Cobalt-Mediated Cyclooligomerization Reactions of Borylacetylenes

Avijit Goswami,[a] Claus-Jürgen Maier,[a] Hans Pritzkow,[a] and Walter Siebert*[a]

Dedicated to Professor Helmut Werner on the occasion of his 70th birthday

Keywords: Boranes / Catalysts / (Cyclobutadiene)cobalt complexes / Mono(boryl)acetylenes / Triborylbenzenes

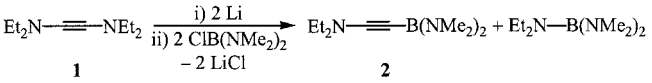
Reaction of bis(diethylamino)acetylene (**1**) with lithium and chlorobis(dimethylamino)borane yields 1-[bis(dimethylamino)boryl]-2-(diethylamino)acetylene (**2**). Treatment of 1-aryl-2-(trimethylstannyl)acetylenes **3** with chlorobis(diisopropylamino)borane results in the quantitative formation of 1-aryl-2-[bis(diisopropylamino)boryl]acetylene compounds **4**. The 1-aryl-2-borylacetylene derivatives **5**, **6**, and **7** are obtained by the reaction of **3** with the appropriate haloborane, or by reacting **4** with two equivalents of HCl and one equivalent of catechol, dithiocatechol and 2-hydroxythiophenol. The catalytic cyclotrimerizations of **5a–d** with $[CpCo(CO)_2]$ or $[Co_2(CO)_8]$ lead to isomeric mixtures of the triborylbenzene derivatives **8a–d** and **8a′–d′**, whereas **6a–d** and **7a–b** undergo cyclotrimerization only with catalytic amount of $[Co_2(CO)_8]$, to give isomeric mixtures of the triborylbenzene derivatives **12a–d/12a′–d′** and **13a–b/13a′–b′**, respectively. The reaction of **2** with a stoichiometric amount of (η^5-cyclopentadienyl)bis(ethene)cobalt leads to (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt complexes **9**. The analogous complexes **10** and **11** are obtained by the reactions of **6** and **7** with a stoichiometric amount of (η^5-cyclopentadienyl)dicarbonylcobalt. Treatment of $Co_2(CO)_8$ with **5a**, **6a**, and **7a** yields the dicobaltatetrahedranes **14a**, **15a** and **16a**. Compound **15a** reacts with two equivalents of diphenylacetylene and 1-(1,3,2-benzodioxaborolyl)-2-phenylacetylene (**5a**), to furnish (1,3,2-benzodithiaborolyl)pentaphenylbenzene (**17**) and bis(1,3,2-benzodioxaborolyl)(1,3,2-benzodithiaborolyl)-triphenylbenzene (**18**), respectively. The new compounds have been characterized by NMR spectroscopy and mass spectrometry, as well as by X-ray structural analyses for **4a**, **5a**, **6a**, and **10a**.

Introduction

Over the past decades, the cyclooligomerization reactions of alkynes with transition metal complexes have received considerable attention.[1] $[CpCo(CO)_2]$[2] is a convenient and efficient reagent for the syntheses of CpCo−cyclobutadiene complexes,[3] cyclopentadienones,[4] and benzene derivatives,[5] whereas $[Co_2(CO)_8]$ is used in Pauson−Khand[6] and [2+2+2] cyclotrimerization reactions.

Recently, we reported the Co-catalyzed [2+2+2] cyclotrimerization of mono-[7] and bis(catecholboryl)acetylenes.[8] With both types of acetylenes, only benzene derivatives were obtained — no CpCo-cyclobutadiene complexes were observed — even when using stoichiometric amounts of $[CpCo(CO)_2]$ and the corresponding acetylene.

To study the influence of the substituents with respect to the formation of CpCo−cyclobutadiene and/or benzene derivatives, we have synthesized new mono(boryl)acetylene derivatives with terminal boryl and amino or aryl substituents. Compound **2**, which has both amino and boryl substituents (Scheme 1), can react similarly to the push−pull acetylene $Me_2N-C\equiv C-COOMe$,[9] and undergoes dimerization.



Scheme 1

The influence of the substituents at the boryl group is of particular interest, as amino groups at the boron center may reduce its Lewis acidity. A large part of this work concentrates on the reactivity of arylalkynyl boranes **5**, **6**, and **7**, in which two oxygen atoms (in **5**), two sulfur atoms (in **6**) and one oxygen and one sulfur atom (in **7**) are bound to the boron atom. It is expected that the heteroatoms have different electronic and steric effects on the reactivity of the acetylenes **5**−**7**. In this paper, we report the syntheses, structures and reactivities of the monoborylacetylene derivatives **2** and **4**−**7**.

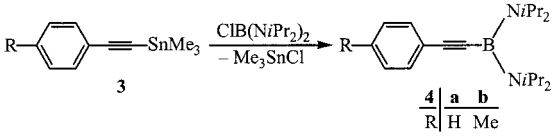
[a] Anorganisch-Chemisches Institut der Universität,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: (internat.) +49-(0)6221-54-5609
E-mail: walter.siebert@urz.uni-heidelberg.de

Results and Discussion

Synthesis and Properties of Mono(boryl)acetylene Derivatives 2, 4, 5, 6 and 7

Bis(diethylamino)acetylene (**1**) is obtained by treating 2-fluoro-1,1-dichloroethene or trichloroethene with *N*,*N*-disubstituted lithium amides and secondary amines.[10] In **1**, the N−C≡C bond is cleaved by lithium in THF to give two lithium compounds (Et_2NLi and $Et_2N-C{\equiv}CLi$), which react with various electrophiles. The mixture was treated with chlorobis(dimethylamino)borane to give $Et_2N-B(NMe_2)_2$ (70%) and 1-amino-2-borylacetylene (**2**) (43%), which were separated by fractional distillation (Scheme 1). Their compositions were determined by mass spectrometric and NMR spectroscopic data.

The reactions of chlorobis(diisopropylamino)borane with 1-trimethylstannyl-2-arylacetylenes **3** led to light-yellow compounds **4** in quantitative yields (Scheme 2). Compounds **4**[11] were characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy, as well as by mass spectrometry.



Scheme 2

In the ^{11}B NMR spectrum, the signal at δ = 26 ppm of **4a** indicates a trigonal-planar boryl group, which we confirmed by X-ray structural analysis. In the linear B−C≡C−C moiety (Figure 1) the C≡C bond is slightly widened relative to other R−C≡C−R compounds (1.18 Å).[12]

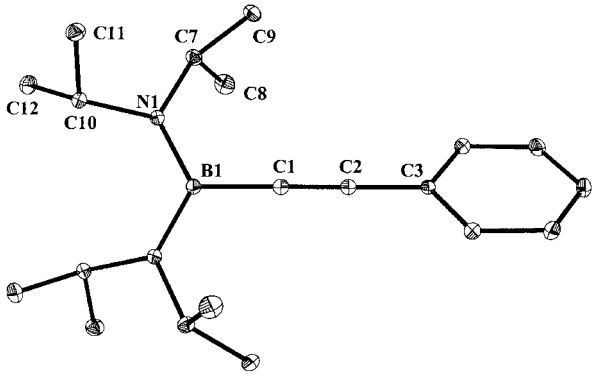
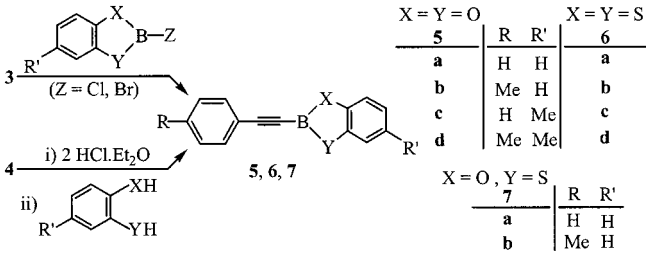


Figure 1. Molecular structure of **4a** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: C1−C2 1.210(14), C2−C3 1.434(14), N1−B1 1.434(8), B1−C1 1.559(15), C1−C2−C3 180.0, C2−C1−B1 180.0

The syntheses of compounds **5**, **6**, and **7** were achieved by two reaction procedures. A solution of 1-aryl-2-(trimethylstannyl)acetylene (**3**) in toluene was reacted with the corresponding haloborane to give **5**−**7**. When compound **4** was treated with two equivalents of HCl and one equivalent of catechol or dithiocatechol or 2-hydroxythiophenol in THF, the corresponding alkynes **5**, **6**, and **7** were obtained as crystalline solids (Scheme 3). These compounds are soluble in benzene and toluene, but are less soluble in hexane and pentane. The ^1H NMR spectra of **5**−**7** show the expected multiplicities of the aromatic protons in the region δ = 6.9−7.9 ppm. In the ^{13}C NMR spectra, the signals for the boron-bound carbon atoms were not observed; the signals for the β carbon atoms (δ = 84−109 ppm) are shifted to lower fields relative to the alkylacetylenes (δ = 70−80 ppm),[13] which may indicate an interaction of the empty orbital at the boron atom with the π system of the triple bond.



Scheme 3

The structures of **5a** and **6a** were determined by performing single-crystal X-ray analyses (Figures 2 and 3). Each compound has a linear B−C≡C−C moiety (**5a**: exactly; **6a**: approximately) and the C≡C bond lengths are slightly longer than those of normal alkyne compounds. The B−C bonds are rather short. This finding is in agreement with structural data for oxygen-substituted bis(catecholboryl)acetylenes.[14]

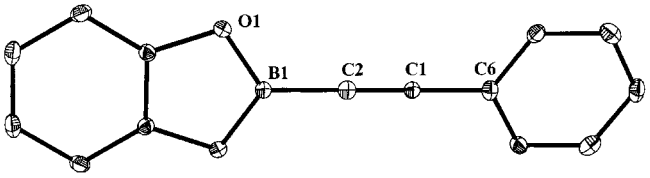


Figure 2. Molecular structure of **5a** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: C1−C2 1.196(5), C1−C6 1.447(5), B1−C2 1.513(5), B1−O1 1.383(15), C1−C2−C6 180.0, C1−C2−B1 180.0

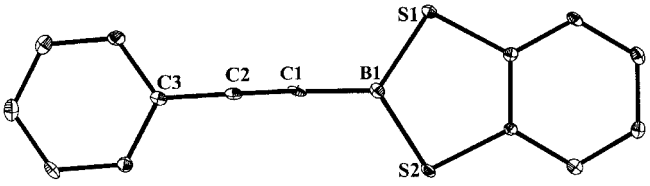
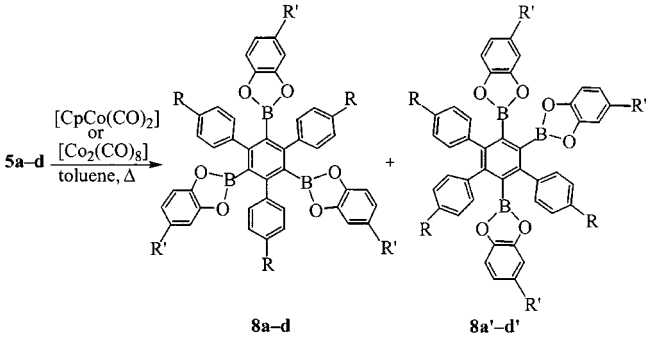


Figure 3. Molecular structure of **6a** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: C1−C2 1.207 (8), C2−C3 1.423(7), B1−C1 1.521(8), B1−S1 1.796(6), C1−C2−C3 178.5(5), C2−C1−B1 177.6(5)

Trimerization of 5 to Triboryl-triarylbenzene Derivatives 8

Only a few triborylbenzene derivatives are known,[15] of which some have been prepared in low yields by Grignard reactions. Recently, we obtained triborylbenzene derivatives[7] by cyclotrimerization of monoborylacetylenes in the presence of catalytic amount of dicarbonyl(η^5-cyclopentadienyl)cobalt. Analogously, in refluxing toluene, the monoborylalkyne derivatives **5a**−**d** formed isomeric mixtures of the 1,3,5- and 1,2,4-triborylbenzene derivatives **8a**−**d** and **8a′**−**d′** in the presence of a catalytic amount of $[CpCo(CO)_2]$ or $[Co_2(CO)_8]$ (Scheme 4). The isomers could not be separated.



