 2.330 g of 4-*tert*-butylcatechol; **1d:** 2.644 g of 2,2′-biphenol) dissolved in 10 mL of THF was added and the reaction mixture was allowed to warm overnight to room temperature. After filtration of the solid the solution was reduced almost to dryness. The products **1a**, **1b**, and **1c** were sublimed, **1d** was crystallized from THF.

1a: 1.227 g (61%), m.p. 53 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.77 (s, 1 H, C≡CH), 7.24−7.14 (m, 4 H, C_6H_4). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 93.7 (br., C≡*C*H), 113.7, 124.3, 148.5 (C_6H_4), B*C* not observed. − ^{11}B NMR (64 MHz, $CDCl_3$): δ = 24.1. − EI-MS: *m*/*z* (%) = 144 (100) [M^+]. − HR-EIMS: *m*/*z* = 144.0382 [M^+], calcd. for $^{12}C_8{}^1H_5{}^{11}B^{16}O_2$: 144.0383 (Δ = 0.1 mmu).

1b: 1.009 g (46%), m.p. 48 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 2.75 (s, 1 H, C≡CH), 7.12−6.88 (m, 3 H, C_6H_3). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3 (CH_3), 93 (br., C≡*C*H), 112.0, 113.3, 123.8, 133.4, 145.4, 147.6 (C_6H_3), B*C* not observed. − ^{11}B NMR (64 MHz, $CDCl_3$): δ = 24.3. − EI-MS: *m*/*z* (%) = 158 (100) [M^+]. − $C_9H_7BO_2$ (158.0): calcd. C 68.43, H 4.47; found C 67.24, H 4.64.

1c: 1.915 g (68%), m.p. 45 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.31 (s, 9 H, CH_3), 2.75 (s, 1 H, C≡CH), 7.28−7.14 (m, 3 H, C_6H_3). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.7 (CH_3), 34.9 [*C*(CH_3)$_3$], 93 (br., C≡*C*H), 110.0, 111.7, 120.1, 144.3, 145.2, 147.4 (C_{ar}), B*C* not observed. − ^{11}B NMR (64 MHz, $CDCl_3$): δ = 24.3. − EI-MS: *m*/*z* (%) = 200 (24.6) [M^+], 185 (100) [$M^+ - CH_3$]. − $C_{12}H_{13}BO_2$ (200.0): calcd. C 72.05, H 6.55; found C 71.38, H 6.51.

1d·THF: 2.715 g (66%), m.p. 115 °C (dec.). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.94 (quint, 4 H, THF), 2.37 (s, 1 H, C≡CH), 4.00 (t, 4 H, THF), 7.45−7.02 (m, 8 H, H_{ar}). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.3 (THF), 69.5, 86 (br., C≡*C*H), 121.3, 124.1, 128.7, 129.2, 129.7, 153.1 (C_{ar}), B*C* not observed. − ^{11}B NMR (64 MHz, $CDCl_3$): δ = 15.9. − EI-MS: *m*/*z* (%) = 220 (100) [M^+]. − HR-EIMS: *m*/*z* = 220.0698 [M^+], calcd. for $^{12}C_{14}{}^1H_9{}^{11}B^{16}O_2$: 220.0696 (Δ = 0.2 mmu).

Tris(1,3,2-benzodioxaborol-2-yl)benzene Isomers (2a,2a′), Tris[1,3,2-(5-methylbenzo)dioxaborol-2-yl]benzene Isomers (2b,2b′), and Tris[1,3,2-(5-*tert*-butylbenzo)dioxaborol-2-yl]benzene Isomers (2c,2c′): Monoborylacetylene (**1a:** 0.865 g; **1b:** 0.956 g; **1c:** 1.209 g; 6.0 mmol) and (η^5-cyclopentadienyl)dicarbonylcobalt (0.055 g, 0.3 mmol, 5 mol-%) were heated in 15 mL of toluene for 24 h under reflux. The solid was separated and washed several times with small amounts of solvent (**2a,2a′:** THF and CH_2Cl_2; **2b,2b′:** toluene and CH_2Cl_2; **2c,2c′:** hexane) and dried in vacuum.

2a,2a′: 1.345 g (52%), m.p. 237 °C. − ^{1}H NMR (200 MHz, [D$_4$]MeOH): δ = 6.76−6.60 (m, 12 H, C_6H_4), 8.10−7.50 (m, 3 H, C_6H_3). − ^{13}C NMR (50 MHz, [D$_4$]MeOH): δ = 116.3, 120.9 (C_6H_4), 131.6 (C_6H_3, central, symm.), 134.7, 137.9, 141.7 (C_6H_3, central, unsymm.), 146.2 (C_6H_4). − ^{11}B NMR (64 MHz, [D$_4$]MeOH): δ = 30.1. − EI-MS: *m*/*z* (%) = 432 (100) [M^+]. − HR-EIMS: *m*/*z* = 432.1183 [M^+], calcd. for $^{12}C_{24}{}^1H_{15}{}^{11}B_3{}^{16}O_6$: 432.1148 (Δ = 3.6 mmu). − $C_{24}H_{15}B_3O_6$ (431.8): calcd. C 66.76, H 3.50; found C 65.28*, H 3.72.

