Synthesis, Structures and Reactivity of Mono- and Diborylacetylenes

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Dedicated to Professor Margot Becke on the occasion of her 90th birthday

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The reaction of [bis(diisopropylamino)boryl]acetylene with 2 equiv. of HCl and 1 equiv. of dithiocatechol or 2-hydroxythiophenol yields the corresponding monoborylacetylenes **1** and **2**, respectively. Diborylacetylenes **3** and **4** are obtained from the reactions of bis(trimethylstannyl)acetylene with 2 equiv. of bromoboranes. Treatment of chlorobis(diisopropylamino)-borane with LiC≡C–EMe$_3$ (E = C, Si) leads to the corresponding element-substituted [bis(diisopropylamino)boryl]-acetylenes **5a**,**b**. The syntheses of monoborylacetylenes **6a**,**b**–**8a**,**b** are achieved by the reaction of **5a**,**b** with 2 equiv. of HCl and 1 equiv. of catechol, dithiocatechol or 2-hydroxythiophenol, respectively. Stoichiometric amounts of [CpCo(CO)$_2$] react with **1**–**4** in refluxing toluene to give the corresponding (η^4-cyclobutadiene)cobalt complexes **9**–**12**. Analogous isomeric mixtures of (η^4-cyclobutadiene)cobalt complexes **13a/13a′**–**15a/15a′** are obtained from 1-*tert*-butyl-2-borylacetylenes **6a**–**8a** and [CpCo(C$_2$H$_4$)$_2$], whereas isomeric mixtures of (η^4-cyclohexatriene)(η^5-cyclopentadienyl)-cobalt complexes **13b/13b′**–**15b/15b′** are formed with 1-boryl-2-silylacetylenes **6b**–**8b** under similar conditions. Hydrolysis of **13a**–**15a** yields the (η^4-1,3-di-*tert*-butylcyclobutadiene)cobalt complex **16**. Catalytic trimerizations of mono- (**1**, **2**) and diborylacetylenes (**3**, **4**) with Co$_2$(CO)$_8$ lead to isomeric mixtures of triboryl- (**17/17′**, **18/18′**) and hexaborylbenzene derivatives (**19**, **20**), respectively. The new compounds are characterized by NMR spectroscopy and mass spectrometry as well as by X-ray structure analyses for **1b**, **5b**, **6b**, **14a**, **15a** and **16**.

Introduction

Over the past three decades, cobalt-mediated cyclooligomerization reactions of acetylenes have been recognized as a powerful tool for the synthesis of various compounds.[1] In general, catalytic cyclotrimerizations of less bulky substituted acetylenes with [CpCoL$_2$] (L = CO, C$_2$H$_4$) lead to benzene derivatives,[2] whereas CpCo complexes of cyclobutadiene[3] and/or cyclopentadienone[4] (with benzene derivatives as side products) are obtained with stoichiometric amounts of [CpCoL$_2$] complexes.

Recently, we have reported the synthesis of oxygen- and sulfur-substituted monoborylacetylenes.[5] Surprisingly, it was found that oxygen-substituted borylacetylenes formed only benzene derivatives in catalytic as well as stoichiometric reactions with [CpCoL$_2$]. On the other hand, with sulfur-substituted borylacetylenes only (η^4-cyclobutadiene)cobalt complexes were achieved. This unique heteroatom effect in borylacetylenes encouraged us to perform further studies. The monoborylacetylenes **1** and **2** and the diborylacetylenes **3** and **4** were synthesized and found to follow the same reaction trend to undergo dimerization with [CpCoL$_2$] to furnish (η^4-cyclobutadiene)cobalt complexes **9**−**12**. This indicated that the aryl groups have less electronic or steric influences on the reactivity of previously reported 1-aryl-2-borylacetylenes.[5]

In order to shed further light on the influence of bulky substituents on the borylacetylenes, we have prepared 1-boryl-2-*tert*-butylacetylenes and 1-boryl-2-silylacetylenes **6**−**8**, in which two oxygen atoms (in **6**), two sulfur atoms (in **7**) and one oxygen and one sulfur atom (in **8**) are bound to the boron atom. It is expected that the bulky substituents have different steric and electronic effects on the reactivity of the acetylenes **6**−**8**. In this paper, we report on the syntheses, structures and reactivity of the above-mentioned acetylenes **1**−**4** and **6**−**8**.