Scheme 4

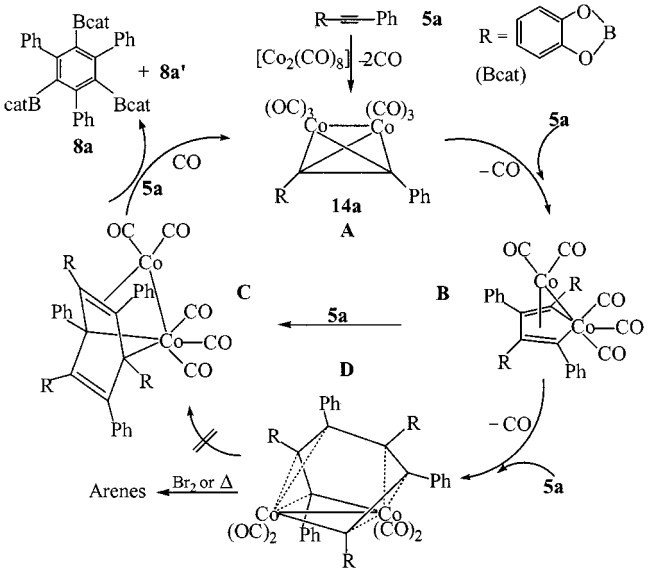
The air-stable solids **8a**−**d** and **8a′**−**8d′** are light-yellow in color and are not soluble in most organic solvents; **8a**/**8a′** dissolve partially in chloroform, whereas **8b**−**d** and **8b′**−**d′** are slightly soluble in dichloromethane and toluene. Compounds **8a**−**d** and **8a′**−**d′** were characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy, elemental analysis, and mass spectrometry. The ^{11}B NMR spectra exhibit broad signals at δ = 24 ppm for **8a**/**8a′**, δ = 22 ppm for **8b**/**8b′** and **8d**/**8d′**, and δ = 23 ppm for **8c**/**8c′**. In the ^{1}H NMR spectrum of **8a**/**8a′**, several peaks appear in the region δ = 7.2−7.6 ppm that are due to aromatic protons of the catechol and phenyl substituents. In the ^{13}C NMR spectrum, three signals at δ = 112.7, 123.2, and 147.8 ppm are observed for the carbon atoms of the catechol groups. The signal at δ = 139.9 ppm is assigned to the *ipso*-carbon atoms of the central ring of the isomer **8a** and three signals at δ = 134.6, 137.3, and 142.5 ppm to the *ipso*-carbon atoms of the central ring of the isomer **8a′**. The ^{13}C NMR spectroscopic signals of the carbon atoms of the phenyl substituents appear at δ = 121.2, 128.5, 130.0, and 132.8 ppm. Similarly, the ^{1}H NMR spectra of **8b**−**d** and **8b′**−**d′** show the expected multiplets (in the region δ = 6.9−7.6 ppm for the aromatic protons) and singlets near δ = 2.3−2.4 ppm (methyl groups). The ^{13}C NMR spectra reveal chemical shifts of the *ipso*-carbon atoms of the central ring of the isomers **8b**−**d** near δ = 140−141 ppm and the *ipso* carbon atoms of the isomers **8b′**−**d′** in the region δ = 136−148 ppm.

Thermal reactions of **5a**−**d** with a stoichiometric amount of $[CpCo(CO)_2]$ did not provide any (cyclobutadiene)cobalt complex: only the cyclotrimerization products were found. Likewise, photochemical activation of $[CpCo(CO)_2]$ and **5a**−**d** did not yield (cyclobutadiene)cobalt complexes: only the starting materials were recovered.

Catalytic Cycles with $[CpCo(CO)_2]$ and $[Co_2(CO)_8]$

The postulated mechanism of $[CpCo(CO)_2]$-catalyzed cyclotrimerization[5a,16] of acetylene is suggested for **5a**. Under thermal conditions, two alkyne ligands displace the CO groups to form a bis(alkyne)cobalt complex, followed by reductive coupling of the alkyne units to give a coordinatively unsaturated cobaltacyclopentadiene complex. Coordination of a third molecule of **5a** could then lead to an 18-VE complex, which undergoes alkyne insertion to form the corresponding cobaltacycloheptatriene compound. Subsequent reductive elimination of the CpCo complex fragment leads to the formation of the triborylbenzene derivatives **8a**/**8a′**. Recently, Vollhardt et al.[17] reported the synthesis of a (η^2-alkyne)cobaltacyclopentadiene complex, which indirectly proves the proposed catalytic cycle, although no direct evidence for the intermediacy of the postulated cobaltacycloheptatriene was obtained. According to ab initio and density functional theory (DFT) investigations of the mechanism,[16] a cobaltacycloheptatriene is in fact very unlikely to form.

Analogously, the catalytic oligomerization of **5a** with octacarbonyldicobalt led to the triborylbenzene derivatives **8a**/**8a′** in 71% yield. One of our aims is to isolate intermediates to shed more light on the catalytic cycle proposed in Scheme 5, which is a short version of the Knox−Pauson−Spicer mechanism.[18] In the first step, elimination of two CO ligands leads to the unsaturated species $[Co_2(CO)_6]$, which reacts with **5a** to give the boryl-substituted dicobaltatetrahedrane complex **14a** (**A**). Subsequent elimination of CO and insertion of one molecule of **5a** should yield the intermediate **B**, of which many examples are known.[19] However, under our conditions, **B** was not detected. A Diels−Alder-type reaction of **B** with **5a** may

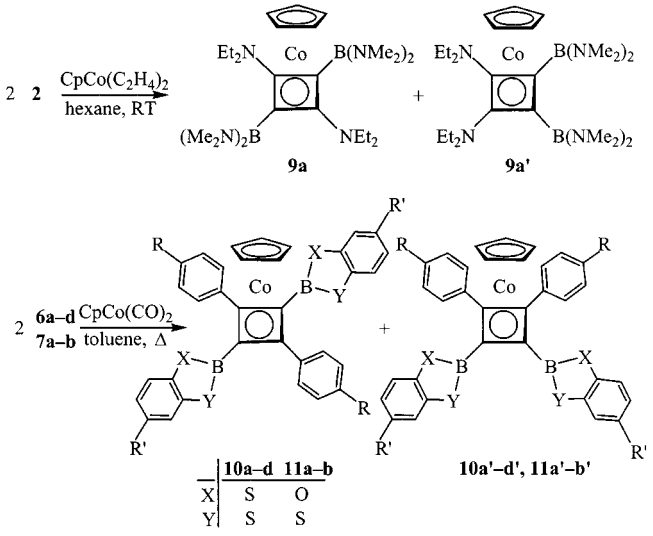


Scheme 5

lead to **C**, which eliminate **8a/8a′** and the pentacarbonyldicobalt fragment reacts with CO and **5a** to give **14a**. We did not observe the postulated intermediates **C** and the "flyover" dicobaltacyclooctadiene complex **D**; several examples have been reported of the latter species.[18,20] It has been demonstrated that drastic conditions[21] or chemical promoters[18] transform **D** into arenes and, therefore, **D** is not on the main path of the catalytic reaction to arenes.[18]

Synthesis of CpCo−Diborylcyclobutadiene Complexes 9, 10 and 11

In 1965, Pettit et al.[22] reported the first generation of the tricarbonyl(η^4-cyclobutadiene)iron complex. Among the various synthetic methods, the reactions of alkynes with transition metal carbonyl complexes in particular have been studied extensively during the last three decades.[23] In an analogous manner, compound **2** was treated with (η^5-cyclopentadienyl)bis(ethene)cobalt in hexane and compounds **6** and **7** with dicarbonyl(η^5-cyclopentadienyl)cobalt in refluxing toluene to give the corresponding (η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt complexes **9**, **10**, and **11** in good yields (Scheme 6). Purification of compounds **9a/9a′** by column chromatography on aluminum oxide led to decomposition. Because of a paramagnetic impurity in the crude product, compounds **9a/9a′** could not be characterized by NMR spectroscopy. EI-MS data confirm the identity of **9a/9a′** through the appearance of the molecular ion peaks with the expected isotopic patterns. Compounds **10** and **11** are partially soluble in toluene and chloroform; in methanol, a fast reaction, leading to the formation of $B(OMe)_3$, takes place.



Scheme 6

Purification of **10** and **11** can be accomplished by washing repeatedly with hexane. Complexes **10** and **11** were characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy, elemental analysis, and mass spectrometry. The ^{11}B NMR spectra show broad signals at $\delta = 58$ ppm for **10a/10d**, and $\delta = 57$ ppm for **10b/10c**. The ^1H NMR spectra of **10** exhibit multiplets in the region $\delta = 7.0-7.9$ ppm that are due to the aromatic protons, in addition to the Cp resonances ($\delta = 4.6-4.9$ ppm). Four quaternary carbon atoms of diboryl-substituted (η^4-cyclobutadiene)cobalt complexes **10** were detected in the ^{13}C NMR spectrum in the region $\delta = 79-89$ ppm. From the NMR spectra, it is not possible to make a distinction between the *trans* (**10a−d**) and *cis* isomers (**10a′−d′**) of the cyclobutadiene complexes. For steric reason, the *trans* isomers **10a−d** seem to be more favored, which is confirmed by the solid state structure of **10a**. However, several complexes are known that have *cis*-bis(trimethylsilyl)cyclobutadiene ligands.[1c,24] The problem was resolved unequivocally by analyzing the major peaks in terms of the degradation of the cyclobutadiene ring in the mass spectra. In general, three different acetylenes are released from the molecular ion of the *cis* isomer, but only a single acetylene is released from the *trans* isomer.[25] Here, in all cases, three kinds of acetylenes were released from the molecular ion. Therefore, mass spectra gave evidence for both the *cis* isomer and the *trans* isomers, but the *cis* isomer could not be identified by NMR spectroscopic measurements.