2b,2b′: 1.550 g (55%), m.p. 220 °C. − ^{1}H NMR (200 MHz, [D$_4$]MeOH): δ = 2.18 (s, 9 H, CH_3), 6.66−6.44 (m, 9 H, C_6H_3, terminal), 7.64−7.50, 7.77 (each br., 3 H, C_6H_3, central). − ^{13}C NMR (50 MHz, [D$_4$]MeOH): δ = 21.0 (CH_3), 116.5, 117.4, 121.4 (C_6H_3, terminal), 130.7 (C_6H_3, central, symm.), 132.1 (C_6H_3, central, unsymm.), 134.5 (C_6H_3, terminal), 137.9, 141.1 (C_6H_3, central, unsymm.), 144.1, 146.3 (C_6H_3, terminal). − ^{11}B NMR (64 MHz, [D$_4$]MeOH): δ = 29.6. − EI-MS: *m*/*z* (%) = 474 (100) [M^+]. − HR-EIMS: *m*/*z* = 474.1643 [M^+], calcd. for $^{12}C_{27}{}^1H_{21}{}^{11}B_3{}^{16}O_6$: 474.1617 (Δ = 2.6 mmu). − $C_{27}H_{21}B_3O_6$ (473.9): calcd. C 68.43, H 4.47; found C 67.39, H 4.71.

2c′: 1.858 g (52%), m.p. 190 °C. − ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.35 (s, 18 H, CH_3), 1.37 (s, 9 H, CH_3), 7.43−7.17 (m, 9 H, C_6H_3, terminal), 8.14 (dd, 3 H, $^3J_{HH}$ = 7.5 Hz, $^5J_{HH}$ = 0.8 Hz), 8.31 (dd, 3 H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.3 Hz, H adj.), 8.74 (pseudo triplet, 3 H, averaged $J_{HH} \approx$ 1 Hz). − ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 31.9 (CH_3), 35.2 [*C*(CH_3)$_3$], 110.32, 110.36, 110.40, 111.87, 111.93, 111.95 [C(H) catechol, adj. to C(O)] 120.06, 120.13, 120.21 [C(H) catechol, adj. to C(CH_3)$_3$], 146.58, 146.62 [*C*(CH_3)$_3$], 147.25, 147.33, 147.42, 148.80, 148.84 [C(O)], BC not observed. − ^{11}B NMR (64 MHz, CD_2Cl_2): δ = 33.9. − EI-MS: *m*/*z* (%) = 600 (90) [M^+], 585 (100) [$M^+ - CH_3$]. − HR-EIMS: *m*/*z* = 600.2994

[M^+], calcd. for $^{12}C_{36}{}^{1}H_{39}{}^{11}B_3{}^{16}O_6$: 600.3026 (Δ = 3.2 mmu). − $C_{36}H_{39}B_3O_6$ (600.1): calcd. C 72.05, H 6.55; found C 70.44*, H 6.53.

1,3,5-Tris(dimesitylboryl)benzene (2e): To a suspension of **2a,2a′** (0.210 g, 0.44 mmol) in toluene (30 mL) was added a solution of MesLi·OEt_2 (1.191 g) in Et_2O (10 mL) at −20 °C. The mixture was then heated for 3 h under reflux. After removal of the solvents the reaction mixture was worked-up by column chromatography (SiO_2/THF). Recrystallization from toluene yielded 0.330 g of **2e** (49%), m.p. 235 °C. − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.88 (s, 36 H, *o*-CH_3), 2.23 (s, 18 H, *p*-CH_3), 6.70 (s, 12 H, C_6H_2), 7.50 (s, 3 H, C_6H_3). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.2 (CH_3), 23.4, 128.0, 138.4, 140.5 (C_6H_2), 145.1 (C_6H_3), B*C* not observed. − ^{11}B NMR (29 MHz, [D_8]toluene): δ = 88. − EI-MS: *m*/*z* (%) = 822 (2) [M^+ − H], 703 (6) [M^+ − Mes − H], 574 (12) [M^+ − $BMes_2$], 324 (54) [M^+ − 2$BMes_2$ − H], 249 (91) [$BMes_2$]$^+$, 120 (100) [MesH]$^+$, 105 (75) [$MesH^+$ − Me].