Results and Discussion

Synthesis and Properties of Mono- and Diborylacetylenes

The preparation of sulfur-substituted borylacetylenes was achieved by treatment of [bis(diisopropylamino)boryl]-acetylene with 2 equiv. of HCl and 1 equiv. of dithiocatechol or 2-hydroxythiophenol in THF, to give the mono-

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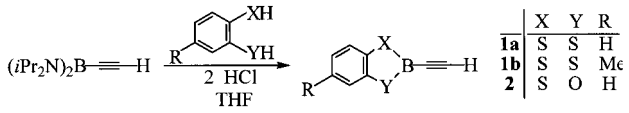
borylacetylenes **1a**,**b** and **2**, respectively, in moderate yields (Scheme 1). The colorless solids were characterized by ^{1}H, ^{11}B and ^{13}C NMR spectroscopy, and by mass spectrometry.



	X	Y	R
1a	S	S	H
1b	S	S	Me
2	S	O	H

Scheme 1

In the ^{11}B NMR spectrum the signals at δ = 47 (**1a**), 48 (**1b**) and 38 (**2**) ppm indicate trigonal-planar boryl groups, which was confirmed by the solid-state structure of **1b** (Figure 1). The ^{1}H NMR spectra of **1a**,**b** and **2** exhibit a characteristic singlet for the acetylenic proton at δ = 3.71 (**1a**), 3.70 (**1b**) and 3.17 (**2**) ppm. In the ^{13}C NMR spectrum the signals for B−C_{sp} are not observed; the signals for H−C_{sp} (δ = 90−100 ppm) are shifted to lower field compared to those of alkylacetylenes (δ = 70−80 ppm).

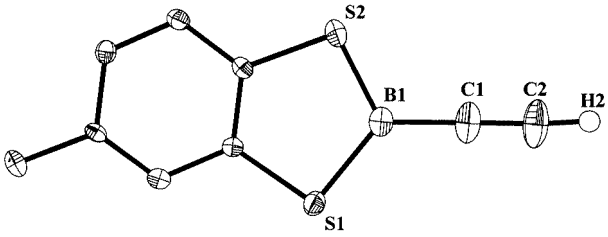
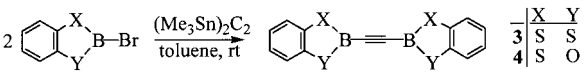


Figure 1. Molecular structure of **1b** in the solid state; selected bond lengths [Å] and bond angles [°]: B1−S1 1.849(3), B1−S2 1.728(3), B1−C1 1.521(2), C1−C2 1.188(3); C2−C1−B1 178.3(2), C1−C2−H2 175.9(2), C1−B1−S2 117.9(2), C1−B1−S1 128.4(2), S2−B1−S1 113.5(1)

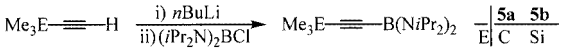
Diborylacetylenes **3** and **4** were prepared by the reaction of bis(trimethylstannyl)acetylene with 2 equiv. of bromoboranes (Scheme 2). The colorless, air-sensitive solids formed are well soluble in chloroform and toluene, but less so in hexane and pentane. The ^{11}B NMR spectra show broad signals at δ = 47 (**3**) and 37 (**4**) ppm.



	X	Y
3	S	S
4	S	O

Scheme 2

The synthesis of the [bis(diisopropylamino)boryl]acetylenes **5a**,**b** was performed according to a literature procedure[6] by treating chlorobis(diisopropylamino)borane with LiC≡C−EMe_3 (E = C, Si). The products were isolated in almost quantitative yields (Scheme 3).



