Syntheses, Structures, and Reactivity of Hexaborylbenzene Derivatives

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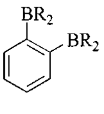
Dedicated to Prof. Heinrich Vahrenkamp on the occasion of his 60th birthday

Keywords: Hexaborylbenzenes / Bis(boryl)acetylenes / Cyclooligomerization / Catalysts / Boranes / Boron

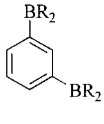
The hexaborylbenzene derivatives **2a** and **2b** have been obtained by transition metal catalyzed {[CpCo(CO)$_2$], [Co$_2$(CO)$_8$], [Ni(cod)$_2$]} cyclotrimerization of bis(1,3,2-benzodioxaborol-2-yl)acetylene (**1a**) and bis[1,3,2-(2,3-naphtho)-dioxaborol-2-yl]acetylene (**1b**). Reaction of [Co$_2$(CO)$_8$] with **1a** yielded the bis(1,3,2-dioxaborol-2-yl)dicobaltatetrahedrane derivative **3a**, which has been subjected to X-ray structure analysis. Reaction of stoichiometric amounts of **3a** and diphenylacetylene was found to give the bis(boryl)tetraphenylbenzene derivative **4**, while **3a** and mono(1,3,2-benzodioxaborol-2-yl)acetylene (**5**) reacted to yield the tetraborylbenzene derivative **6**. AlMe$_3$ and AlEt$_3$ were found to react with **2a**,**b** to furnish C$_6$(BMe$_2$)$_6$ (**7a**) and C$_6$(BEt$_2$)$_6$ (**7b**), respectively. With pyridine, the hexafunctional Lewis acid **7a** formed the crystalline bis(pyridine) adduct C$_6$(BMe$_2$)$_6$·(NC$_5$H$_5$)$_2$ (**8a**). Thermolysis of C$_6$(BEt$_2$)$_6$ (**7b**) resulted in the intramolecular elimination of ethane to give the 1,2,3,4-bis(2′,3′-dihydro-1′,3′-diborole)-5,6-bis(diethylboryl)benzene compound **9b**. The molecular structure of the hexaborylbenzene pyridine adduct **8a** has been determined by X-ray structure analysis.

Introduction

Over the past two decades, borylbenzene compounds have become an area of particular interest in relation to the syntheses of boraheterocycles[1] and of polymeric graphite-like boron−carbon frameworks.[2] Several derivatives of the bis(boryl)benzene isomers **A**, **B**, and **C** are known. Kaufmann[3] obtained 1,2-bis(dichloroboryl)benzene **A** (R = Cl) by silicon−boron exchange with BCl$_3$, while Eisch et al.[4] synthesized the bis(diethylboryl)benzene derivatives of **A**, **B**, and **C** (R = Et) through tin−boron exchange by reacting the corresponding bis(trimethylstannyl)benzenes with Et$_2$BX (X = Cl, Br).



A



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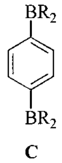

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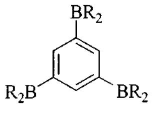

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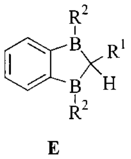

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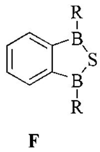
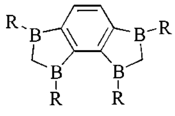


F

The formation and electrochemical properties of bis(boryl)benzene derivatives **C** (R = Ph, Mes) have been studied by Kaim and Schulz.[5] The synthesis of a 1,3,5-tris(boryl)-benzene derivative of **D** (R = Br, OH) was achieved by Stern and Washburn[6] by means of a Friedel−Crafts reaction. Okada, Oda, et al.[7] obtained the mesityl derivatives of **B** and **D** by treating dimesitylfluoroborane with Grignard solutions prepared from 1,3-dibromo- and 1,3,5-tribromobenzene.



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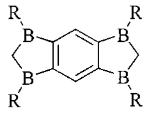

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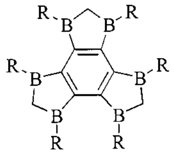

I

The benzo-1,3-diborole heterocycle **E** (R^1 = H, Me; R^2 = Cl, Me, NMe$_2$) has been synthesized by tin−boron exchange of 1,2-bis(trimethylstannyl)benzene with bis(dichloroboryl)methane derivatives, and its ligand properties have been studied in the context of complex formation.[8] The redox reaction between 1,2-diiodobenzene, BI$_3$, and (IBS)$_3$ led to the formation of the benzo-2,5-diiodo-1,2,5-thiadiborole derivative **F** (R = I), in which the iodine could easily be substituted, thereby allowing access to a variety of derivatives.[9] Its dimethyl derivative (**F**, R = Me) formed the first stable tricarbonylironthiaborane complex.[10] Bis- and tris(2,3-dihydro-1,3-diborole)benzene compounds **G**−**I** are of interest with regard to the synthesis of doubly- and triply-stacked complexes with bridging 1,3-diborolyl ligands. Tetra- and hexaborylbenzenes are potential precursors for the preparation of boron-containing polymers. A graphite-like web (C$_3$B)$_n$, in which each boron atom is connected to three carbon atoms, should be feasible by polycondensation of C$_6$(BR$_2$)$_6$ with elimination of BR$_3$. We report herein on the synthesis of hexaborylbenzene derivatives by transition metal catalyzed cyclotrimerization of

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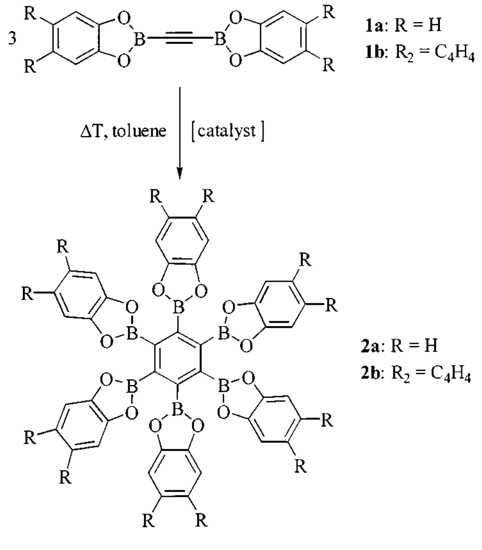
bis(boryl)acetylene derivatives and on the reactivities of these compounds. A preliminary account of our work has been reported previously.[11]

Results and Discussion

Hexakis(1,3,2-benzodioxaborolyl)benzene (2a) and Hexakis{1,3,2-naphtho[2,3-*d*]dioxaborolyl}benzene (2b)