The structure of **10a** was characterized by performing a single-crystal X-ray diffraction analysis. Two independent molecules were found; the structure of one is shown in Figure 4. The solid state structure of **10a** reveals that both phenyl groups, as well as one of dithiacatecholboryl groups, do not lie in the plane of the cyclobutadiene ring. From the internal bond angles of the cyclobutadiene ring of **10a**, it is found that there is a little deviation from the exact square-planar shape because the internal bond angles for both the carbon atoms attached to the boron atom are smaller than those attached to the phenyl groups.

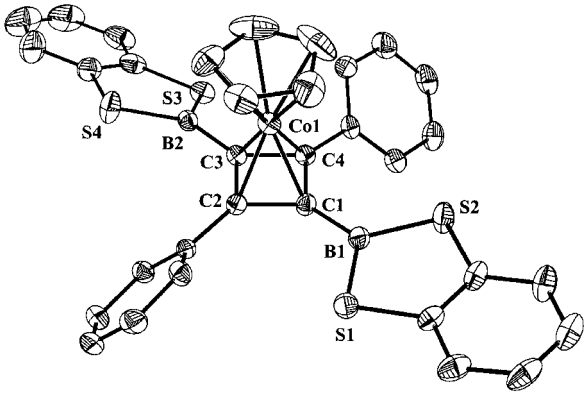


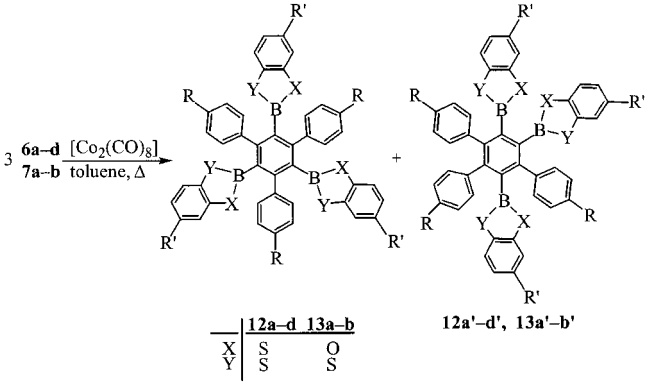
Figure 4. Molecular structure of **10a** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: C1−C2 1.460 (5), C2−C3 1.465(5), C3−C4 1.476(5), C4−C1 1.462(5), C1−B1 1.528(6), C3−B2 1.527(6), C2−C1−C4 89.2(3), C1−C2−C3 91.4(3), C2−C3−C4 88.5(3), C1−C4−C3 90.9(3)

Similarly, ^{11}B NMR spectra show broad signals at $\delta = 45$ ppm for **11a/11a′** and $\delta = 46$ ppm for **11b/11b′**. The ^1H NMR spectra exhibit multiplets in the region $\delta =$

7.1−7.9 ppm that are due to aromatic protons. In the ^{13}C NMR spectra of **11a/11a′** and **11b/11b′**, the signals in the region δ = 84−86 ppm are assigned to the *ipso*-carbon atoms of the central C_4 ring and to the signals of the Cp carbon atoms (δ = 83−87 ppm). The EI mass spectra of **11a**−**b** and **11a′**−**b′** show ion fragmentations similar to those mentioned above, with the expected isotopic patterns. It is important to mention that no benzene derivatives were observed in the reactions of $[CpCo(CO)_2]$ with the alkynes **6** and **7** (Scheme 6).

$[Co_2(CO)_8]$-Catalyzed Cyclotrimerization of 6 and 7 to Triborylbenzenes 12 and 13

Arnett et al.[26] prepared the sterically encumbered hexaisopropylbenzene by $[Co_2(CO)_8]$-catalyzed trimerization of bis(isopropyl)acetylene. Analogously, in refluxing toluene, the mono(boryl)acetylene derivatives **6** and **7** formed the triborylbenzene derivatives **12** and **13** in the presence of a catalytic amount of $[Co_2(CO)_8]$ (Scheme 7). The isomeric mixture (1,3,5- and 1,2,4-substituted) could not be separated. Purifications of **12** and **13** were achieved by washing repeatedly with hexane, toluene and CH_2Cl_2.



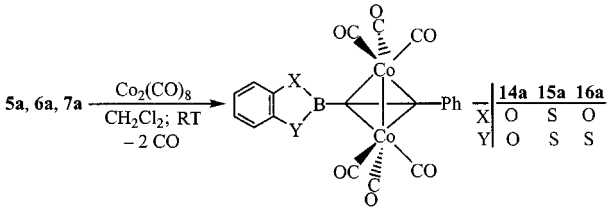
Scheme 7

The compounds **12** and **13** are air-stable solids and are not soluble in most common organic solvents; slight solubility in chloroform enables NMR spectra to be measured. All compounds were characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy, elemental analysis, and mass spectrometry. The ^{11}B NMR spectra show broad signals at δ = 62 ppm for **12a/12a′** and δ = 60 ppm for **12b/12b′**, **12c/12c′**, and **12d/12d′**. In the ^1H NMR spectra, multiplets (δ = 6.9−7.9 ppm) are observed for the aromatic protons of **12a**−**d** and **12a′**−**d′**. In the ^{13}C NMR spectra, the signals in the region δ = 126−128 ppm are assigned to the *ipso*-carbon atoms of the central ring of the isomers **12a**−**c** and those in the region δ = 128−141 ppm to the *ipso* carbon atoms of the isomers **12a′**−**c′**. The quaternary carbon atoms of **12d/12d′** were not observed.

The ^{11}B NMR spectra of **13a/13a′** exhibit broad signals at δ = 53 ppm and of **13b/13b′** at δ = 52 ppm. The ^1H NMR spectra show multiplets in the aromatic region for the aryl protons of **13a/b** and **13a′/b′**. The ^{13}C NMR spectra reveal the signals of the *ipso*-carbon atoms of the central ring of **13a** at δ = 132.8 ppm and at δ = 132.7 ppm for **13b**.

Synthesis and Properties of Dicobaltatetrahedranes 14a, 15a, and 16a

(Alkyne)hexacarbonyldicobalt complexes are obtained by treating alkynes with $Co_2(CO)_8$.[27] Analogously, the mono(boryl)acetylene derivatives **5a**, **6a**, and **7a** reacted with $Co_2(CO)_8$ in CH_2Cl_2; elimination of two CO units resulted in the corresponding complexes **14a**, **15a** and **16a** (Scheme 8). These compounds were isolated by column chromatography as brown-red oils,[28] which we characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopy, IR spectroscopy, and mass spectrometry.

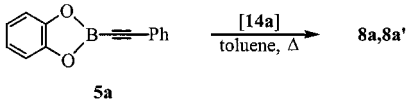


Scheme 8

The ^{11}B NMR spectrum of **14a** shows a broad signal at δ = 33 ppm. The ^1H NMR spectrum exhibits the signals of the aromatic protons in the region δ = 7.2−7.7 ppm. In the ^{13}C NMR spectrum, the arene carbon atoms give rise to signals at δ = 112.6, 123.2, and 147.8 ppm for the catechol unit and at δ = 121.2, 128.5, 130.0, and 130.2 ppm for the phenyl group. The signal of the carbon atom bound to the boron atom are not observed, while the carbon atom attached directly to the phenyl group appears at δ = 104.3 ppm. The carbonyl ligands exhibit a signal in the ^{13}C NMR spectrum at δ = 200.2 ppm.

Similarly, in their ^{11}B NMR spectra, the signals of the complexes **15a** and **16a** appear at δ = 59 and 47 ppm, respectively. The ^1H NMR spectra show multiplets in the regions δ = 7.1−7.8 ppm for **15a** and δ = 7.1−7.5 ppm for **16a**. The characteristic carbonyl ligands in the ^{13}C NMR spectra appear at δ = 199.5 ppm for **15a** and δ = 200.6 ppm for **16a**.

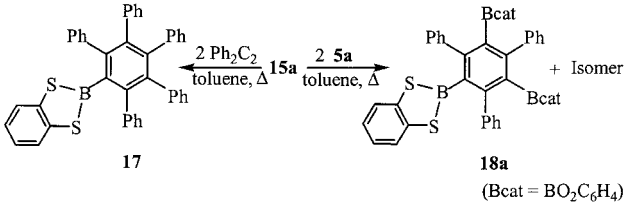
Complex **14a** can also act as a catalyst for the cyclotrimerization of **5a**. When a catalytic amount of **14a** and 1-(catecholboryl)-2-phenylacetylene (**5a**) were heated in toluene, the triborylbenzene derivatives **8a/8a′** were obtained in good yield (Scheme 9).



Scheme 9

(1,3,2-Benzodithiaborolyl)pentaphenylbenzene and Bis(1,3,2-benzodioxaborolyl)(1,3,2-benzodithiaborolyl)triphenylbenzene (17 and 18)

Recently, we have shown the use of C_2Co_2 clusters for the preparation of different substituted arenes.[8] Analogously, we have heated diphenylacetylene and a stoichiometric amount of **15a** in toluene, which resulted in the formation of (1,3,2-benzodithiaborolyl)pentaphenylbenzene (**17**) in good yield (Scheme 10). Compound **17** is not soluble in common organic solvents and, therefore, NMR spectroscopic measurements were not possible. Compound **17** was characterized by mass spectrometry, which confirms the identity of **17** through the appearance of the molecular ion peak at $m/z = 608$.



Scheme 10

Similarly, compound **15a** was treated with two equivalents of 1-(catecholboryl)-2-phenylacetylene (**5a**) in toluene under reflux, which led to the formation of an isomeric mixture **18** in moderate yield. Because of the complete insolubility of compound **18**, NMR spectroscopic measurements were not possible. Compound **18** was characterized by EI mass spectrometry, which indicated the molecular ion peak of **18** at $m/z = 692$.