E	5a	5b
	C	Si

Scheme 3

The light-yellow acetylenes **5a**,**b** were characterized by ^{1}H, ^{11}B and ^{13}C NMR spectroscopy, and by mass spectrometry. The X-ray structure analysis of **5b** (Figure 2) reveals an almost linear B−C≡C−Si moiety; the C≡C distance (1.21 Å) is slightly longer than in other R−C≡C−R compounds (1.18 Å).[7]

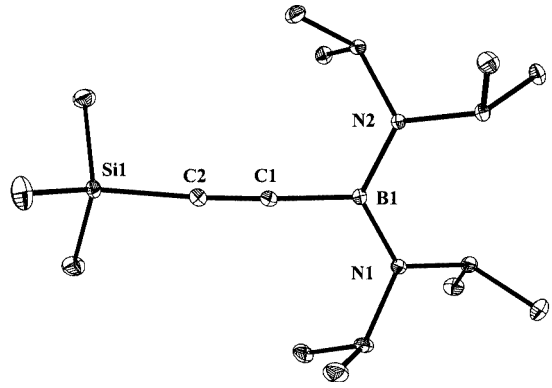
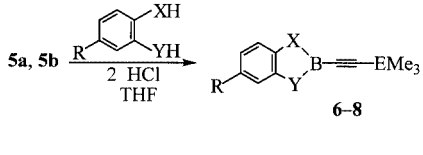


Figure 2. Molecular structure of **5b** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: B1−C1 1.564(1), C1−C2 1.214(1), Si1−C2 1.830(1), N1−B1 1.428(1), N2−B1 1.439(1); C2−C1−B1 177.3(1), C1−C2−Si1 174.54(9), N1−B1−N2 124.40(8), N2−B1−C1 117.46(8), N1−B1−C1 118.13(8)

The synthesis of compounds **6**−**8** was achieved by the reaction of the [(diisopropylamino)boryl]acetylenes **5a**,**b** with 2 equiv. of HCl and 1 equiv. of catechol, dithiocatechol or 2-hydroxythiophenol, respectively, in THF (Scheme 4). Compounds **7a** and **7b** are colorless solids, whereas **6a**,**b**[8] and **8a**,**b** are pale-yellow liquids, which are readily soluble in common organic solvents.



	X	Y	E	R
6a	O	O	C	H
6b	O	O	Si	H
7a	S	S	C	Me
7b	S	S	Si	Me
8a	S	O	C	H
8b	S	O	Si	H

Scheme 4

The ^{11}B NMR spectra exhibit broad signals at δ = 24 (**6a**), 23 (**6b**), 48 (**7a**), 47 (**7b**), 38 (**8a**) and 37 (**8b**) ppm. In the ^{1}H NMR spectra of **6b**−**8b** and **6a**−**8a** singlets appear at δ = 0.2−0.3 ppm ($SiMe_3$) and 1.2−1.3 ppm (CMe_3). Single crystals of **6b** were obtained at −20 °C. The molecular structure of **6b** (Figure 3) indicates an almost linear B−C≡C−Si moiety with a slightly elongated C≡C bond. The boron atom is trigonal coordinated and the heterocycle is almost planar.

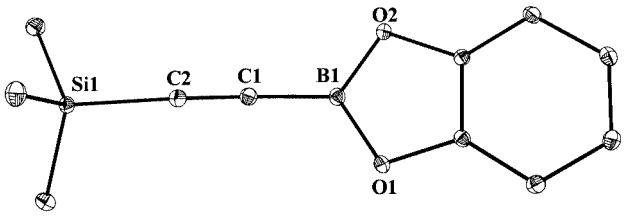
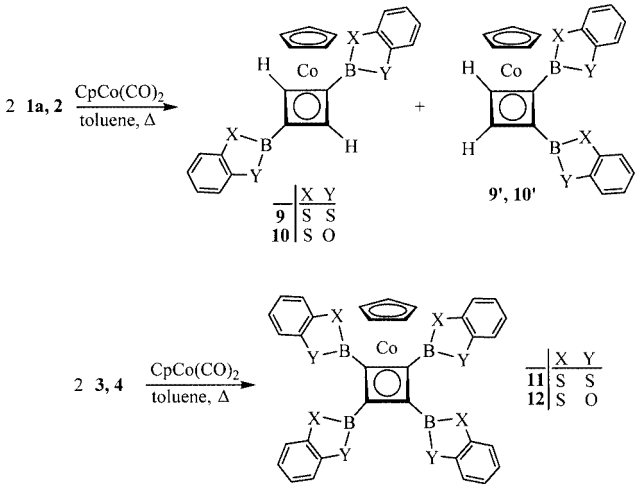