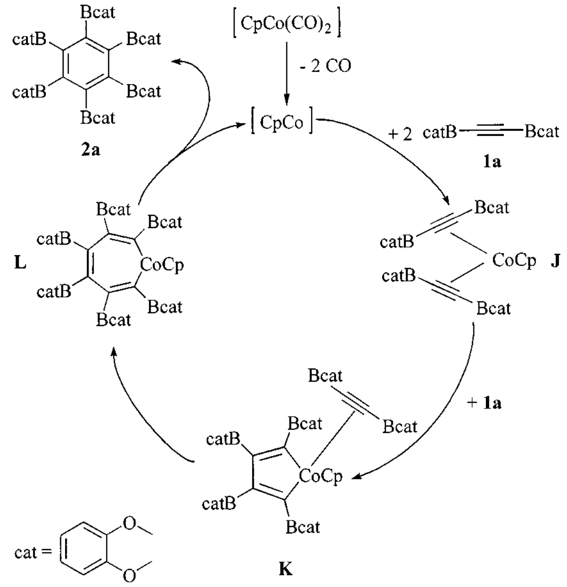
Since the early report of thermal trimerization of acetylene to benzene by Berthelot,[12] and the first transition metal catalyzed version of this reaction by Reppe,[13] the [2+2+2] cyclotrimerization of acetylenes has been extensively studied. A large number of transition metal complexes as well as Ziegler-type catalysts[14] are known to catalyze this reaction.[15] The formation of substituted arenes by cobalt-catalyzed [2+2+2] cyclotrimerization of alkynes is well-known and has found widespread application in organic synthesis.[16] In an analogous manner, the diborylacetylene **1a**[17] (R = H) has been cyclotrimerized in the presence of (η^5-cyclopentadienyl)dicarbonyl-cobalt in refluxing toluene to give the hexaborylbenzene derivative **2a** (R = H) in 75% yield (Scheme 1).[11]



catalysts: [CpCo(CO)$_2$], [Co$_2$(CO)$_8$], [Ni(cod)$_2$]

Scheme 1

Compound **2a** is only slightly soluble in most organic solvents; in methanol, a slow reaction leading to the formation of $H_4C_6O_2BOMe$ takes place. Purification of **2a** can be accomplished by repeated washing with toluene. The ^{11}B NMR spectrum in [D$_4$]MeOH shows a broad signal at δ = 29 due to **2a** and a sharp one at δ = 19.0 attributable to the methanolysis product $H_4C_6O_2BOCD_3$. A characteristic feature of borylbenzenes is the broad ^{13}C NMR resonance signal of the *ipso* carbon atom(s) of the central C$_6$ ring (δ = 130−150).[18] **2a** exhibits a resonance at δ = 143 due to the *ipso* carbon atoms, which is shifted by 50 ppm to lower field as compared to that of the bis(boryl)acetylene **1a**. This reflects the change of the hybridization of the carbon atoms from sp to sp^2. The ^{13}C NMR signals of the aromatic carbons of the catecholyl substituents appear at δ = 116.3, 120.8, and 146.2. The ^{1}H NMR spectrum features one multiplet at δ = 6.61−6.77 due to the aromatic protons. EI-MS data confirm the identity of **2a** through the appearance of ion peaks at *m*/*z* = 785 [M$^+$] and 667 [M$^+$ − $H_4C_6O_2B$].



Scheme 2

Similarly, the bis(boryl)acetylene **1b** (R$_2$ = C$_4$H$_4$) could be trimerized in the presence of a catalytic amount of CpCo(CO)$_2$ to give hexakis{1,3,2-naphtho[2,3-*d*]dioxaborolyl}benzene (**2b**, R$_2$ = C$_4$H$_4$) in good yield (Scheme 1). Compound **2b** was characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy, elemental analysis, and mass spectrometry. The ^{1}H NMR spectrum shows the expected multiplet at δ = 7.14−7.59 due to the aromatic protons. In the ^{13}C NMR spectrum, the signals due to the naphthol substituent are seen at δ = 110.8, 124.4−131.0, and 147.8, while that due to the carbons of the benzene ring appears at δ = 144. The ^{11}B NMR shift of δ = 28.3 is comparable with that seen for **2a** (R = H). In the EI mass spectrum of **2b**, the molecular ion appears at *m*/*z* = 1085 and shows the expected isotopic pattern.

Catalytic Cycles with [CpCo(CO)$_2$], [Co$_2$(CO)$_8$], and [Ni(cod)$_2$]

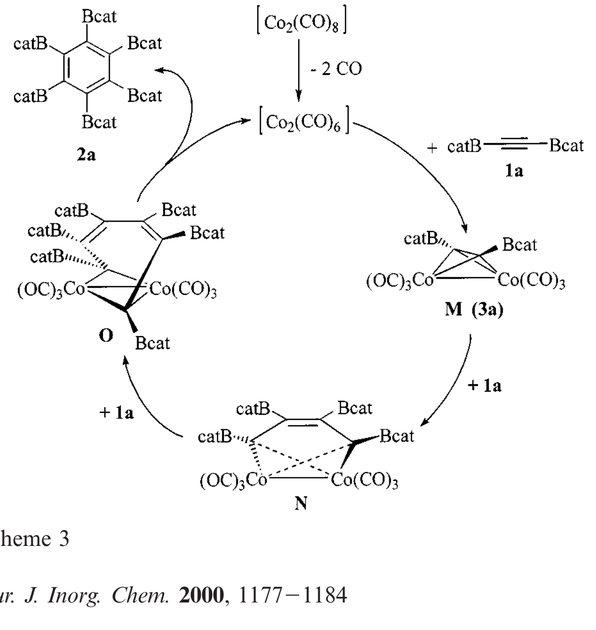
The postulated mechanism of [CpCo(CO)$_2$]-catalyzed cyclotrimerization[16] of acetylene is illustrated for diborylacetylenes in Scheme 2. It is likely that under thermal conditions two alkyne moieties displace the two CO ligands at the metal to form the diborylacetylene complex **J**. Subsequent reductive coupling of the alkynes would then give a coordinatively unsaturated cobaltacyclopentadiene complex. Complexation of a third molecule of **1a** could then lead to **K**, which would be followed by alkyne insertion to form the cobaltacycloheptatriene **L**. Finally, reductive elimination of the CpCo complex fragment would account for the formation of the observed hexaborylbenzene **2a**. Recently, Vollhardt et al.[19] succeeded in synthesizing a cobaltacyclopentadiene−alkyne complex of type **K**, thus seemingly proving this mechanism, although no direct evidence for the intermediacy of the postulated cobaltacycloheptatriene was obtained. Indeed, theoretical investigations of the mechanism at ab initio and density functional (DFT) levels[20] indicate that a cobaltacycloheptatriene (in Scheme 2) is in fact very unlikely to occur.