Conclusions

We have studied the reactions of boryl-substituted acetylenes with catalytic and stoichiometric amounts of $[CpCo(C_2H_4)_2]$, $[CpCo(CO)_2]$, and $[Co_2(CO)_8]$. [2+2+2] Cyclotrimerization products **8** are obtained from the reactions of (catecholboryl)acetylenes **5** with a catalytic amount of $[CpCo(CO)_2]$ or $[Co_2(CO)_8]$. (η^4-Cyclobutadiene)cobalt complexes are not formed from (thermal and photochemical) reactions of **5** with stoichiometric amount of $[CpCo(CO)_2]$. Treatment of nitrogen- and sulfur-bound borylacetylenes **2**, **6**, and **7** with a stoichiometric amount of $[CpCo(C_2H_4)_2]$ or $[CpCo(CO)_2]$ opened a long-sought route to the new class of boryl-substituted (η^4-cyclobutadiene)cobalt complexes. Possibly because of steric reasons, the nitrogen-substituted borylacetylene **2** does not undergo catalytic cyclotrimerization with $[CpCo(C_2H_4)_2]$ or $[CpCo(CO)_2]$. On the other hand, triborylbenzene derivatives **12** and **13** are obtained from the reactions of **6** and **7**, respectively, with a catalytic amount of $[Co_2(CO)_8]$. Surprisingly, we found that changing the heteroatom(s) bound to the boron atom causes a remarkable difference in the reactivities of **6** and **7** when compared to that of **5**. Most likely, this behavior of **6** and **7** arises from interactions of the sulfur atom(s) with the cobalt center, which might prevent the formation of coordinatively unsaturated cobaltacyclopentadiene complexes (the postulated precursor en route to cyclotrimerization products). Instead of cyclotrimerization products, (η^4-cyclobutadiene)cobalt complexes **10** and **11** are obtained. Reactions of **5a**, **6a**, and **7a** with a stoichiometric amount of $[Co_2(CO)_8]$ lead to the Co_2C_2 clusters **14a**, **15a**, and **16a**, respectively.

Experimental Section

General: All reactions were performed under nitrogen using standard Schlenk techniques. Solvents were dried with the appropriate drying agents and distilled under nitrogen. Glassware was dried with a heat gun under high vacuum. ^1H, ^{13}C, and ^{11}B NMR spectroscopy: Bruker AC 200 spectrometer; ^1H and ^{13}C spectra were referenced to $(CH_3)_4Si$ and ^{11}B spectra to $F_3B{\cdot}OEt_2$. IR spectra were recorded on a Bruker IFS 28 FT spectrometer. Mass spectra were obtained on Finnigan MAT 8230 plus spectrometers using the EI technique. Elemental analyses were carried out at the Microanalytical Laboratory, University of Heidelberg. Melting points (uncorrected) were obtained on a Büchi apparatus, using capillaries that were filled under nitrogen and sealed. Bis(diethylamino)acetylene[10] (**1**), $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{BCl}$,[29] 1-aryl-2-(trimethylstannyl)acetylenes[30] **3**, and chlorocatecholborane[31] were prepared according to literature procedures. Bromo(dithiocatechol)borane and bromo(1,3,2-benzothiaoxaborol), which have not been reported previously in the literature, were prepared by the reactions of dithiocatechol and 2-hydroxythiophenol with excess BBr_3. Catechol, 4-methylcatechol, dithiocatechol, 4-methyldithiocatechol, and 2-hydroxymercaptanol were purchased from Aldrich.

1-[Bis(dimethylamino)boryl]-2-(diethylamino)acetylene (2): Bis(diethylamino)acetylene (**1**, 1.18 g, 7.0 mmol) was added slowly at room temperature to a stirred suspension of lithium powder (0.34 g, 49.7 mmol) in diethyl ether (20 mL). The reaction mixture was heated under reflux for 3 h. After cooling, the mixture was stirred at ambient temperature for 40 h. The ether was evaporated by vacuum, THF (20 mL) was added, and the THF solution was heated for 1 h. The solid that formed was separated by filtration and washed with a small amount of THF. After drying under high vacuum, a green solid (a mixture of Et_2NC_2Li and $LiNEt_2$) was obtained. Chlorobis(dimethylamino)borane (1.26 g, 9.4 mmol) was added within 10 min at −60 °C to a solution of lithium compounds (0.85 g, 4.7 mmol) in THF (10 mL). The reaction mixture was stirred for 16 h. After filtration, the solvent was evaporated under high vacuum. Compound **2** and $Et_2B(NMe)_2$ were obtained by fractional distillation. Yield 0.39 g (43%), colorless liquid, b.p. 50 °C/0.2 Torr. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{H,H}$ = 7.2 Hz, 6 H, CH_2CH_3), 2.68 (s, 12H, NCH_3), 2.90 (q, $^3J_{H,H}$ = 7.2 Hz, 4 H, CH_2CH_3) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 12.90 (CH_2CH_3), 40.60 (NCH_3), 48.20 (CH_2CH_3) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 26 ppm. MS (70 eV, EI): m/z (%) = 195 (100) [M^+], 180 (31) [$M^+ - CH_3$], 123 (93) [$M^+ - NEt_2$].

1-[Bis(diisopropylamino)boryl]-2-phenylacetylene (4a) and 1-[Bis(diisopropylamino)boryl]-2-tolylacetylene (4b): Chlorobis(diisopropylamino)borane (2.59 g, 10.5 mmol) in toluene (10 mL) was added slowly at −78 °C to a stirred solution of 1-trimethylstannyl-2-arylacetylene (**3a**: 2.80 g; **3b**: 2.94 g; 10.5 mmol) in toluene (40 mL). The reaction mixture was stirred overnight to reach room temperature, the solvent was evaporated under high vacuum, and the residue was distilled.

4a: Yield 3.1 g (94%), pale-yellow liquid, b.p. 102 °C/0.01 Torr. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.38 [d, $^3J_{H,H}$ = 6.9 Hz, 24 H, $CH(CH_3)_2$], 3.55 [sept., $^3J_{H,H}$ = 6.9 Hz, 4 H, $CH(CH_3)_2$], 7.4−7.5 (m, C_6H_5, 5H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 24.23 [$CH(CH_3)_2$], 46.71 [$CH(CH_3)_2$], 104.6 (C_{sp}−C_i), 125.1, 127.8, 128.3, 130.9 (C_6H_5) ppm; C_{sp}−B not found. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 26 ppm. MS (70 eV, EI): *m*/*z* (%) = 312 (13) [M^+], 297 (100) [$M^+ - CH_3$], 269 (87) [$M^+ - i$Pr], 212 (31) [$M^+ - N(i\text{Pr})_2$]. MS (70 eV, HR-EI): *m*/*z* (%) = 312.2759 (8) [M^+; $^{12}C_{20}{}^1H_{33}{}^{11}B^{14}N_2$: 312.2736]; Δmmu = 2.3.

4b: Yield: 3.0 g (87%), yellow liquid, b.p. 112 °C/0.02 Torr. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.35 [d, $^3J_{H,H}$ = 7.0 Hz, 24H, $CH(CH_3)_2$], 2.32 (s, CH_3, 3 H), 3.53 [sept., $^3J_{H,H}$ = 6.9 Hz, 4H, $CH(CH_3)_2$], 7.3−7.6 (m, 4H, C_6H_5) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.32 (CH_3), 24.25 [$CH(CH_3)_2$], 46.81 [$CH(CH_3)_2$], 104.5 (C_{sp}−C_i), 125.3, 127.5, 128.7, 131.2 (C_6H_4) ppm; C_{sp}−B not found. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 26 ppm. MS (70 eV, EI): *m*/*z* (%) = 326 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 326.2899 (100) [M^+; $^{12}C_{21}{}^1H_{35}{}^{11}B^{14}N_2$: 326.2893]; Δmmu = 0.6.

Two General Procedures for 1-Aryl-2-borylacetylenes 5, 6, and 7. Procedure A: The appropriate 1-aryl-2-(trimethylstannyl)acetylene **3** was dissolved in toluene (50 mL) and then the corresponding haloborane in toluene (10 mL) was added slowly at −20 °C. The reaction mixture was stirred overnight at ambient temperature. After evaporation of the solvent under high vacuum, a crystalline solid was obtained.

Procedure B: The appropriate 1-aryl-2-[bis(diisopropylamino)-boryl]acetylene **4** was dissolved in THF (50 mL) and then 2 equiv. of HCl·Et_2O (2 M) was added slowly at −78 °C. Stirring was continued for 45 min and NH_2iPr_2Cl formed as a white solid. The corresponding aromatic diol in THF (15 mL) was then added dropwise and the reaction mixture was stirred overnight at room temperature. After filtration of the solid, the solution was reduced to near dryness, and a crystalline product was obtained.

1-(Catecholboryl)-2-phenylacetylene (5a): Starting materials: **3a** (4.8 g, 18 mmol), $H_4C_6O_2BCl$ (2.78 g, 18 mmol). Yield 2.8 g (71%), orange-red solid, m.p. 76 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.2−7.7 (m, 9 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 105.1 (C_{sp}−C_i), 112.7, 123.3, 147.9 (catechol), 121.2, 128.6, 130.1, 132.8 (C_6H_5) ppm; C_{sp}−B not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 25 ppm. MS (70 eV, EI): *m*/*z* (%) = 220 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 220.0715 (100) [M^+; $^{12}C_{14}{}^1H_9{}^{11}B^{16}O_2$: 220.0695]; Δmmu = 2.0.

1-(Catecholboryl)-2-tolylacetylene (5b): Starting materials: **3b** (2.4 g, 8.6 mmol), $H_4C_6O_2BCl$ (1.32 g, 8.6 mmol). Yield 1.4 g (69%), yellow solid, m.p. 72 °C (dec.). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 7.0−7.5 (m, 8 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.67 (CH_3), 103.4 (C_{sp}−C_i), 112.6, 123.1, and 147.8 (catechol), 115.5, 121.3, 129.2, 132.7 (tolyl) ppm; C_{sp}−B not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 25 ppm. MS (70 eV, EI): *m*/*z* (%) = 234 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 234.0833 (100) [M^+; $^{12}C_{15}{}^1H_{11}{}^{11}B^{16}O_2$: 234.0852]; Δmmu = 1.9.

1-(4-Methylcatecholboryl)-2-phenylacetylene (5c): Starting materials: **3a** (4.1 g, 15.4 mmol), $CH_3C_6H_3O_2BCl$ (2.59 g, 15.4 mmol). Yield 2.4 g (66%), yellow solid, m.p. 75 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.39 (s, CH_3, 3 H), 6.9−7.6 (m, 8 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.38 (CH_3), 93.37 (C_{sp}−C_i), 111.9, 113.2, 123.6, 130.0, 145.7, 147.8 (catechol), 121.2, 128.8, 132.7, 133.2 (C_6H_5) ppm; C_{sp}−B not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 24 ppm. MS (70 eV, EI): *m*/*z* (%) = 234 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 234.0834 (100) [M^+; $^{12}C_{15}{}^1H_{11}{}^{11}B^{16}O_2$: 234.0852]; Δmmu = 1.8.