Figure 3. Molecular structure of **6b** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: Si1−C2 1.853(1), B1−C1 1.524(2), C1−C2 1.209(2), O1−B1 1.386(1), O2−B1 1.387(1); C2−C1−B1 172.8(1), C1−C2−Si1 175.3(1), O1−B1−O2 112.13(9), O1−B1−C1 122.7(1), O2−B1−C1 125.0(1)

(η^4-Cyclobutadiene)cobalt Complexes 9−12

CpCo-mediated cyclodimerization has proved particularly efficient for tolerating the presence of varied functionalities on the alkyne.[9] As a result, the $[CpCoL_2]$ (L = CO, PR_3, olefin) complex family has been utilized for intensive studies, culminating in the isolation of numerous (η^4-cyclobutadiene)cobalt complexes. In refluxing toluene the mono- (**1a**, **2**) and diborylacetylenes (**3**, **4**) formed the (η^4-cyclobutadiene)cobalt complexes **9**−**12** in the presence of stoichiometric amounts of $[CpCo(CO)_2]$ (Scheme 5). Purification of complexes **9**−**12** was performed by repeated washing with hexane and toluene. The red-brown solids of **9**−**12** are partially soluble in chloroform; in methanol a fast reaction leads to the formation of $B(OMe)_3$.

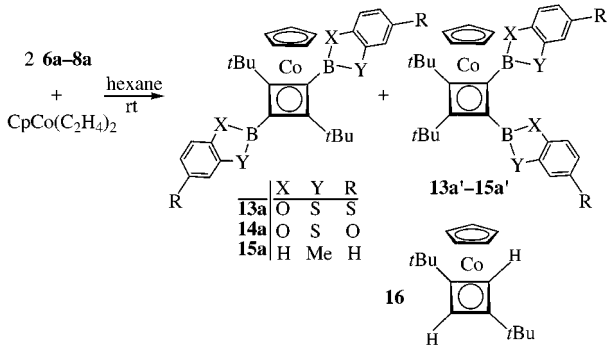


Scheme 5

Complexes **9**−**12** were characterized by ^1H, ^{11}B and ^{13}C NMR spectroscopy, and by mass spectrometry. The ^{11}B NMR spectra show broad signals at δ = 60 (**9**), 48 (**10**), 63 (**11**) and 50 (**12**) ppm. The ^1H NMR spectra of **9**−**12** exhibit multiplets in the region δ = 6.6−8.2 ppm for thr aromatic protons in addition to the Cp resonances (δ = 4.7−5.4 ppm). The *cis* isomers **9′**, **10′** could not be identified by NMR spectroscopy; however, analysis of the fragmentation patterns in the mass spectra in terms of the degradation of the cyclobutadiene ring clearly indicates the presence of trace amounts of *cis* isomers in the isomeric mixtures. It is worth mentioning that no benzene derivative was formed in the catalytic cyclotrimerization (thermal or photochemical) reactions of $[CpCo(CO)_2]$ with the borylacetylenes **1**−**4**.

Reactions of $[CpCo(C_2H_4)_2]$ with 6a−8a

The reaction of borylacetylenes **6a**−**8a** with stoichiometric amounts of $[CpCo(CO)_2]$ in refluxing toluene led only to 50−60% conversion of the starting acetylenes to an isomeric mixture of (η^4-cyclobutadiene)cobalt complexes **13a/13a′**, **14a/14a′** and **15a/15a′**, respectively. Using the more reactive complex $[CpCo(C_2H_4)_2]$[10] resulted in complete conversion of the borylacetylenes to the CpCo complexes **13a/13a′**−**15a/15a′** (Scheme 6).



Scheme 6

Attempts to separate the isomeric mixtures of the cobalt complexes **13a/13a′**−**15a/15a′** by column chromatography led to the known complex $[CpCo(\eta^4\text{-}C_4tBu_2H_2)]$ (**16**).[11] Compounds **13a/13a′**−**15a/15a′** and **16** are soluble in common organic solvents and were characterized by ^1H, ^{11}B and ^{13}C NMR spectroscopy, mass spectrometry as well as by X-ray analyses for **14a**, **15a** and **16**. The ^{11}B NMR spectra show broad signals at δ = 36 (**13a/13a′**), 63 (**14a/14a′**) and 50 (**15a/15a′**) ppm. The ^1H NMR spectra of **13a**−**15a** exhibit singlets in the region δ = 4.8−5.2 ppm for H_{Cp} in addition to the *tert*-butyl group resonances (δ = 1.2−1.4 ppm). The molecular-ion peaks of **13a**−**15a** were detected with the expected isotopic pattern by mass spectrometry. The presence of very small amounts of *cis* isomers (**13a′**, **14a′** and **15a′**) in the isomeric mixtures was confirmed by analyzing the major peaks in the mass spectra (analogous to **9′**, **10′**).