Analogously, the catalytic trimerization of **1a** with octacarbonyldicobalt leads to the hexaborylbenzene derivative **2a** in 70% yield. The proposed mechanism of this catalytic cyclotrimerization is outlined in Scheme 3. In the first step of the catalytic cycle, the elimination of two CO ligands leads to the unsaturated species $[Co_2(CO)_6]$, which then reacts with **1a** to give the bis(boryl)dicobaltatetrahedrane **M** (**3a**) (Scheme 3). Insertion of one molecule of bis(boryl)acetylene **1a** leads to complex **N**, which reacts with a third acetylene molecule to give **O**. Subsequent reductive elimination yields the hexaborylbenzene **2a**. An intermediate of the type **O** obtained from the reaction of acetylene, *tert*-butylacetylene, and octacarbonyldicobalt has been characterized by X-ray structure analysis.[21]

In the past, numerous compounds incorporating benzene or cyclooctatetraene derivatives have been synthesized in the presence of nickel catalysts.[22a][22b] It was found that the [2+2+2] cycloaddition of **1a** to give the hexaborylbenzene derivative **2a** was also catalyzed by $[Ni(cod)_2]$ in 80% yield. The proposed mechanism of the catalytic cyclotrimerization with $[Ni(cod)_2]$ is similar to that with $[CpCo(CO)_2]$ (Scheme 2).

Synthesis and Properties of Bis(borolyl)dicobaltatetrahedrane (3a)

In 1956, it was found that acetylene and substituted acetylenes are capable of displacing two carbonyl groups from $[Co_2(CO)_8]$ to yield dicobaltatetrahedranes.[23] To investigate the mechanism of the cyclotrimerization with $[Co_2(CO)_8]$ as catalyst, the first intermediate **M** of the catalytic cycle was synthesized. Thus, the bis(borolyl)dicobaltatetrahedrane **3a** was prepared in 45% yield by treating the bis(boryl)ethyne **1a** with one equivalent of $[Co_2(CO)_8]$ in dichloromethane at room temperature (Scheme 4). **3a** was isolated by column chromatography on Florisil® and characterized by ^1H, ^{13}C, and ^{11}B NMR, IR, mass spectrometry, as well as an X-ray structure analysis.



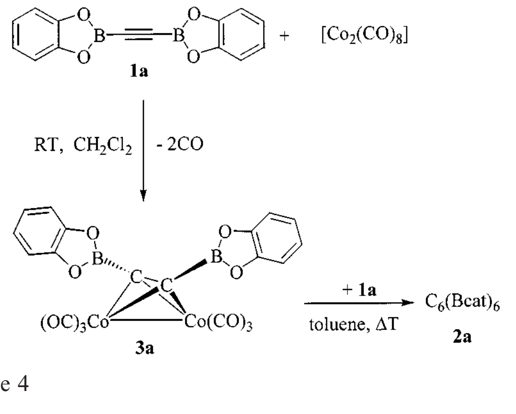
Scheme 3

The ^1H NMR spectrum shows the signal due to the aromatic protons at δ = 6.85−7.29. In the ^{13}C NMR spectrum, the arene carbon atoms give rise to signals at δ = 111.5, 122.0, and 147.4. The signals of the carbon atoms bonded to boron are observed at δ = 96, while those of the carbonyl ligands appear at δ = 197.4. The ^{11}B NMR signal, seen at δ = 33.1, is shifted to low field (Δδ = 10 ppm) as compared to that of the bis(boryl)acetylene **1a**. The IR spectrum of **3a** features three absorption bands at ṽ = 2102, 2066, and 2038 cm^{-1} attributable to the CO ligands. In the mass spectrum (EI) of **3a**, the molecular ion peak appears at *m/z* = 548 and shows the expected isotopic distribution as well as the appropriate fragmentation pattern arising from the stepwise loss of the six CO ligands.

The bis(1,3,2-benzodioxaborolyl)dicobaltatetrahedrane (**3a**) was shown to catalyze the trimerization of **1a**, thus verifying the catalytic cycle with $[Co_2(CO)_8]$. Catalytic amounts of **3a** and the diborylacetylene **1a** were allowed to react in refluxing toluene for 24 h. The resulting product was the expected hexakis(1,3,2-benzodioxaborolyl)benzene (**2a**, Scheme 4).

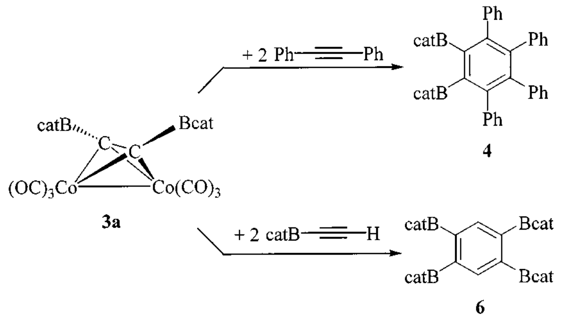
Bis(1,3,2-benzodioxaborolyl)tetraphenylbenzene and Tetrakis(1,3,2-benzodioxaborolyl)benzene

Since the syntheses of the first dicobaltatetrahedranes,[23] numerous cobalt complexes have been reported.[24] However, the use of C_2Co_2 clusters for the preparation of substituted arenes has not been studied in detail. We have explored this route and have found that heating of diphenylacetylene and a stoichiometric amount of **3a** in toluene results in the formation of bis(1,3,2-benzodioxaborolyl)tetraphenylbenzene (**4**) in good yield (Scheme 5). Compound **4** was characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy, and by mass spectrometry. The ^1H NMR spectrum shows the expected multiplet due to the aromatic protons at δ = 6.60−7.30. In the ^{13}C NMR spectrum, the signals attributable to the benzodioxaborolyl substituent appear at δ = 112.6, 122.5, and 148.5, while those of the phenyl substituents are seen at δ = 125.8, 127.3, 131.4, and 141.7. The ^{11}B NMR spectrum features one signal at δ = 32.3. In the HR-



Scheme 4

EI mass spectrum, the molecular ion peak of **4** is seen at $m/z = 618$ and shows the expected isotopic pattern.