1-(4-Methylcatecholboryl)-2-tolylacetylene (5d): Starting materials: **4b** (4.44 g, 13.6 mmol), HCl·OEt_2 (13.6 mL, 27.2 mmol), 4-methylcatechol (1.68 g, 13.6 mmol). Yield 2.1 g (62%), brown solid, m.p. 73 °C (dec.). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 6.9−7.5 (m, 7 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.40 and 21.65 (CH_3), 83.81 (C_{sp}−C_i), 111.9, 113.1, 123.1, 138.9, 145.4, 147.5 (catechol), 119.0, 129.2, 132.0, 132.8 (tolyl) ppm; C_{sp}−B not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 23 ppm. MS (70 eV, EI): *m*/*z* (%) = 248 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 248.1008 (100) [M^+; $^{12}C_{16}{}^1H_{13}{}^{11}B^{16}O_2$: 248.1015]; Δmmu = 0.7.

1-(Dithiocatecholboryl)-2-phenylacetylene (6a): Starting materials: **3a** (4.1 g, 15.4 mmol), $H_4C_6S_2BBr$ (3.55 g, 15.4 mmol). Yield 2.8 g (72%), brown-red solid, m.p. 82 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.4−7.8 (m, 9 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 84.01 (C_{sp}−C_i), 125.7, 126.5, 140.9 (dithiocatechol), 128.4, 129.7, 131.1, 132.2 (C_6H_5) ppm; C_{sp}−B not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 47 ppm. CI-MS: *m*/*z* (%) = 252.1 [M^+] (70)

1-(Dithiocatecholboryl)-2-tolylacetylene (6b): Starting materials: **3b** (1.7 g, 6.09 mmol), $H_4C_6S_2BBr$ (1.4 g, 6.09 mmol). Yield 1.2 g (74%), light-yellow solid, m.p. 86 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 7.15−7.50 (m, 8 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.07 (CH_3), 92.43 (C_{sp}−C_i), 122.2, 126.0, 140.9 (dithiocatechol), 126.8, 127.1, 128.4, 132.2 (tolyl) ppm; C_{sp}−B not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 48 ppm. MS (70 eV, EI): *m*/*z* (%) = 266 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 266.0401 (100) [M^+; $^{12}C_{15}{}^1H_{11}{}^{11}B^{32}S_2$: 266.0395]; Δmmu = 0.6.

1-(4-Methyldithiocatecholboryl)-2-phenylacetylene (6c): Starting materials: **4a** (3.5 g, 11.2 mmol), HCl·OEt_2 (11.2 mL, 22.4 mmol), 4-methyldithiocatechol (1.75 g, 11.2 mmol). Yield 2.3 g (77%), yellow solid, m.p. 88 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 7.13, 7.41, 7.64 (m, 8 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.07 (CH_3), 93.37 (C_{sp}−C_i), 126.1, 126.8, 127.1, 135.9, 137.6, 140.9 (dithiocatechol), 122.2, 128.4, 129.7, 132.2 (C_6H_5) ppm; C_{sp}−B not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 47 ppm. MS (70 eV, EI): *m*/*z* (%) = 266 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 266.0399 (100) [M^+; $^{12}C_{15}{}^1H_{11}{}^{11}B^{32}S_2$: 266.0395]; Δmmu = 0.4.

1-(4-Methyldithiocatecholboryl)-2-tolylacetylene (6d): Starting materials: **3b** (3.05 g, 10.9 mmol), $CH_3C_6H_3S_2BBr$ (2.66 g, 10.9 mmol). Yield 2.2 g (72%), brown solid, m.p. 93 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, CH_3), 2.38 (s, 3 H, CH_3), 7.1−7.6 (m, 7 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.07, 21.67 (CH_3), 83.81 (C_{sp}−C_i), 126.0, 126.8, 127.0, 135.8, 137.6, 140.9 (thiocatechol), 119.1, 129.2, 132.1, 140.2 (tolyl) ppm; C_{sp}−B not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 48 ppm. MS (70 eV, EI): *m*/*z* (%) = 280 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 280.0562 (100) [M^+; $^{12}C_{16}{}^1H_{13}{}^{11}B^{16}S_2$: 280.0551]; Δmmu = 1.1.

1-(1,3,2-Benzothiaoxaborolyl)-2-phenylacetylene (7a): Starting materials: **4a** (3.1 g, 9.93 mmol), HCl·OEt_2 (9.93 mL, 19.86 mmol), 2-hydroxyphenol (1.25 g, 9.93 mmol). Yield 1.8 g (76%), brown-red solid, m.p. 66 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.2−7.6 (m, 9 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 108.9 (C_{sp}−C_i), 114.2, 123.5, 125.4, 126.3, 126.9, 156.7 (2-hydroxythio-

phenol), 119.7, 128.5, 129.9, 132.6 (C_6H_5) ppm; C_{sp}−B not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 38 ppm. MS (70 eV, EI): *m/z* (%) = 236 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 236.0462 (100) [M^+; $^{12}C_{14}{}^1H_9{}^{11}B^{16}O_1{}^{32}S_1$: 236.0467]; Δmmu = 0.5.

1-(1,3,2-Benzothiaoxaborolyl)-2-tolylacetylene (7b): Starting materials: **3b** (2.75 g, 9.85 mmol), H_4C_6OSBr (2.0 g, 9.85 mmol). Yield: 2.1 g (86%), yellow solid, m.p. 71 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 7.2−7.6 (m, 8 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.66 (CH_3), 109.3 ($C_{sp}-C_i$), 114.8, 123.8, 125.4, 126.2, 126.9, 156.6 (2-hydroxythiophenol), 118.4, 129.3, 132.5, 140.4 (tolyl) ppm; C_{sp}−B not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 38 ppm. MS (70 eV, EI): *m/z* (%) = 250 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 250.0622 (100) [M^+; $^{12}C_{15}{}^1H_{11}{}^{11}B^{16}O_1{}^{32}S_1$: 250.0627]; Δmmu = 0.5.

Isomers of Tris(catecholboryl)triphenylbenzene (8a/8a′), Tris(catecholboryl)tritolylbenzene (8b/8b′), Tris(4-methylcatecholboryl)triphenylbenzene (8c/8c′), and Tris(4-methylcatecholboryl)tritolylbenzene (8d/8d′). Catalyst = [CpCo(CO)$_2$]: Borylacetylene (**5a:** 1.32 g; **5b**: 1.42 g; **5c**: 1.42 g; **5d**: 1.50 g; 6 mmol) and dicarbonylcobalt(η^5-cyclopentadienyl) (0.055 g, 0.3 mmol, 5 mol%) were heated at 90 °C in toluene (20 mL) for 3 days. The solid that formed was separated and washed several times with small amount of solvents (**8a/8a′**: toluene and CH_2Cl_2; **8b/8b′**: hexane and toluene; **8c/8c′** and **8d/8d′**: hexane) and dried in vacuo.

8a/8a′: Yield 1.02 g (77%), yellow solid, m.p. 230 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.2−7.6 (m, 27 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 112.7, 123.2, 147.8 (catechol), 121.2, 128.5, 130.0, 132.8 (C_6H_5), 139.9 (central benzene, symm.), 134.6, 137.3, 142.5 (central benzene, unsymm.) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 24 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 660 (100) [M^+], 542 (42) [M^+ − catB + 1], 424 (15) [M^+ − 2catB + 1]. MS (70 eV, HR-EI): *m/z* (%) = 660.2087 (100) [M^+; $^{12}C_{42}{}^1H_{27}{}^{11}B_3{}^{16}O_6$: 660.2086]; Δmmu = 0.1. $C_{42}H_{27}B_3O_6$ (660.1): calcd. C 76.42, H 4.12; found C 76.15, H 4.75.

8b/8b′: Yield 1.10 g (78%), yellow solid, m.p. 241 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.35 (s, 9 H, CH_3), 7.0−7.4 (m, 24 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.67 (CH_3), 112.6, 123.1, 147.8 (catechol), 118.1, 129.2, 132.0, 132.7 (tolyl), 140.6 (central benzene, symm.), 135.9, 139.2, 147.5 (central benzene, unsymm.) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 22 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 702 (8) [M^+], 584 (65) [M^+ − catB + 1], 466 (100) [M^+ − 2catB + 1]. MS (70 eV, HR-EI): *m/z* (%) = 702.2551 (5) [M^+; $^{12}C_{45}{}^1H_{33}{}^{11}B_3{}^{16}O_6$: 702.2556]; Δmmu = 0.5. $C_{45}H_{33}B_3O_6$ (702.2): calcd. C 76.97, H 4.74; found C 77.95, H 4.98.

8c/8c′: Yield 0.95 g (67%), yellow solid, m.p. 245 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.42 (s, 9 H, CH_3), 7.1−7.6 (m, 24 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.60 (CH_3), 112.0, 113.3, 123.3, 129.4, 145.6, 147.7 (catechol), 123.7, 129.2, 132.2, 132.9 (C_6H_5), 140.7 (central benzene, symm.), 139.1, 146.0, 148.0 (central benzene, unsymm.) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 23 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 702 (100) [M^+], 570 (95) [M^+ − $H_3CC_6H_3O_2B$ + 1]. MS (70 eV, HR-EI): *m/z* (%) = 702.2596 (100) [M^+; $^{12}C_{45}{}^1H_{33}{}^{11}B_3{}^{16}O_6$: 702.2556]; Δmmu = 4.0. $C_{45}H_{33}B_3O_6$ (702.2): calcd. C 76.97, H 4.74; found C 76.45, H 5.08.

8d/8d′: Yield 1.12 g (75%), pale yellow solid, m.p. 261 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.35 (s, 9 H, CH_3), 2.39 (s, 9 H, CH_3), 6.9−7.5 (m, 21 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.37 and 21.48 (CH_3), 111.9, 113.2, 123.1, 133.1, 145.7, 147.8 (catechol), 118.1, 129.0, 132.0, 132.7 (tolyl), 140.5 (central benzene, symm.), 138.9, 145.3, 147.5 (central benzene, unsymm.) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 22 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 744 (100) [M^+], 612 (49) [M^+ − $H_3CC_6H_3O_2B$ + 1]. MS (70 eV, HR-EI): *m/z* (%) = 744.3028 (100) [M^+; $^{12}C_{48}{}^1H_{39}{}^{11}B_3{}^{16}O_6$: 744.3025]; Δmmu = 0.3. $C_{48}H_{39}B_3O_6$ (744.2): calcd. C 77.46, H 5.28; found C 77.05, H 5.59.

Catalyst = [Co$_2$(CO)$_8$]: Mono(boryl)acetylene (**5a:** 1.76 g; **5b:** 1.87 g; **5c:** 1.87 g; **5d:** 1.98 g; 8 mmol) and octacarbonyldicobalt (0.136 g, 0.4 mmol, 5 mol%) were heated at 90 °C in toluene (20 mL) for 2 days. Workup was carried out as above.