Complexes **14a** and **15a** were characterized by performing a single-crystal X-ray diffraction analysis (Figures 4 and 5), which revealed that the *tert*-butyl and boryl groups are in *trans* positions. Neither of the boron heterocycles of **14a** lies in the cyclobutadiene plane, whereas one of the boron heterocycles of **15a** is coplanar with the cyclobutadiene ring.

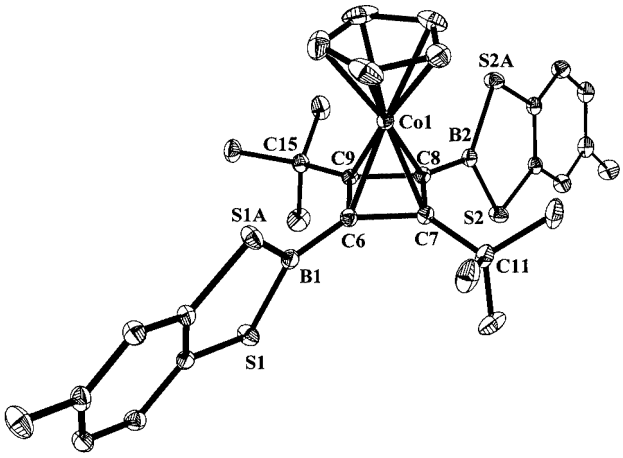


Figure 4. Molecular structure of **14a** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [A] and bond angles [°]: C6−C9 1.467(3), C6−C7 1.475(3), C7−C8 1.468(3), C8−C9 1.467(3), B1−S1 1.803(3), B2−S2 1.795(3); C9−C6−C7 88.6(2), C6−C7−C8 91.1(2), C9−C8−C7 88.8(2), C6−C9−C8 91.5(2)

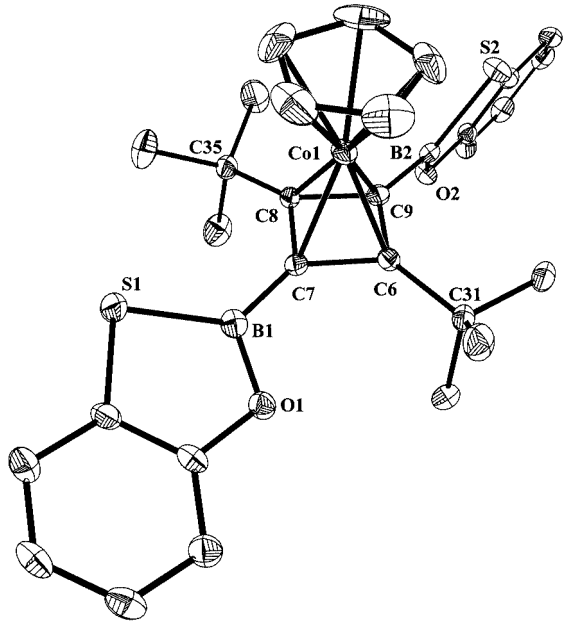


Figure 5. Molecular structure of **15a** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [A] and bond angles [°]: C6−C9 1.459(4), C6−C7 1.477(4), C7−C8 1.482(4), C8−C9 1.467(4), B1−O1 1.379(4), B2−O2 1.376(4), B1−S1 1.824(4), B2−S2 1.814(4); C9−C6−C7 91.3(2), C6−C7−C8 88.3(2), C9−C8−C7 90.8(2), C6−C9−C8 89.6(2)

A solid-state structure analysis of **16** was carried out on a single crystal. This complex crystallizes with two independent molecules in the asymmetric unit with very similar distances and angles; only one structure is shown in Figure 6 and the average values are listed in the caption.