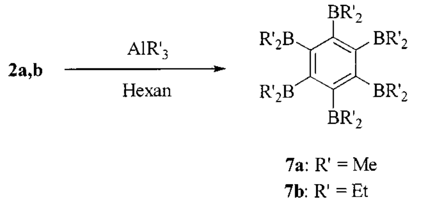
Scheme 5

Analogously, the bis(borolyl)dicobaltatetrahedrane (**3a**) reacts with the monoborylacetylene **5** to give the tetrakis(1,3,2-benzodioxaborolyl)benzene (**6**) (Scheme 5). To the best of our knowledge, this represents the first example of the synthesis of a tetraborylbenzene derivative through a stoichiometric reaction of a transition metal cluster and an acetylene.

Tetrakis(1,3,2-benzodioxaborolyl)benzene (**6**) is − in contrast to the hexaboryl derivatives **2a**,**b**, which are only slightly soluble in most organic solvents − highly soluble in toluene and chlorinated solvents. The molecular ion peak of **6** is detected in the HR-EI mass spectrum at $m/z = 550$. In the ^{11}B NMR spectrum, one signal is seen at $\delta = 22.2$, while the ^{1}H NMR spectrum shows a signal at $\delta = 6.83-7.20$ due to the protons of the catecholyl ligand. The signals of the two aromatic protons of the central benzene ring are not detected. In the ^{13}C NMR spectrum, the carbon atoms of the catecholyl ligand give rise to signals at $\delta = 111.6$, 121.8, and 146.5. It would seem that **6** consists not only of the 1,2,4,5-isomer, but is rather a mixture of the 1,2,4,5-, 1,2,3,4-, and 1,2,3,5-isomers.

Substitution of the Catechol Groups in 2a,b

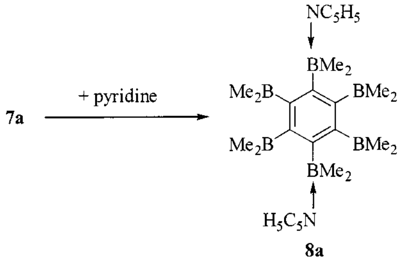
In analogy to the cleavage of the B−O bonds in 2-alkyl-1,3,2-benzodioxaborole derivatives with Grignard reagents,[25] treatment of a suspension of **2a**,**b** in hexane with trimethylaluminum furnishes hexakis(dimethylboryl)benzene (**7a**) (Scheme 6). Purification of the crude product could only be achieved by column chromatography on Florisil®, which allowed pure **7a** to be isolated in 24% yield. Compound **7a** is a low melting, colorless solid, which, in contrast to **2a**,**b**, is extremely sensitive to air and moisture. It was characterized by ^{1}H-, ^{13}C-, and ^{11}B NMR spectroscopy, and by mass spectrometry. The ^{1}H NMR spectrum shows only one signal at $\delta = 0.95$, attributable to the B−CH$_3$ groups. In the ^{13}C NMR spectrum, the *ipso* carbon atoms of the benzene ring give rise to signals at $\delta = 149.1$, while the B−CH$_3$ groups resonate at $\delta = 18.6$. The ^{11}B NMR spectrum features one broad signal at $\delta = 85.1$, which is in the range typical for alkylated boron compounds.[26] In the HR-EI mass spectrum of **8a**, the molecular ion peak is seen at $m/z = 317$ and shows the expected isotopic distribution.



Scheme 6

On treating **2a**,**b** with triethylaluminum, the hexakis(diethylboryl)benzene (**7b**) is formed. As in the case of the methyl analogue, purification could only be achieved by chromatography on a column of Florisil®. Compound **7b** was found to be soluble in hexane and also proved to be sensitive to air and moisture. In the ^{1}H NMR spectrum, a triplet ($J = 7.1$ Hz) is seen at $\delta = 1.07$ due to the methyl groups, along with a quadruplet at $\delta = 1.34$ due to the methylene units. The ^{13}C NMR spectrum of **7b** features two signals at $\delta = 9.9$ and 23.9 attributable to the ethyl substituents, while the resonances of the benzene carbon atoms are seen at $\delta = 146.8$. The ^{11}B NMR shift of $\delta = 83.7$ is comparable with the shift of **7a** quoted above. In the HR-EI mass spectrum, the molecular ion peak appears at $m/z = 485.5$.

The hexaborylbenzene derivatives **7a**,**b** possess six electron-poor boryl groups and may be regarded as hexafunctional Lewis acids. Therefore, pyridine was added to a solution of **7a** in hexane (Scheme 7). At −15 °C, a white precipitate was obtained, which was found to consist of two crystalline products, a microcrystalline compound and colorless needles.

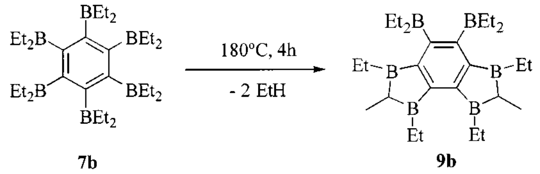


Scheme 7

NMR and mass spectral data showed this precipitate to be composed of C$_6$(BMe)$_6$ and pyridine. The ^{11}B NMR spectrum in [D$_8$]THF shows signals at $\delta = 55.4$, 3.1, and 48.8, the latter being attributable to the protolysis product Me$_2$BOH. The signal at $\delta = 55.4$ can be assigned to $[C_6(BMe_2)_6\cdot(NC_5H_5)_2]$ (**8a**), in which only two pyridines are coordinated, while the broad peak centered at $\delta = 3.1$ corresponds to a compound in which all the boron atoms are tetracoordinated. It is likely that the boron atoms in **7a** are completely coordinated by pyridine, although we are unable to prove this. Evidently, the two pyridine ligands in **8a** are not fixed, but undergo rapid exchange with the neighboring boryl groups so that only an averaged signal (δ = 55.4) is seen in the ^{11}B NMR spectrum. In the mass spectrum (EI) of **8a**, the molecular ion peak of **2a** (*m*/*z* = 317), without the two pyridine molecules, is observed.