Yields: 1.25 g (71%) of **8a/8a′**; 1.45 g (77%) of **8b/8b′**; 1.32 g (70%) of **8c/8c′**; 1.49 g (75%) of **8d/8d′**.

[η^4-Bis(diethylamino)bis(dimethylaminoboryl)cyclobutadiene](η^5-cyclopentadienyl)cobalt(I) (9): A solution of **2** (0.39 g, 2 mmol) in hexane (5 mL) was added within 15 min at room temparature to a solution of $CpCo(C_2H_4)_2$ (0.36 g, 2 mmol) in hexane (20 mL). The reaction mixture was stirred for 3 h. After filtration, the solvent was evaporated under high vacuum and a brown-green cobalt complex **9** was obtained. MS (70 eV, EI): *m/z* (%) = 515 (5) [M^+ + 1], 341 (4) [$C_{15}H_{24}B_2CoN_4{}^+$], 205 (7) [$C_9H_{19}B_2N_4{}^+$], 58 (37) [$C_3H_8N^+$], 28 (100) [$C_2H_4{}^+$].

[η^4-Bis(dithiocatecholboryl)diphenylcyclobutadiene](η^5-cyclopentadienyl)cobalt(1) (10a/10a′), [η^4-Bis(dithiocatecholboryl)ditolylcyclobutadiene](η^5-cyclopentadienyl)cobalt(1) (10b/10b′), [η^4-Bis(4-methyldithiocatecholboryl)diphenylcyclobutadiene](η^5-cyclopentadienyl)cobalt(1) (10c/10c′), [η^4-Bis(4-methyldithiocatecholboryl)ditolylcyclobutadiene](η^5-cyclopentadienyl)cobalt(1) (10d/10d′), [η^4-bis(1,3,2-benzo-thiaoxaborolyl)diphenylcyclobutadiene](η^5-cyclopentadienyl)cobalt(1) (11a/11a′), and [η^4-Bis(1,3,2-benzothiaoxaborolyl)ditolylcyclobutadiene](η^5-cyclopentadienyl)cobalt(1) (11b/11b′): Borylalkyne (**6a:** 2.01 g; **6b:** 2.12 g; **6c:** 2.12 g; **6d:** 2.24 g; **7a:** 1.88 g; **7b:** 2.00 g; 8 mmol) was added at room temperature to a solution of dicarbonylcobalt(η^5-cyclopentadienyl) (0.72 g, 4 mmol) in toluene (30 mL). The reaction mixture was heated under reflux for 3 d. After cooling, the precipitate was collected by filtration, washed several times with hexane, and dried in vacuo.

10a/10a′: Yield 1.42 g (56%), orange solid, m.p. 241 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 4.72 (s, 5 H, Cp−H), 7.4−7.9 (m, 18 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 81.05, 82.10 (C_{4ring}), 86.25 (Cp−C), 125.7, 126.5, 140.9 (dithiocatechol), 128.4, 129.7, 131.1, 132.2 (C_6H_5) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 58 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 628 (100) [M^+], 478 (50) [M^+ − $BS_2C_6H_4$ + 1], 450 (2) [M^+ − PhC≡CPh], 376 (70) [M^+ − $C_6H_4S_2BC{\equiv}CPh$], 302 (4) [M^+ − $C_6H_4S_2BC{\equiv}CBS_2C_6H_4$]. MS (70 eV, HR-EI): *m/z* (%) = 628.0222 (100) [M^+; $^{12}C_{33}{}^1H_{23}{}^{11}B_2{}^{59}Co^{32}S_4$: 628.0200]; Δmmu = 2.2. $C_{33}H_{23}B_2CoS_4$ (628.0): calcd. C 63.06, H 3.39; found C 62.21, H 3.58.

10b/10b′: Yield 1.53 g (58%), orange-red solid, m.p. 245 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.35 (s, 6 H, CH_3), 4.82 (s, 5 H, Cp−H), 6.9−7.3 (m, 16 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.69 (CH_3), 84.86 (Cp−C), 82.84, 83.41 (CBD), 124.8, 125.6, 139.9 (dithiocatechol), 127.5, 128.8, 130.2, 131.2 (tolyl) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 57 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 656 (100) [M^+], 506 (30) [M^+ − $BS_2C_6H_4$ + 1], 450 (3) [M^+ − $H_3CC_6H_4C{\equiv}CC_6H_4CH_3$], 390 (70) [$M^+$ − $C_6H_4S_2BC{\equiv}CC_6H_4CH_3$], 330 (5) [$M^+$ − $C_6H_4S_2BC{\equiv}CBS_2C_6H_4$]. MS (70 eV, HR-EI): *m/z* (%) = 656.0519 (100) [M^+; $^{12}C_{35}{}^1H_{27}{}^{11}B_2{}^{59}Co^{32}S_4$: 656.0513]; Δmmu = 0.6. $C_{35}H_{27}B_2CoS_4$ (656.0): calcd. C 64.02, H 4.15; found C 64.34, H 4.59.

10c/10c′: Yield 1.45 g (55%), yellow solid, m.p. 247 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 2.36 (s, 6 H, CH_3), 4.86 (s, 5 H, Cp−H),

7.1−7.9 (m, 16 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 20.96 (CH_3), 79.72 (Cp−C), 82.45, 83.23 (C_{4ring}), 124.5, 126.8, 127.0, 135.9, 137.7 (dithiocatechol), 122.2, 128.8, 129.3, 132.8 (C_6H_5) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 57 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 656 (100) [M^+], 492 (50) [M^+ − $BS_2C_6H_3CH_3$ + 1], 478 (5) [M^+ − PhC≡CPh], 390 (70) [M^+ − $H_3CC_6H_3S_2BC$≡CPh], 302 (10) [M^+ − $H_3CC_6H_3S_2BC$≡$CBS_2C_6H_3CH_3$]. MS (70 eV, HR-EI): *m/z* (%) = 656.0533 (100) [M^+; $^{12}C_{35}{}^1H_{27}{}^{11}B_2{}^{59}Co^{32}S_4$: 656.0513]; Δmmu = 2.0. $C_{35}H_{27}B_2CoS_4$ (656.0): calcd. C 64.02, H 4.15; found C 64.49, H 4.77.

10d/10d′: Yield 1.56 g (57%), orange solid, m.p. > 300 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 2.38 (s, 6 H, CH_3), 2.42 (s, 6 H, CH_3), 4.68 (s, 5 H, Cp−H), 7.0−7.8 (m, 14 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.07 and 21.56 (CH_3), 83.90 (Cp−C), 79.72, 89.76 (C_{4ring}), 125.7, 126.4, 126.5, 135.2, 137.2, 140.8 (dithiocatechol), 128.2, 129.0, 130.0, 132.7 (tolyl) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 58 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 684 (15) [M^+], 520 (18) [M^+ − $BS_2C_6H_3CH_3$ + 1], 478 (10) [M^+ − $H_3CC_6H_4C$≡$CC_6H_4CH_3$], 404 (100) [M^+ − $H_3CC_6H_3S_2$-BC≡$CC_6H_4CH_3$], 330 (22) [M^+ − $H_3CC_6H_3S_2BC$≡$CBS_2C_6H_3CH_3$]. MS (70 eV, HR-EI): *m/z* (%) = 684.0851 (100) [M^+; $^{12}C_{37}{}^1H_{31}{}^{11}B_2{}^{59}Co^{16}S_4$: 684.0826]; Δmmu = 2.5. $C_{37}H_{31}B_2CoS_4$ (684.4): calcd. C 64.90, H 4.57; found C 64.38, H 5.07.

11a/11a′: 1.64 g (68%), red-brown solid, m.p. 210 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 5.35 (s, 5 H, Cp−H), 7.4−7.9 (m, 18 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 83.98, 85.26 (C_{4ring}), 87.26 (Cp−C), 113.8, 122.8, 125.3, 125.9, 127.4, 155.6 (2-hydroxythiophenol), 120.5, 124.4, 128.9, 131.5 (C_6H_5) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 45 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 596 (50) [M^+], 462 (50) [M^+ − $BSOC_6H_4$ + 1], 418 (3) [M^+ − PhC≡CPh], 360 (65) [M^+ − C_6H_4SOBC≡CPh], 302 (4) [M^+ − C_6H_4SOBC≡$CBOSC_6H_4$]. MS (70 eV, HR-EI): *m/z* (%) = 596.0665 (82) [M^+; $^{12}C_{33}{}^1H_{23}{}^{11}B_2{}^{59}Co^{16}O_2{}^{32}S_2$: 596.0657]; Δmmu = 0.8. $C_{33}H_{23}B_2CoO_2S_2$ (596.2): calcd. C 66.44, H 3.89; found C 65.89, H 4.56.

11b/11b′: 1.56 g (62%), red solid, m.p. 221 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 2.32 (s, 6 H, CH_3), 5.37 (s, 5 H, Cp−H), 7.1−7.5 (m, 16 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.39 (CH_3), 83.86 (Cp−C), 84.49, 86.23 (C_{4ring}), 114.5, 123.5, 125.1, 125.9, 126.7, 156.3 (2-hydroxythiophenol), 118.1, 128.9, 132.2, 140.1 (tolyl) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 46 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 624 (80) [M^+], 490 (50) [M^+ − $BSOC_6H_4$ + 1], 418 (2) [M^+ − $H_3CC_6H_4C$≡$CC_6H_4CH_3$], 374 (45) [M^+ − C_6H_4SOBC≡$CC_6H_4CH_3$], 330 (9) [M^+ − C_6H_4SOBC≡$CBOSC_6H_4$]. MS (70 eV, HR-EI): *m/z* (%) = 624.0985 (100) [M^+; $^{12}C_{35}{}^1H_{27}{}^{32}S_2{}^{16}O_2{}^{11}B_2{}^{59}Co$: 624.0970]; Δmmu = 1.5. $C_{35}H_{27}B_2CoO_2S_2$ (624.2): calcd. C 67.30, H 4.36; found C 66.95, H 4.72.