Bis(1,3,2-benzodioxaborol-2-yl)ethenes (3a and **4a):** A solution of **1a** (0.800 g, 5.6 mmol) and CatBH·THF (1.067 g, 5.6 mmol) in 20 mL of THF was heated at 80 °C under reflux for 4 h. Then the solvent was partially removed in vacuum and a white solid (1.267 g, 86%, m.p. 105 °C dec.) separated. It contained **3a** and a small amount of **4a**, which was not detected by NMR spectroscopy but obtained by crystallization from toluene.
3a: ^{1}H NMR (200 MHz, C_6D_6): δ = 6.93−6.60 (m, 8 H, C_6H_4), 6.99 (s, 2 H, BCH). − ^{13}C NMR (50 MHz, C_6D_6): δ = 112.8, 123.0, 148.8 (C_6H_4), 154.9 (CH_2). − ^{11}B NMR (64 MHz, C_6D_6): δ = 32.2. − EI-MS: *m*/*z* (%) = 264 (30) [M^+]. − $C_{14}H_{10}B_2O_4$ (263.8): calcd. C 63.73, H 3.82; found C 63.18, H 4.13.

1,1,1-Tris(1,3,2-benzodioxaborol-2-yl)ethane (5a): Procedure A: To a solution of **1a** (1.941 g, 13.5 mmol) in 50 mL of pentane was added BCl_3 (6 mL, 69.1 mmol) at −20 °C. Then triethylsilane (4.00 g, 34.4 mmol) in 10 mL of pentane was added very slowly at −20 °C. After 2 h of stirring at room temperature the solution was cooled to −20 °C and catechol (3.053 g, 27.7 mmol) in 10 mL of THF was added within 40 min. After 18 h of stirring at room temperature the solid was isolated by filtration, washed several times with hexane and dried in vacuum. Recrystallization from toluene yielded **5a** (4.282 g, 83%).
Procedure B: To a suspension of **3a** (1.543 g, 5.8 mmol) in 30 mL of pentane was added BCl_3 (2 mL, 23.0 mmol) at −20 °C. Then, triethylsilane (0.900 g, 7.7 mmol) in 20 mL of pentane was very slowly added. After 2 h of stirring at room temperature the solution was cooled to −20 °C and catechol (0.644 g, 5.8 mmol) in 5 mL of THF was added within 30 min. The reaction mixture was stirred for 18 h at −20 °C. Thereafter the solid was separated, washed several times with hexane, and dried in vacuum. Recrystallization from toluene yielded **5a** (1.731 g, 78%), m.p. 155 °C (dec.) − ^{1}H NMR (200 MHz, C_6D_6): δ = 2.04 (s, 3 H, CH_3), 6.97−6.67 (m, 12 H, C_6H_4). − ^{13}C NMR (50 MHz, C_6D_6): δ = 12.2 (CH_3), 112.8, 122.9, 149.0 (C_6H_4). − ^{11}B NMR (64 MHz, C_6D_6): δ = 35.4. − EI-MS: *m*/*z* (%) = 384 (100) [M^+]. − HR-EIMS: *m*/*z* = 384.1169 [M^+], calcd. for $^{12}C_{20}{}^{1}H_{15}{}^{11}B_3{}^{16}O_6$: 384.1147 (Δ = 2.1 mmu). − $C_{20}H_{15}B_3O_6$ (383.8): calcd. C 62.59, H 3.94; found C 61.01*, H 4.27.

1,1,1-Tris[di(*tert*-butyl)boryl]ethane (6a): A suspension of **5a** (1.00 g, 2.6 mmol) in 70 mL of hexane was reacted at −70 °C with 9 mL of *t*BuLi. After stirring at −20 °C the mixture was heated for 5 h under reflux. Separation of the solid resulted in a yellow solution, which was slowly concentrated under reduced pressure (50 Torr). The yellow, oily residue was distilled at 80 °C/0.4 Torr to yield **6a** (0.122 g, 12%). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.11 [s, 54 H, $C(CH_3)_3$], 1.92 (s, 3 H, CH_3). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.1 (CH_3), 30.3 [$C(CH_3)_3$], B*C* not observed. − ^{11}B NMR (29 MHz, $CDCl_3$): δ = 83.4. − EI-MS: *m*/*z* (%) = 325 (0.8) [M^+(**8a**) − H], 258 (1.2) [M^+(**7a**)], 243 (1.9) [M^+(**7a**) − Me], 41 (100).