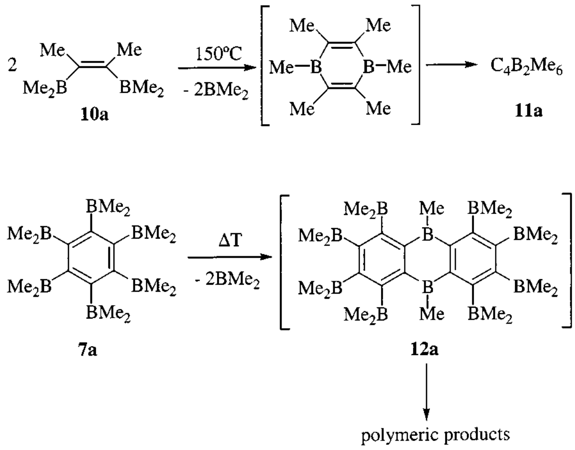
Thermolysis of Hexakis(diethylboryl)benzene (7b)

In 1968, Binger reported the first synthesis of the derivative 1,3,4,5-tetraethyl-2,3-dihydro-2-methyl-1,3-diborole, which involved thermolysis of *cis*-3,4-diethyl-3,4-bis(diethylboryl)hexene[27] at 160 °C. Similarly, a sample of **7b** was heated to 180 °C for 4 h in an argon stream. The reaction was accompanied by the evolution of ethane and the color changed from white to yellow. NMR and mass spectral data indicated that 1,2,3,4-bis(1′,3′-diborole-2′,3′-dihydro)-5,6-bis(boryl)benzene (**9b**) had been formed (Scheme 8). This represents the first example of a benzo derivative with two attached 1,3-diborole rings. In the ^{11}B NMR spectrum, one broad signal is seen at δ = 77.0, which is shifted upfield by 8 ppm compared to that of $C_6(BEt_2)_6$ (**7b**). The ^{13}C NMR spectrum of **9b** features three signals at δ = 7.8, 9.8, and 10.9 due to the three different methyl groups. The resonances of the methylene carbon atoms are found at δ = 24.2 and 25.6, while the bridging methylene carbon atoms give a signal at δ = 67.8. The signal due to the arene carbon atoms is seen at δ = 154.0. In the mass spectrum (EI) of **9b**, the molecular ion peak is seen at *m*/*z* = 425 and shows the expected isotopic distribution.



Scheme 8

Binger also reported the thermolysis of the *cis*-2,3-dimethyl-2,3-bis(dimethylboryl)hexene[27] at 150 °C to give, via the 1,4-hexamethyldiboracyclohexadiene, the *nido*-tetracarbahexaborane(6) (**11a**) (Scheme 9). Analogously, methyl derivative **7a** was heated to 150 °C in the hope of isolating the condensation product **12a** (Scheme 9). However, no low molecular weight species such as **12a** could be detected; only insoluble brown products were obtained, which may have web-like structures.



Scheme 9

Crystal Structures

The structure of **3a** was characterized by performing a single-crystal X-ray analysis (crystal data and structure refinement parameters for **3a** and **8a** are presented in Table 1). The dark-red crystals of **3a**, grown at 4 °C from a solution in toluene, belong to the monoclinic system, space group *C*2/*c* and have four formula units in the unit cell.

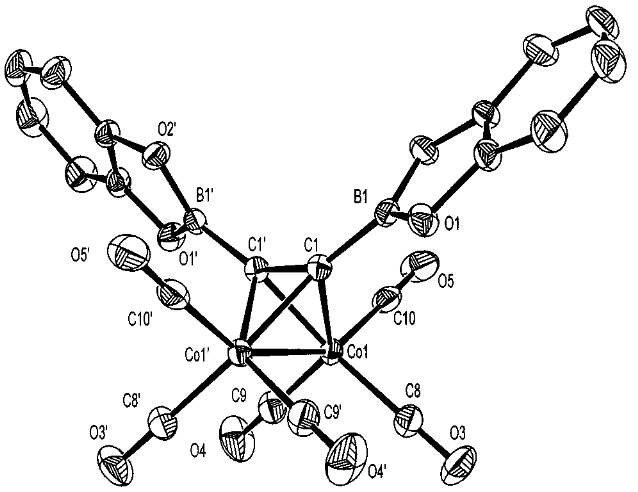


Figure 1. Structure of **3a** in the crystal; selected bond lengths [Å] and angles [°]: Co1−Co1′ 2.472(2), C1−C1′ 1.345(7), Co1−C1 1.983(4), Co1−C1′ 1.953(4), B1−C1 1.518(5), B1−O1 1.379(5), B1−O2 1.387(5); Co1−C1−Co1′ 77.8(1), Co1−C1−C1′ 68.8(2), Co1′−C1−C1′ 71.2(2), B1−C1−C1′ 145.2(2), O1−B1−O2 111.8(3), B1−C1−Co1 127.8(3), B1−C1−Co1′ 137.0(3)

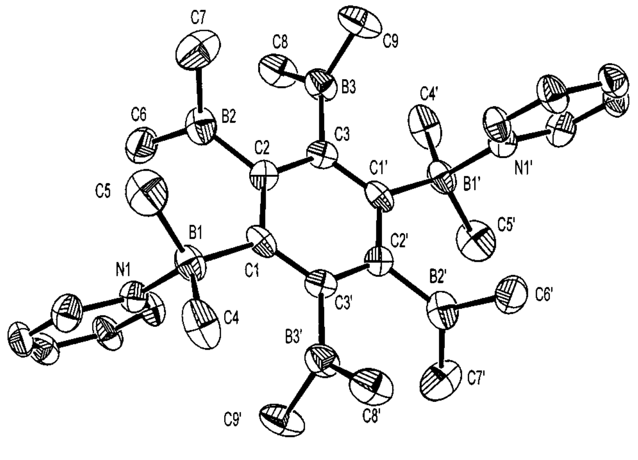


Figure 2. Structure of **8a** in the crystal; selected bond lengths [Å]: B1−C1 1.668(11), B1−N1 1.667(10), B2−C2 1.585(12), B3−C3 1.561(11), C1−C2 1.437(9), C2−C3 1.391(9), C3−C1′ 1.422(9)

The molecular structure (Figure 1) shows the Co_2C_2 framework; each cobalt atom is surrounded by three CO ligands and each carbon atom bears a terminal $BO_2C_6H_4$ group. The C1−C14 distance of 1.345 Å is similar to that in other Co_2C_2 tetrahedrane compounds.[28a,28b] The

Tabelle 1. Crystal data and structure refinement for **3a** and **8a**

	3a	**8a**
Empirical formula	$C_{20}H_8B_2Co_2O_{10}\cdot C_7H_8$	$C_{28}H_{46}B_6N_2$
Formula mass	639.9	475.6
Crystal system	monoclinic	trigonal
Space group	$C2/c$	$R\bar{3}$
Unit cell		
a [Å]	16.290(12)	31.25(2)
b [Å]	14.573(10)	31.25(2)
c [Å]	14.148(11)	9.942(7)
α [deg]	90	90
β [deg]	124.31	90
γ [deg]	90	120
Volume [Å^3]	2774(4)	8408(10)
Z	4	9
Calcd. density [g/cm^3]	1.532	1.306
Absorp. coeff. [mm^{-1}]	1.251	0.05
F(000)	1288	2322
Crystal size [mm]	0.3 × 0.4 × 0.6	0.2 × 0.2 × 0.3
Θ-range [deg]	25	22.5
Index ranges	−19/+16, 0/+17, 0/+16	−26/+28, 0/+33, 0/+9
No. of reflections		
unique	2439	1926
observed [$I > 2\sigma(I)$]	2067	731
Transmission	0.631−0.787	−
Parameters	171	171
Final R indices		
$R1$ [$I > 2\sigma(I)$]	0.047	0.086
$wR2$	0.133	0.242
T [°C]	−65	−70
Largest diff. peak/hole [e/Å]	1.08/−0.45	0.17/−0.17

Co1−Co1 distance (2.472 Å) falls within the normal range.[28a][28b]

To elucidate the structure of **8a**, an X-ray diffraction study was carried out. A single crystal was grown from a solution in hexane at −15 °C. The determined structure is shown in Figure 2. **8a** crystallizes in the trigonal space group $R\bar{3}$ with nine formula units in the unit cell.