Isomers of Tris(dithiocatecholboryl)triphenylbenzene (12a/12a′), Tris(dithiocatecholboryl)tritolylbenzene (12b/12b′), Tris(4-methyldithiocatecholboryl)triphenylbenzene (12c/12c′), Tris(4-methyldithiocatecholboryl)tritolylbenzene (12d,12d′), Tris(1,3,2-benzothiaoxaborolyl)triphenylbenzene (13a/13a′), and Tris(1,3,2-benzothiaoxaborolyl)tritolylbenzene (13b/13b′). Catalyst = [$Co_2(CO)_8$]: Borylalkyne (**6a:** 2.26 g; **6b:** 2.39 g; **6c:** 2.39 g; **6d:** 2.52 g; **7a:** 2.12 g; **7b:** 2.25 g; 9 mmol) and octacarbonyldicobalt (0.155 g, 0.45 mmol, 5 mole-%) were heated under reflux in toluene (20 mL) for 48 h. The solid was separated and washed several times with small amounts of solvents (**12a/12a′**: toluene and CH_2Cl_2; **12b/12b′**: hexane and toluene; **12c/12c′** and **12d/12d′**: hexane; **13a/13a′**: toluene and CH_2Cl_2; **13b/13b′**: hexane and toluene) and dried in vacuo.

12a/12a′: 1.74 g (77%), black solid, m.p. > 300 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 7.4−7.9 (m, 36 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 125.8, 126.6, 141.0 (dithiocatechol), 126.9 (central benzene, symm.), 128.4, 128.9, 138.0 (central benzene, unsymm.), 128.6, 129.9, 131.2, 132.3 (C_6H_5) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 62 (v. br.) ppm. MS (70 eV, EI): *m/z* (%) = 756 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 756.0742 (100) [M^+; $^{12}C_{42}{}^1H_{27}{}^{11}B_3{}^{32}S_6$: 756.0716]; Δmmu = 2.6. $C_{42}H_{27}B_3S_6$ (756.4): calcd. C 66.66, H 3.60; found C 65.21, H 3.84.

12b/12b′: 1.83 g (76%), black solid, m.p. 295 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 2.39 (s, 9 H, CH_3), 7.2−7.5 (m, 24 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.27 (CH_3), 122.4, 127.3, 141.2 (dithiocatechol), 126.3 (central benzene, symm.), 136.0, 137.8, 140.6 (central benzene, unsymm.), 127.0, 128.6, 129.9, 132.4 (tolyl) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 60 (v. br.) ppm. MS (70 eV, EI): *m/z* (%) = 798 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 798.1197 (100) [M^+; $^{12}C_{45}{}^1H_{33}{}^{11}B_3{}^{32}S_6$: 798.1185]; Δmmu = 1.2. $C_{45}H_{33}B_3S_6$ (798.5): calcd. C 67.66, H 4.17; found C 67.74, H 4.59.

12c/12c′: 1.90 g (79%), black solid, m.p. 297 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 2.33 (s, 9 H, CH_3), 6.9−7.6 (m, 24 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.77 (CH_3), 122.9, 126.8, 127.8, 136.6, 138.3, 141.7 (dithiocatechol), 128.5 (central benzene, symm.), 136.2, 138.0, 141.1 (central benzene, unsymm.), 127.5, 129.1, 130.4, 132.9 (C_6H_5) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 60 (v. br.) ppm. MS (70 eV, EI): *m/z* (%) = 798 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 798.1185 (100) [M^+; $^{12}C_{45}{}^1H_{33}{}^{11}B_3{}^{32}S_6$: 798.1185]; Δmmu = 0.0. $C_{45}H_{33}B_3S_6$ (798.5): calcd. C 67.66, H 4.17; found C 67.89, H 4.75.

12d/12d′: 2.05 g (81%), black solid, m.p. > 310 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 2.38 (s, 9 H, CH_3), 2.41 (s, 9 H, CH_3), 7.2−7.7 (m, 21 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.17 and 21.78 (CH_3), 126.2, 126.9, 127.1, 135.9, 137.7, 141.0 (dithiocatechol), 119.2, 129.3, 132.2, 140.3 (tolyl) ppm; because of the low solubility, the *ipso*-carbon atoms were not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 60 (v. br.) ppm. MS (70 eV, EI): *m/z* (%) = 840 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 840.1680 (100) [M^+; $^{12}C_{48}{}^1H_{39}{}^{11}B_3{}^{16}S_6$: 840.1655]; Δmmu = 2.5. $C_{48}H_{39}B_3S_6$ (840.6): calcd. C 68.56, H 4.68; found C 67.38, H 5.15.

13a/13a′: 1.50 g (70%), red solid, m.p. 282 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 7.2−7.6 (m, 27 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 113.8, 122.8, 124.4, 125.3, 125.9, 155.6 (2-hydroxythiophenol), 132.8 (central benzene, symm.), 135.2, 138.4, 141.2 (central benzene, unsymm.), 120.5, 128.0, 128.9, 131.5 (C_6H_5) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 53 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 708 (100) [M^+], 574 (10) [M^+ − $OSBC_6H_4$ + 1]. MS (70 eV, HR-EI): *m/z* (%) = 708.1415 (100) [M^+; $^{12}C_{42}{}^1H_{27}{}^{11}B_3{}^{16}O_3{}^{32}S_3$: 708.1401]; Δmmu = 1.4. $C_{42}H_{27}B_3O_3S_3$ (708.2): calcd. C 71.17, H 3.84; found C 71.07, H 4.26.

13b/13b′: Yield: 1.85 g (82%), red solid, m.p. 293 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 2.38 (s, 9 H, CH_3), 7.2−7.6 (m, 24 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.39 (CH_3), 114.5, 123.5, 125.1, 125.9, 131.7, 156.3 (2-hydroxythiophenol), 132.7 (central benzene, symm.), 118.1, 126.7, 128.9, 132.2 (tolyl) ppm; *ipso* carbon atoms of unsymm. ring were not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 52 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 750 (70) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 750.1872 (100) [M^+; $^{12}C_{45}{}^1H_{33}{}^{11}B_3{}^{16}O_3{}^{32}S_3$: 750.1871]; Δmmu = 0.1. $C_{45}H_{33}B_3O_3S_3$ (750.3): calcd. C 71.98, H 4.43; found C 71.09, H 4.93.

3-(1,3,2-Benzodioxaborolyl)-4-phenyl-1,2-bis(tricarbonylcobalta)-tetrahedrane (14a), 3-(1,3,2-Benzodithiaborolyl)-4-phenyl-1,2-bis-

(tricarbonylcobalta)tetrahedrane (15a), and 3-(1,3,2-Benzothiaoxaborolyl)-4-phenyl-1,2-bis(tricarbonylcobalta)tetrahedrane (16a): A solution of an alkyne (**5a:** 1.29 g; **6a:** 1.48 g; **7a:** 1.39 g; 5.9 mmol) in CH_2Cl_2 (10 mL) was added at −20 °C to a solution of $Co_2(CO)_8$ (2.03 g, 5.9 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 48 h at room temperature and the solvent was evaporated to near dryness. The residue was separated by column chromatography (Florisil®; hexane) to give two fractions. Using hexane as the eluent, $[Co_2(CO)_8]$ was obtained first. The second fraction (hexane/toluene, 1:4) contained the corresponding dicobalt complex.

14a: Yield 1.51 g (50%), red oil. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.2−7.7 (m, 9 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 104.3 (C_{ipso}), 112.7, 123.2, 147.8 (catechol), 121.2, 128.5, 130.0, 132.8 (C_6H_5), 200.1 (CO) ppm; CB was not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 33 ppm. IR (hexane): $\tilde{\nu}$ = 2021 (vs), 2039 (s), 2057 (vs), 2081 (w), 2098 (s) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 506 (2) [M$^+$], 478 (16) [M$^+$ − CO], 450 (6.5) [M$^+$ − 2 CO], 422 (13) [M$^+$ − 3 CO], 394 (30) [M$^+$ − 4 CO], 366 (53) [M$^+$ − 5 CO], 338 (27) [M$^+$ − 6 CO], 279 (30) [M$^+$ − 6 CO − Co], 220 (100) [M$^+$ − 6 CO − 2 Co]. MS (70 eV, HR-EI): *m/z* (%) = 505.9105 (2) [M$^+$; $^{12}C_{20}{}^1H_9{}^{11}B^{59}Co_2{}^{16}O_8$: 505.9054]; Δmmu = 5.1.

15a: Yield 1.52 g (48%), brown-red oil. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.1−7.8 (m, 9 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 72.56 (br., CB), 122.5 (C_{ipso}), 125.5, 126.9, 137.4 (dithiocatechol), 128.1, 128.3, 130.2, 131.2 (C_6H_5), 199.5 (CO) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 59 ppm. IR (hexane): $\tilde{\nu}$ = 2007 (s), 2025 (s), 2044 (vs), 2060 (vs), 2088 (w) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 538 (2) [M$^+$], 510 (3) [M$^+$ − CO], 482 (5) [M$^+$ − 2 CO], 454 (2) [M$^+$ − 3 CO], 426 (7) [M$^+$ − 4 CO], 398 (12) [M$^+$ − 5 CO], 370 (15) [M$^+$ − 6 CO], 311 (4) [M$^+$ − 6 CO − Co], 252 (100) [M$^+$ − 6 CO − 2 Co]. MS (70 eV, HR-EI): *m/z* (%) = 537.8536 (2) [M$^+$; $^{12}C_{20}{}^1H_9{}^{11}B^{59}Co_2{}^{16}O_6{}^{32}S_2$: 537.8597]; Δmmu = 6.1.

16a: 1.40 g (45%), brown-red oil. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.1−7.5 (m, 9 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 108.7 (C_{ipso}), 114.8, 123.8, 125.4, 126.2, 126.9, 156.6 (2-hydroxythiophenol), 121.5, 128.4, 129.9, 132.5 (C_6H_5), 200.6 (CO) ppm; CB was not observed. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 47 ppm. IR (hexane): $\tilde{\nu}$ = 2007 (s), 2022 (vs), 2044 (vs), 2060 (vs), 2076 (s) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 522 (3) [M$^+$], 494 (7) [M$^+$ − CO], 466 (10) [M$^+$ − 2 CO], 438 (12) [M$^+$ − 3 CO], 410 (31) [M$^+$ − 4 CO], 382 (15) [M$^+$ − 5 CO], 354 (13), [M$^+$ − 6 CO], 295 (6) [M$^+$ − 6 CO − Co], 236 (100) [M$^+$ − 6 CO − 2 Co]. MS (70 eV, HR-EI): *m/z* (%) = 521.8856 (3) [M$^+$; $^{12}C_{20}{}^1H_9{}^{11}B^{59}Co_2{}^{16}O_7{}^{32}S_1$: 521.8826]; Δmmu = 3.0.

(1,3,2-Benzodithiaborolyl)pentaphenylbenzene and Bis(1,3,2-benzodioxaborolyl)(1,3,2-benzodithiaborolyl)triphenylbenzene (17 and 18): Diphenylacetylene (0.75 g, 4.2 mmol) or 1-(catacholboryl)-2-phenylacetylene (**5a**; 0.92 g, 4.2 mmol) was added at room temperature to a solution of **15a** (1.12 g, 2.1 mmol) in toluene (30 mL). The resulting mixture was stirred for 48 h under reflux. After cooling, the dark-black precipitate was collected by filtration and washed several times with hexane and toluene, and then dried in vacuo.