3-(1,3,2-Benzodioxaborol-2-yl-1,2-bis(tricarbonylcobalta)tetrahedrane (9a): To a solution of $Co_2(CO)_8$ (2.034 g, 5.9 mmol) in 30 mL of hexane at −20 °C was slowly added **1a** (0.856 g,

Table 1. Data for the crystal structure analyses

	1a	**4a**	**5a(thf)$_3$**	**5a**	**9a**
Empirical formula	$C_8H_5BO_2$	$C_{14}H_{10}B_2O_4$	$C_{20}H_{15}B_3O_6{\cdot}3C_4H_8O$	$C_{20}H_{15}B_3O_6$	$Co_2C_{14}H_5BO_8$
Formula weight	143.93	263.84	600.06	383.50	429.85
Crystal system	tetragonal	monoclinic	monoclinic	orthorhombic	triclinic
Space group	$I4_1/a$	$P2_1/n$	$P2_1/n$	*Pbca*	$P\bar{1}$
Unit cell *a* [Å]	16.96(3)	5.870(3)	11.883(9)	11.996(2)	6.7766(1)
b [Å]	16.96(3)	6.002(3)	11.959(10)	30.683(4)	7.6633(1)
c [Å]	10.43(2)	17.693(9)	22.725(16)	39.120(5)	15.5942(3)
α [°]	90	90	90	90	100.385(1)
β [°]	90	96.95(4)	91.09(6)	90	94.252(1)
γ [°]	90	90	90	90	102.229(1)
Volume [Å^3]	2999(9)	618.8(5)	3229(4)	14399(3)	773.15(2)
Z	16	2	4	32	2
Density [g/cm^3]	1.275	1.416	1.234	1.416	1.846
μ [mm^{-1}]	0.089	0.100	0.087	0.101	2.186
F(000)	1184	272	1272	3168	424
Crystal size [mm]	0.80 × 0.50 × 0.20	0.35 × 0.35 × 0.30	0.90 × 0.60 × 0.35	0.38 × 0.21 × 0.13	0.46 × 0.17 × 0.03
θ-range[°]	24.94	23.96	22.50	26.36	28.28
Index ranges (*h*, *k*, *l*)	0/20, 0/20, 0/12	−6/6, 0/6, 0/20	−12/11, 0/12, 0/24	0/14, 0/38, 0/48	−9/8, −10/9, 0/20
No. of reflections	1325	876	4183	14670	3750
observed [$I > 2\sigma_I$]	949	590	2307	9532	3087
Parameters	120	111	403	1285	246
*R*1 [$I > 2\sigma_I$]	0.0384	0.0598	0.0588	0.0444	0.0279
*wR*2	0.0917	0.2013	0.1544	0.1162	0.0697
T (K)	203(2)	203(2)	203(2)	173(2)	173(2)
Max. residual electron density [e/Å^3]	0.13/−0.15	0.30/−0.33	0.22/−0.19	0.29/−0.25	0.67/−0.36

5.9 mmol) in 20 mL of hexane. After stirring for 3 days at 20 °C the solvent was removed and the reaction mixture separated by column chromatography (florisil): with n-hexane red-brown $Co_2(CO)_8$, and with toluene brown **9a** was eluted (1.082 g, 42%), m.p. 125 °C (dec.). – ^{1}H NMR (200 MHz, C_6D_6): δ = 5.83 (s, 1 H, CH), 6.94–6.70 (m, 4 H, H_{ar}),. – ^{13}C NMR (50 MHz, C_6D_6): δ = 71 (br., CB), 81.9 (CH), 112.8, 123.2, 149.0 (C_{ar}), 200 (br., CO). – ^{11}B NMR (64 MHz, C_6D_6): δ = 32.6. – EI-MS: *m/z* (%) = 430 (12) [M^+], 402 (39) [M^+ – CO], 374 (6) [M^+ – 2CO], 346 (16) [M^+ – 3CO], 318 (36) [M^+ – 4CO], 290 (91) [M^+ – 5CO], 262 (46) [M^+ – 6CO], 118 (100) [Bcat – H]$^+$. – HR-EIMS: *m/z* = 429.8763 [M^+], calcd. for $^{12}C_{14}{}^1H_5{}^{11}B^{16}O_8{}^{59}Co_2$: 429.8741 (Δ = 2.2 mmu).

X-ray Crystal Structure Analyses of 1a, 4a, 5a, 5a(thf)$_3$ and 9a: Table 1 contains details of the structures. The intensities for **1a**, **4a**, and **5a(thf)$_3$** were measured with a four-circle diffractometer, and for **9a** and **5a** with a CCD area detector (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, ω-scans). The structures were solved by direct methods (SHELXS-86)[25] and refined by least-square methods based on F^2 with all measured reflections (SHELXL-97)[26]. For **1a**, **4a**, **5a** and **9a** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically; for **5a(thf)$_3$** the hydrogen atoms were inserted in calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-148514 (**1a**), -148515 (**4a**), -148516 [**5a(thf)$_3$**], -150265 (**5a**), and -148517 (**9a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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