The crystal structure analysis reveals that in the donor−acceptor compound **8a**, two pyridines are coordinated to *para*-BMe$_2$ groups in *anterti* positions (Figure 2). The boron atoms of the remaining four boryl groups are coordinated in a planar fashion, the BC$_2$ planes being perpendicular to the central benzene plane. The distances C1−C2 (1.438 Å), C2−C3 (1.391 Å), and C3−C1 (1.422 Å) in the aromatic ring are somewhat elongated.

Experimental Section

General: All manipulations of compounds were performed with rigorous exclusion of air and moisture under an argon atmosphere using standard Schlenk techniques. Solvents were dried with the appropriate drying agents and distilled under a nitrogen atmosphere. − Column chromatography: Florisil® (Fluka), 100−200 mesh. − Elemental analyses were carried out at the Microanalytical Laboratory, Universität Heidelberg. − Melting points (uncorrected) were obtained on a Büchi apparatus using samples sealed in capillaries under argon. − ^{1}H, ^{13}C, and ^{11}B NMR: Bruker AC 200 spectrometer; ^{1}H and ^{13}C spectra were referenced to $(CH_3)_4Si$; ^{11}B spectra to $BF_3\cdot Et_2O$. − IR spectra were recorded on a Bruker IFS 28 FT spectrometer. − Mass spectra were obtained on Finnigan MAT 8230 and Jeol MStation IMS-700 spectrometers operating in EI and FD modes. − Bis(1,3,2-benzodioxaborol-2-yl)acetylene (**1a**),[17] $(Me_3Sn)_2C_2$,[29] [Ni(cod)$_2$],[30] and [CpCo(C$_2$H$_4$)$_2$][31] were prepared according to literature procedures. [CpCo(CO)$_2$], [Co$_2$(CO)$_8$], and 2,3-dihydroxynaphthalene were purchased from Aldrich®.

2-Chloro-[1,3,2-(2,3-naphtho)dioxaborole]: To a solution of BCl$_3$ (39.0 g, 0.33 mol) in CH$_2$Cl$_2$ (500 mL), 2,3-dihydroxynaphthalene (50.0 g, 0.31 mol) was added at −78 °C. The mixture was allowed to warm to room temperature and stirred for a further 12 h. It was then concentrated and the resulting crystalline precipitate was collected by filtration. Yield: 61.3 g (96%), colorless needles; m.p. 152 °C. − ^{1}H NMR (200.1 MHz, CDCl$_3$): δ = 7.84−7.44 (m, 6 H, arene H). − ^{13}C NMR (50.3 MHz, CDCl$_3$): δ = 108.8, 125.3, 127.8, 130.4, 147.3 (C$_{10}$H$_6$). − ^{11}B NMR (64.2 MHz, CDCl$_3$): δ = 29.9. − MS (70 eV, EI): *m*/*z* (%) = 204 (100) [M$^+$].

Bis[1,3,2-(2,3-naphtho)dioxaborol-2-yl]acetylene (1b): To a solution of $(Me_3Sn)_2C_2$ (4.00 g, 11.4 mmol) in toluene (50 mL), $C_{10}H_6O_2BCl$ (4.65 g, 22.8 mmol) in toluene (150 mL) was added at −78 °C. The mixture was allowed to warm to room temperature and stirred for a further 24 h. It was then concentrated and the resulting precipitate was collected by filtration. Yield: 3.73 g (91%) of **1b** as a colorless, crystalline, air-stable solid; m.p. 255 °C. − ^{1}H NMR (200.1 MHz, [D$_4$]MeOH): δ = 7.54−7.10 (m, 12 H, arene H). − ^{13}C NMR (50.3 MHz, [D$_4$]MeOH): δ = 110.2, 124.1, 126.4, 131.5, 148.3 (C$_{10}$H$_6$), 98 (BCCB). − ^{11}B NMR (64.2 MHz, [D$_4$]MeOH): δ = 22.1. − MS (70 eV, EI): *m*/*z* (%) = 362 (100) [M$^+$].

Hexakis(1,3,2-benzodioxaborolyl)benzene (2a). − Catalyst [CpCo(CO)$_2$]: To a suspension of **1a** (2.28 g, 8.7 mmol) in toluene (30 mL), (η^5-cyclopentadienyl)dicarbonylcobalt (0.09 g, 0.5 mmol) was added at room temperature. The mixture was then heated under reflux for 48 h. After cooling, the resulting precipitate was collected by filtration, washed several times with toluene, and dried in vacuo. Yield: 1.71 g (75%) of **2a** as a white, air-stable powder; m.p. > 310 °C. − ^{1}H NMR (200.1 MHz, [D$_4$]MeOH): δ = 6.61−6.77

(m, 24 H, arene H). − ^{13}C NMR (50.3 MHz, [D$_4$]MeOH): δ = 116.3, 120.8, 146.2 (C_6H_4), 143 (br., C_{ar}−B). − ^{11}B NMR (64.2 MHz, [D$_4$]MeOH): δ = 29.3. − MS (70 eV, HR-EI): *m/z* (%) = 785.1879 (100) [M$^+$; calcd. $^{12}C_{42}{}^{1}H_{24}{}^{10}B_{1}{}^{11}B_{5}{}^{16}O_{12}$: 785.1862]. − $C_{42}H_{24}B_6O_{12}$ (785.51): calcd. C 64.22, H 3.08; found C 64.06, H 3.26.

Catalyst [$Co_2(CO)_8$]: A suspension of **1a** (1.02 g, 3.9 mmol) and octacarbonyldicobalt (0.13 g, 0.4 mL) in toluene (30 mL) was heated for 24 h under reflux. Workup was carried out as above. Yield: 0.69 g (68%) of **2a**.