17: 0.90 g (70%), dark solid, m.p. > 300 °C. MS (70 eV, EI): *m/z* (%) = 608 (100) [M$^+$]. MS (70 eV, HR-EI): *m/z* (%) = 608.1818 (100) [M$^+$; $^{12}C_{42}{}^1H_{29}{}^{11}B^{32}S_2$: 608.1803]; Δmmu = 1.5.

18: 1.10 g (75%), black solid, m.p. > 300 °C. MS (70 eV, EI): *m/z* (%) = 692 (100) [M$^+$]. MS (70 eV, HR-EI): *m/z* (%) = 692.1633 (100) [M$^+$; $^{12}C_{42}{}^1H_{27}{}^{11}B_3{}^{16}O_4{}^{32}S_2$: 692.1629]; Δmmu = 0.4.

Crystal Structure Determinations of 4a, 5a, 6a, and 10a: Crystal data and details of the structure determinations are listed in Table 1. Unique sets of intensity data were collected using a Bruker−AXS SMART 1000 diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, ω-scan). Empirical absorp-

Table 1. Crystal data and structural refinement for **4a, 5a, 6a**, and **10a**

	4a	**5a**	**6a**	**10a**
Empirical formula	$C_{20}H_{33}N_2B$	$C_{14}H_9O_2B$	$C_{14}H_9S_2B$	$C_{33}H_{23}B_2CoS_4$
Molecular mass	312.29	220.02	252.14	628.30
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic
Space group	*C*2/*c*	F*dd*2	$P2_1$	$P\bar{1}$
Unit cell				
a [Å]	13.9717(7)	19.626(5)	14.419(2)	12.7008(7)
b [Å]	14.9033(8)	7.1519(18)	5.4955(8)	15.9541(9)
c [Å]	11.0036(6)	15.422(4)	15.466(2)	17.364(1)
α [°]	90	90	90	87.270(1)
β [°]	118.881(1)	90	102.885(3)	69.319(1)
γ [°]	90	90	90	88.105(1)
Volume [Å^3]	2006.25(18)	2164.8(9)	1194.6(3)	3287.5(3)
Z	4	8	4	4
Calcd. density [g cm^{-3}]	1.034	1.350	1.402	1.269
μ [mm^{-1}]	0.059	0.088	0.414	0.796
F(000)	688	912	520	1288
Crystal size [mm]	0.50 × 0.34 × 0.26	0.35 × 0.23 × 0.07	0.17 × 0.10 × 0.01	0.18 × 0.07 × 0.05
$\theta_{max.}$ [°]	32.01	32.10	27.11	25.03
Index ranges	−20/18, 0/22, 0/16	0/29, 0/10, −21/22	−18/17, −7/ 6, 0/19	−14/15, −18/18, 0/20
Reflections collected	9223	5076	7208	35994
independent	3421(0.0216)	1717(0.0673)	4370(0.0625)	11615(0.0763)
Parameters	173	98	308	725
Goodness-of-fit on F^2	1.045	1.072	0.993	0.870
R_1 [$I > 2\sigma_I$]	0.0438	0.0713	0.0532	0.0503
wR_2 (all reflections)	0.1230	0.1678	0.1195	0.1162
T [K]	103(2)	103(2)	103(2)	298(2)
Residual electron density [e/A^3]	0.532/−0.125	0.926/−0.367	0.462/−0.581	0.281/−0.542

tion corrections were applied. The structures were solved by direct methods (SHELXS-86)[32] and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-97).[33] All non-hydrogen atoms were refined anisotropically.

CCDC-227235 (for **4a**), -227236 (for **5a**), -227237 (for **6a**), and -227238 (for **10a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the SFB 623 and the Fonds der Chemischen Industrie. We thank Prof. R. Gleiter for fruitful discussions.

[1] [1a] S. Saito, Y. Yamamoto, *Chem. Rev.* **2000**, *100*, 2901−2915. [1b] Y. Yamamoto, A. Nagata, H. Nagata, Y. Ando, Y. Avikawa, K. Tatsumi, K. Itoh, *Chem. Eur. J.* **2003**, *9*, 2469−2483. [1c] E. R. F. Gesing, K. P. C. Vollhardt, *J. Organomet. Chem.* **1981**, *217*, 105−118. [1d] L. P. M. Bushnell, E. R. Evirt, R. G. Bergman, *J. Organomet. Chem.* **1978**, *157*, 445−456.

[2] [2a] T. S. Piper, F. A. Cotton, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1955**, *1*, 165−174. [2b] E. O. Fischer, R. Jira, *Z. Naturforsch., Teil B* **1955**, *10*, 355.

[3] [3a] A. Efraty, *Chem. Rev.* **1977**, *77*, 691−744. [3b] R. Gleiter, *Angew. Chem.* **1992**, *104*, 29−46; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 27−44. [3c] A. Nakamura, N. Hagihara, *Bull. Chem. Soc., Jpn.* **1961**, *34*, 452−453. [3d] M. D. Rausch, R. A. Genetti, *J. Am. Chem. Soc.* **1967**, *89*, 5502−5503. [3e] J. L. Boston, D. W. A. Sharp, G. Wilkinson, *J. Chem. Soc.* **1962**, 3488−3494.

[4] N. Schore, *Chem. Rev.* **1988**, *88*, 1081−1119.

[5] [5a] K. P. C. Vollhardt, *Angew. Chem.* **1984**, *96*, 525−542; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 539−644. [5b] H. Bönnemann, W. Brijoux, R. Brinkmann, W. Meurers, R. Mynott, W. Von Phillipsbon, T. Egolf, *J. Organomet. Chem.* **1984**, *272*, 231−249.

[6] [6a] I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, *J. Chem. Soc., Chem. Commun.* **1971**, 36. [6b] I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, *J. Chem. Soc., Perkin Trans. 1* **1973**, 975−977. [6c] P. L. Pauson, *Tetrahedron* **1985**, *41*, 5855−5860.

[7] Y. Gu, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **2001**, 373−379.

[8] C. Ester, A. Maderna, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **2000**, 1177−1184.

[9] [9a] M. Neuenschwander, P. Bigler, *Helv. Chim. Acta* **1973**, *56*, 959−965. [9b] A. Niederhauser, M. Neuenschwander, *Helv. Chim. Acta* **1973**, *56*, 1331−1343.

[10] S. Y. Delavarenne, H. G. Viehe, *Chem. Ber.* **1970**, *103*, 1209−1215.

[11] C. Blanchard, E. Framery, M. Vaultier, *Synthesis* **1996**, 45−47.

[12] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

[13] M. Hesse, H. Meier, B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie,* 4th ed., Thieme Verlag, Stuttgart, **1991**.

[14] [14a] H. Schulz, G. Gabbert, H. Pritzkow, W. Siebert, *Chem. Ber.* **1993**, *126*, 1593−1595. [14b] M. Bluhm, A. Maderna, H. Pritzkow, S. Bethke, R. Gleiter, W. Siebert, *Eur. J. Inorg. Chem.* **1999**, 1693.

[15] K. Okada, T. Sugawa, M. Oda, *J. Chem. Soc., Chem. Commun.* **1992**, 74.

[16] J. H. Hardesty, J. B. Koerner, T. A. Albright, G. Y. Lee, *J. Am. Chem. Soc.* **1999**, *121*, 6055− 6067.

[17] R. Diercks, B. E. Eaton, S. Gürtzgen, S. Jalisatgi, A. J. Matzger, R. H. Radde, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1998**, *120*, 8247−8248.

[18] R. J. Baxter, G. R. Knox, J. H. Mori, P. L. Pauson, M. D. Spicer, *Organometallics* **1999**, *18*, 206−214.

[19] [19a] R. J. Baxter, G. R. Knox, P. L. Pauson, M. D. Spicer, *Organometallics* **1999**, *18*, 197−205. [19b] M. A. Bennett, P. B. Donaldson, *Inorg. Chem.* **1978**, *17*, 1995−2000. [19c] R. J. Kaufman, R. S. Sidhu, *J. Org. Chem.* **1982**, *47*, 4941−4947.

[20] [20a] O. S. Mills, G. Robinson, *Proc. Chem. Soc.* **1964**, 187. [20b] G. Gervasio, E. Sappa, L. Marko, *J. Organomet. Chem.* **1993**, *444*, 203−209. [20c] R. S. Dickson, P. J. Fraser, *Aust. J. Chem.* **1972**, *25*, 1179.

[21] [21a] W. Hübel, C. Hoogzand, *Chem. Ber.* **1960**, *93*, 103. [21b] U. Krüerke, W. Hübel, *Chem. Ber.* **1961**, *94*, 2829. [21c] U. Krüerke, W. Hübel, *Chem. Ber.* **1961**, *94*, 2917.

[22] G. F. Emerson, L. Watts, R. Pettit, *J. Am. Chem. Soc.* **1965**, *87*, 131.

[23] F. L. Bowden, A. B. P. Lever, *Organomet. Chem. Rev.* **1968**, *3*, 227.

[24] J. R. Fritch, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1978**, *100*, 3643.

[25] H. Sakurai, J. Hayashi, *J. Organomet. Chem.* **1972**, *39*, 365−370.

[26] M. E. Arnett, J. M. Bollinger, *J. Am. Chem. Soc.* **1964**, *86*, 4729−4731.

[27] [27a] P. Galow, A. Sebald, B. Wrackmeyer, *J. Organomet. Chem.* **1983**, *259*, 253. [27b] H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby, I. Wender, *J. Am. Chem. Soc.* **1956**, *78*, 120.

[28] [28a] J. Perez, L. Riera, V. Riera, S. G. Granda, E. G. Rodriguez, D. G. Churchill, M. R. Churchill, T. S. Janik, *Inorg. Chim. Acta* **2003**, *347*, 189−193. [28b] M. Akita, M. Terada, M. Tanaka, Y. Moro-Oka, *Organometallics* **1992**, *11*, 3468.

[29] P. Y. Chavant, M. Vaultier, *J. Organomet. Chem.* **1993**, *455*, 37−46.

[30] M. Younus, N. J. Long, P. R. Raithby, J. Lewis, N. A. Page, A. J. P. White, D. J. Williams, M. C. B. Colbert, A. J. Hodge, M. S. Khan, D. G. Parker, *J. Organomet. Chem.* **1999**, *578*, 198−209.

[31] W. Gerrard, M. F. Lappert, B. A. Mountfield, *J. Chem. Soc., II* **1959**, 1529−1535.

[32] G. M. Sheldrick, *SHELXS-86*, University of Göttingen, **1986**.

[33] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**.

Received January 23, 2004
Early View Article
Published Online May 25, 2004