[CpCo(η⁴-cyclohexatriene)] Complexes 13b/13b′−15b/15b′

Reaction of **6b−8b** with $[CpCo(C_2H_4)_2]$[12] led to the [CpCo(η⁴-cyclohexatriene)] complexes **13b/13b′−15b/15b′**

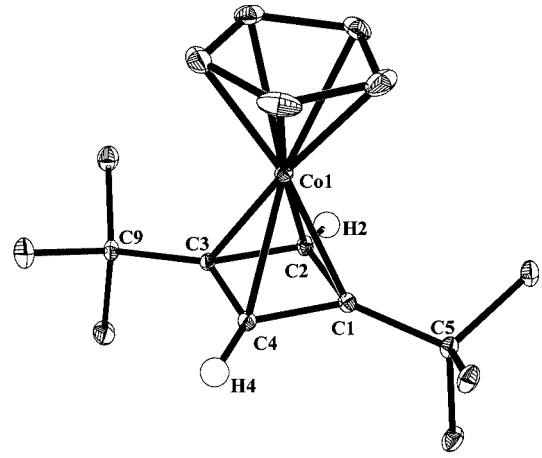
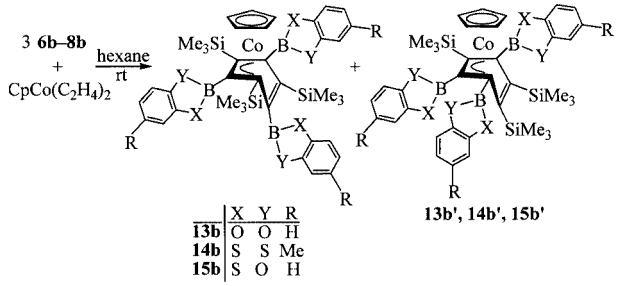


Figure 6. Molecular structure of **16** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [A] and bond angles [°]: C1−C2 1.449(3), C1−C4 1.455(3), C2−C3 1.455(3), C3−C4 1.461(3); C2−C1−C4 89.8(2), C1−C2−C3 90.7(2), C2−C3−C4 89.3(2), C1−C4−C3 90.2(2)



Scheme 7

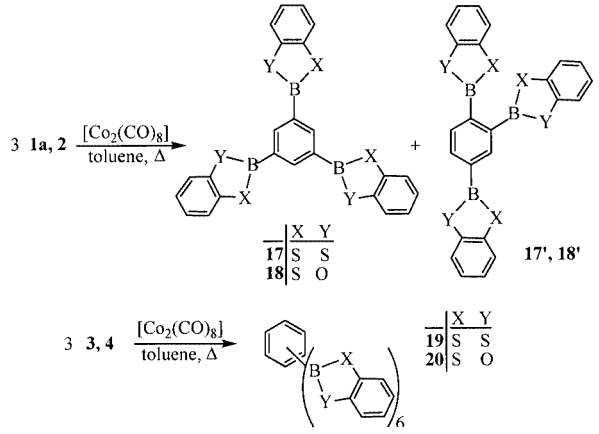
in moderate yields (Scheme 7). They were purified by column chromatography on Florosil and isolated as reddish-brown oils, which were characterized by ^1H, ^{11}B, ^{13}C and ^{29}Si NMR spectroscopy, and by mass spectrometry.

The ^{11}B NMR spectra show broad signals at $\delta = 32$ (**13b/13b′**), 60 (**14b/14b′**) and 49 (**15b/15b′**) ppm and the ^1H NMR spectra exhibit multiplets in the aromatic region of $\delta = 6.3-7.5$ ppm in addition to the Cp resonances ($\delta = 4.9-5.3$ ppm). The EI-MS data confirm the identity of complexes **13b−15b** by the appearance of the molecular-ion peaks with the correct isotopic pattern.