Catalyst [Ni(cod)$_2$]: A suspension of **1a** (1.38 g, 5.3 mmol) and [Ni(C_8H_8)$_2$] (0.08 g, 0.3 mmol) in toluene (40 mL) was heated for 20 h under reflux. Workup was carried out as above. Yield: 1.07 g (77%) of **2a**.

Catalyst 3a: A suspension of **1a** (1.12 g, 4.3 mmol) and bis(1,3,2-benzodioxaborolyl)dicobalttetrahedrane (**3a**) (0.11 g, 0.2 mmol) in toluene (30 mL) was heated for 24 h under reflux. Workup was carried out as above. Yield: 0.63 g (56%) of **2a**.

Hexakis{1,3,2-naphtho[2,3-*d*]dioxaborolyl}benzene (2b): A suspension of **1b** (2.03 g, 5.6 mmol) and (η^5-cyclopentadienyl)dicarbonylcobalt (0.08 g, 0.4 mmol) in toluene (30 mL) was heated for 48 h under reflux. Workup was carried out as for **2a**. Yield: 1.28 g (63%) of **2b** as a white, air-stable powder; m.p. > 310 °C. − ^{1}H NMR (200.1 MHz, [D$_4$]MeOH): δ = 7.14−7.59 (m, 36 H, arene H). − ^{13}C NMR (50.3 MHz, [D$_4$]MeOH): δ = 110.8, 124.4, 127.0, 131.0, 147.8 ($C_{10}H_6$), 144 (br., C_{ar}−B). − ^{11}B NMR (64.2 MHz, [D$_4$]MeOH): δ = 28.3. − MS (70 eV, EI): *m/z* (%) = 1085 (7) [M$^+$], 917 (4) [M$^+$ − $C_{10}H_6O_2B$], 749 (3) [M$^+$ − 2 $C_{10}H_6O_2B$]. − $C_{66}H_{36}B_6O_{12}$ (1086): calcd. C 73.00, H 3.34; found C 71.40, H 3.39.

Bis(borolyl)dicobaltatetrahedrane (3a): To a solution of bis(1,3,2-benzodioxaborole-2-yl)acetylene (**1a**; 1.22 g, 4.7 mmol) in CH_2Cl_2 (40 mL), a solution of octacarbonyldicobalt (1.61 g, 4.7 mmol) in CH_2Cl_2 (20 mL) was added dropwise at room temperature. An immediate reaction ensued, as indicated by the evolution of carbon monoxide. The mixture was stirred for 20 h at room temperature and thereafter for 2 h at reflux temperature. To the red-brown solution was then added Florisil® (10 g) and the solvent was removed in vacuo. The residue was separated by column chromatography (Florisil®/hexane) to give two fractions. Using hexane as eluent, [$Co_2(CO)_8$] was obtained first. The second fraction (hexane/toluene, 1:1) was found to contain **3a**. Yield: 1.17 g (45%) of **3a** as a red, air-sensitive solid; m.p. 102 °C. − ^{1}H NMR (200.1 MHz, C_6D_6): δ = 6.85−7.29 (m, 8 H, C_{ar}H). − ^{13}C NMR (50.3 MHz, C_6D_6): δ = 111.5, 122.0, and 147.4 (C_{ar}), 96 (br., C−B), 197.4 (CO). − ^{11}B NMR (64.2 MHz, C_6D_6): δ = 33.1. − IR (hexane): ṽ [cm^{-1}] = 2102 (s), 2066 (vs), 2038 (vs). − MS (70 eV, EI): *m/z* (%) = 548 (2) [M$^+$], 520 (7) [M$^+$ − CO], 492 (9) [M$^+$ − 2 CO], 464 (6) [M$^+$ − 3 CO], 436 (9) [M$^+$ − 4 CO], 408 (23) [M$^+$ − 5 CO], 380 (13) [M$^+$ − 6 CO], 321 (8) [M$^+$ − 6 CO − Co], 262 (100) [M$^+$ − 6 CO − 2 Co].

Bis(1,3,2-benzodioxaborolyl)tetraphenylbenzene (4): To a solution of **3a** (1.14 g, 2.1 mmol) in toluene (30 mL), diphenylacetylene (0.75 g, 4.2 mmol) was added at room temperature. The resulting mixture was stirred for 24 h under reflux. After cooling, the brown solution thus obtained was filtered and the filtrate was concentrated to dryness in vacuo. The residue was washed several times with hexane and dried in vacuo. Yield: 1.01 g (76%) of **4** as a white, air-stable powder. − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 6.60−7.30 (m, 28 H, arene H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 112.6, 122.5, 148.5 (C_6H_4), 125.8, 127.3, 131.4, 141.7 (C_6H_5), 145 (br., C_{ar}−B). − ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 32.3. − MS (70 eV, HR-EI): *m/z* (%) = 618.21839 (45) [M$^+$; calcd. $^{12}C_{42}{}^{1}H_{28}{}^{11}B_{2}{}^{16}O_{4}$: 618.21869].

Tetrakis(1,3,2-benzodioxaborolyl)benzene (6): To a solution of **3a** (1.06 g, 1.9 mmol) in toluene (25 mL), monoborylacetylene[32] **5** (0.56 g, 3.9 mmol) was added at room temperature. The resulting mixture was stirred for 24 h under reflux. After cooling, the brown solution thus obtained was filtered and the filtrate was concentrated to dryness in vacuo. The residue was washed several times with hexane and dried in vacuo. Yield: 0.83 g (79%) of **6** as a white, air-stable powder. − ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 6.83−7.20 (m, 16 H, arene H, catecholyl); C_{ar}−H not observed . − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 111.6, 121.8, 146.5 (C_6H_4); C_{ar}−B and C_{ar}−H not observed. − ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 22.2. − MS (70 eV, HR-EI): *m/z* (%) = 550.1371 (83) [M$^+$; calcd. $^{12}C_{30}{}^{1}H_{18}{}^{11}B_{4}{}^{16}O_{8}$: 550.1365]; Δmmu = 0.6.