[$Co_2(CO)_8$]-Catalyzed Cyclotrimerization of 1−4

In refluxing toluene the mono- and diborylacetylenes **1−4** form the corresponding benzene derivatives **17−20** in the presence of a catalytic amount of $Co_2(CO)_8$ (Scheme 8).[13] The air-stable colorless solids **17−20** are not soluble in common organic solvents, although triborylbenzene derivatives **17** and **18** are partially soluble in chloroform. In general, for unsymmetrical acetylenes one can expect to achieve mixtures of both 1,3,5 and 1,2,4 isomers in variable ratios. Due to their low solubility, the mixtures of isomers **17/17′** and **18/18′** could not be separated by column chromatography.[14] Purification of the compounds was accomplished by repeated washing with hexane and toluene. Compounds **17** and **18** were characterized by ^1H, ^{11}B and

^{13}C NMR spectroscopy, and by mass spectrometry. In the ^{13}C NMR spectra of **17** and **18** the signals for the central benzene rings are not observed. Therefore, one cannot rule out the possibility that the isomers **17**/**17′** and **18**/**18′** are present. The hexaborylbenzene derivatives **19** and **20** were identified by mass spectrometry by the appearance of molecular-ion peaks with the correct isotopic pattern. Owing to their very low solubility, NMR measurements were not possible for **19** and **20**.



Scheme 8

Under similar reaction conditions no triborylbenzene derivative was found from the reactions with 1-alkyl-2-borylacetylenes **6**−**8**.

Conclusions

The reaction of borylacetylenes with catalytic as well as stoichiometric amounts of $[CpCo(CO)_2]$, $[CpCo(C_2H_4)_2]$ and $[Co_2(CO)_8]$ have been studied. Benzene derivatives are not formed by [2+2+2] catalytic cyclotrimerization reactions of $[CpCoL_2]$ (L = CO, C_2H_4) with borylacetylenes **1**−**4** and **6**−**8**. The (η^4-cyclobutadiene)cobalt complexes **9**−**12** are, however, formed by the reaction of mono- (**1**, **2**) and diborylacetylenes (**3**, **4**) with stoichiometric amounts of $[CpCo(CO)_2]$. Analogous (η^4-cyclobutadiene)cobalt complexes **13a**−**15a** have been prepared by the reaction of the corresponding *tert*-butylborylacetylenes **6a**−**8a** in the presence of $[CpCo(C_2H_4)_2]$. The interaction of a sulfur atom with the cobalt atom in the coordinatively unsaturated cobaltacyclopentadiene derivative probably does not allow the approach of a third acetylene molecule to the cobalt center; therefore formation of benzene derivatives does not occur by [2+2+2] catalytic cycloaddition reactions of the monoboryl acetylenes **1**−**4**, **7a** and **8a**. As similar oxygen−cobalt interactions are not known, steric bulkiness may be the reason for obtaining only (η^4-cyclobutadiene)cobalt complexes from the reaction of **6a** with $[CpCo(C_2H_4)_2]$. In **7a** and **8a**, the presence of the bulky *tert*-butyl group obviously hinders the formation of benzene derivatives.

Surprisingly, such types of cyclobutadienylcobalt complexes are not found in the reactions of 1-boryl-2-silylacetylenes **6b**−**8b** under similar reaction conditions. On the other hand, treatment of **6b**−**8b** with $[CpCo(C_2H_4)_2]$ at ambient temperature led to the novel (η^4-cyclohexatriene)(η^5-cyclopentadienyl)cobalt complexes **13b**−**15b**. Reaction of mono- and diborylalkynes (**1**−**4**) with catalytic amounts of $[Co_2(CO)_8]$ gives rise to triboryl- (**17**/**17′** and **18**/**18′**) and hexaborylbenzene derivatives (**19** and **20**), 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. Column chromatography: Florosil® (Fluka), 100−200 mesh. ^1H, ^{11}B and ^{13}C NMR: Bruker AC 200 spectrometer; ^1H and ^{13}C spectra were referenced to $Si(CH_3)_4$; ^{11}B spectra to $F_3B{\cdot}OEt_2$. Mass spectra were obtained with Finnigan MAT 8230 plus spectrometers using the EI technique. Melting points (uncorrected) were obtained with a Büchi apparatus, using capillaries which were filled under nitrogen and sealed. (iPr$_2$N)$_2$BCl[15] and [bis(diisopropylamino)boryl]acetylene[16] were prepared according to literature procedures. Bromo(dithiocatechol)-borane and bromo-1,3,2-benzooxathiaborole, not previously reported in the literature, were prepared by the reactions of dithiocatechol and 2-hydroxythiophenol with excess of BBr_3. Catechol, dithiocatechol, 4-methyldithiocatechol, 2-mercaptophenol and bis(trimethylstannyl)acetylene were purchased from Aldrich.