Hexakis(dimethylboryl)benzene (7a): To a suspension of **2a** (1.51 g, 1.9 mmol) [or **2b** (1.67 g, 1.5 mmol)] in hexane (40 mL), trimethylaluminum (0.56 g, 7.8 mmol) [0.45 g, 6.2 mmol] was added dropwise at −20 °C. The reaction mixture was allowed to warm to room temperature, stirred for 24 h, and then heated under reflux for 2 h. The brown-yellow solution thus obtained was filtered and the filtrate was concentrated to dryness in vacuo. The oily residue was redissolved in hexane (10 mL) and separated by column chromatography (Florisil®/hexane). Yield: 0.14 g (24%) [0.10 g (20%)] of **7a** as a colorless, air-sensitive solid; m.p. 34 °C. − ^{1}H NMR (200.1 MHz, C_6D_6): δ = 0.96 (s, 36 H, BCH_3). − ^{13}C NMR (50.3 MHz, C_6D_6): δ = 18.6 (BCH_3), 149.1 [C_{ar}−B(CH_3)$_2$]. − ^{11}B NMR (64.2 MHz, C_6D_6): δ = 85.1. − MS (70 eV, EI): *m/z* (%) = 317 (27) [M$^+$], 302 (7) [M$^+$ − CH_3], 246 (13) [M$^+$ − B(CH_3)$_2$ − 2 CH_3]; HR-EI: *m/z* (%) = 317.34155 (29) [M$^+$; calcd. $^{12}C_{18}{}^{1}H_{36}{}^{10}B_{1}{}^{11}B_{5}$: 317.34116]; Δ mmu = 0.39.

Hexakis(diethylboryl)benzene (7b): To a suspension of **2a** (1.32 g, 1.7 mmol) [or **2b** (1.53 g, 1.4 mmol)] in hexane (35 mL), triethylaluminum (0.77 g, 6.7 mmol) [0.64 g, 5.6 mmol] was added dropwise at −20 °C. Workup was carried out as for **7a**. Yield: 0.33 g (40%) [0.19 g (28%)] of **7b** as a colorless, air-sensitive solid; m.p. 48 °C. − ^{1}H NMR (200.1 MHz, C_6D_6): δ = 1.07 (t, *J* = 7.1 Hz, 36 H, CH_2CH_3), 1.34 (q, *J* = 7.3 Hz, 24 H, CH_2CH_3). − ^{13}C NMR (50.3 MHz, C_6D_6): δ = 9.9 (CH_2CH_3), 23.9 (CH_2CH_3), 146.8 [C_{ar}−B(CH_2CH_3)$_2$]. − ^{11}B NMR (64.2 MHz, C_6D_6): δ = 83.7. − MS (70 eV, EI): *m/z* (%) = 485.5 (54) [M$^+$], 456 (9) [M$^+$ − C_2H_5], 428 (5) [M$^+$ − 2 C_2H_5], 348 (22) [M$^+$ − 2 B(C_2H_5)$_2$]; HR-EI: *m/z* (%) = 485.5330 (5) [M$^+$; calcd. $^{12}C_{30}{}^{1}H_{60}{}^{10}B_{1}{}^{11}B_{5}$: 485.5290]; Δ mmu = 4.0.

Hexakis(dimethylboryl)benzene−Bipyridine Adduct (8a): Hexakis(-dimethylboryl)benzene **7a**, obtained from **2a** (1.21 g, 1.5 mmol) and trimethylaluminum (0.44 g, 6.0 mmol), was dissolved in hexane (12 mL) and then pyridine (2 mL) was added. The reaction mixture was cooled to −15 °C, whereupon a white precipitate was deposited. Yield: 0.22 g (30%) of **8a** as colorless, air-sensitive needles; m.p. 110 °C. − ^{1}H NMR (200.1 MHz, [D$_8$]THF): δ = 0.90 (s, BCH_3), 1.28 [s, B(CH_3)$_2$−NC_5H_5], 6.96 (m, C_5H_5N), 7.71 (m, C_5H_5N), 8.49 (m, C_5H_5N). − ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 1.5 [B(CH_3)$_2$−NC_5H_5], 19.3 (BCH_3), 128.5, 134.3, 146.2 (C_5H_5N), 144.7 [CB(CH_3)$_2$]. − ^{11}B NMR (64.2 MHz, [D$_8$]THF): δ = 55.4. − MS (70 eV, EI): *m/z* (%) = 317 (35) [M$^+$ − 2 C_5H_5N], 302 (7) [M$^+$ − 2 C_5H_5N − CH_3], 246 (11) [M$^+$ − 2 C_5H_5N − B(CH_3)$_2$ − 2 CH_3], 79 (100) [C_5H_5N].

1,2,3,4-Bis(1,3-diborole)-5,6-bis(boryl)benzene (9b): Under argon, hexakis(diethylboryl)benzene (**7b**; 0.21 g, 0.4 mmol) was slowly heated without a solvent to 180 °C and maintained at this temperature for 4 h. Yield: 0.14 g (77%) of a yellow, air-sensitive oily residue. − $^{1}\mathrm{H}$ NMR (200.1 MHz, $\mathrm{C_6D_6}$): δ = 1.04 (m, $\mathrm{CH_2C}\mathit{H}_3$), 1.52 (m, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 3.5 ($\mathrm{C}\mathit{H}\mathrm{CH_3}$). − $^{13}\mathrm{C}$ NMR (50.3 MHz, $\mathrm{C_6D_6}$): δ = 7.8 ($\mathrm{CH}\mathit{C}\mathrm{H_3}$), 9.8 [$\mathrm{B(CH_2}\mathit{C}\mathrm{H_3)_2}$], 10.9 [$\mathrm{B(CH_2}\mathit{C}\mathrm{H_3)}$], 24.2 [$\mathrm{B(}\mathit{C}\mathrm{H_2CH_3)_2}$], 25.6 [$\mathrm{B(}\mathit{C}\mathrm{H_2CH_3)}$], 67.8 ($\mathit{C}\mathrm{HCH_3}$), 154 [$\mathit{C}\mathrm{-B(CH_2CH_3)_2}$]. − $^{11}\mathrm{B}$ NMR (64.2 MHz, $\mathrm{C_6D_6}$): δ = 77. − MS (70 eV, EI): *m*/*z* (%) = 425 (42) [$\mathrm{M^+}$], 396 (71) [$\mathrm{M^+ - C_2H_5}$], 327 (21) [$\mathrm{M^+ - C_2H_5 - B(C_2H_5)_2}$], 298 (13) [$\mathrm{M^+ - 2\ C_2H_5 - B(C_2H_5)_2}$].

Crystal Structure Determinations of 3a and 8a: Crystal data and details of the structure determinations are listed in Table 1. Unique sets of intensity data were collected at −65 °C and −70 °C on a Siemens−Stoe AED four-circle diffractometer (Mo-K_α radiation, λ = 0.7107 Å, graphite monochromator, ω-scans). Empirical absorption corrections (ψ-scans) were applied. The structures were solved by direct methods (SHELXS-86)[33] and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-97).[34] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions or as part of rigid groups ($\mathrm{CH_3}$).

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-137769 (**3a**) and CCDC-137770 (**8a**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk]

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