(1,3,2-Benzodithiaborol-2-yl)acetylene (1a), (5-Methyl-1,3,2-benzodithiaborol-2-yl)acetylene (1b) and (1,3,2-Benzooxathiaborol-2-yl)-acetylene (2): $HCl{\cdot}OEt_2$ (2 M; 10.5 mL, 21 mmol) was added to a stirred solution of [bis(diisopropylamino)boryl]acetylene (2.40 g, 10.1 mmol) in 50 mL of THF at −78 °C within 15 min. Stirring was continued at room temp. for 2 h. Then, 10.1 mmol of the corresponding aromatic diol (**1a**: 1.43 g of dithiocatechol; **1b**: 1.57 g of 4-methyldithiophenol; **2**: 1.27 g of 2-hydroxythiophenol; in 15 mL of THF) was added to the white suspension and the reaction mixture was stirred overnight at room temp. After filtration, the solution was concentrated almost to dryness, and a crystalline solid was obtained.

1a: Yield: 0.98 g (55%), m.p. 62 °C (dec.). ^1H NMR (200.1 MHz, $CDCl_3$): δ = 3.71 (s, 1 H, C≡CH), 7.20, 7.80 (m, 4 H, C_6H_4) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 47 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 94.10 (C≡*C*H), 126.0, 126.8, 140.8 (C_6H_4) ppm; C_{sp}−B signal not observed. MS (70 eV, EI): *m*/*z* (%) = 176 (20) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 175.9915 (13) [M^+; $^{12}C_8{}^1H_5{}^{32}S_2{}^{11}B$: 175.9926]; Δmmu = −1.1.

1b: Yield: 0.97 g (51%), m.p. 71 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 3.70 (s, 1 H, C≡CH), 7.20, 7.62 (m, 3 H, C_6H_3) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 48 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.06 (CH_3), 96.24 (C≡*C*H), 126.2, 126.9, 127.3, 136.2, 137.6, 140.9 (C_6H_3) ppm; C_{sp}−B not observed.

2: Yield: 0.79 g (49%), m.p. 56 °C. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 3.17 (s, 1 H, C≡CH), 7.1−7.7 (m, 4 H, C_6H_4) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 38 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 97.23 (C≡*C*H), 115.1, 120.9, 124.1, 126.4, 127.8, 156.5 (C_6H_4) ppm; C_{sp}−B signal not observed. MS (70 eV, EI): *m*/*z* (%) = 160 (10) [M^+].

[Bis(1,3,2-benzodithiaborol-2-yl)]acetylene (3) and [Bis(1,3,2-benzooxathiaborol-2-yl)]acetylene (4): The bromoborane (2.62 g of $C_6H_4S_2BBr$; 2.43 g of C_6H_4OSBBr; 11.4 mmol; in 10 mL of toluene) was added to a solution of $(Me_3Sn)_2C_2$ (2.0 g, 5.7 mmol) in toluene (50 mL) at −78 °C. The reaction mixture was allowed to warm to room temp. and stirred overnight. After removal of the solvent under vacuum, the brown-red residue was sublimed to yield colorless, air-sensitive crystals.

3: Yield: 1.18 g (64%), m.p. 132 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.37, 7.85 (m, 8 H, C_6H_4) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 47 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 93.14 (BC), 126.0, 126.7, 140.8 (C_6H_4) ppm. MS (70 eV, EI): *m*/*z* (%) = 326 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 325.9699 (100) [M^+; $^{12}C_{14}{}^1H_8{}^{32}S_4{}^{11}B_2$: 325.9694]; Δmmu = 0.5.

4: Yield: 1.0 g (60%), m.p. 102 °C (dec.). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.3−7.6 (m, 8 H, C_6H_4) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 37 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 115.1, 124.2, 125.5, 126.6, 127.9, 156.5 (C_6H_4) ppm; C_{sp}−B signal not observed. MS (70 eV, EI): *m*/*z* (%) = 294 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 294.0164 (3.6) [M^+; $^{12}C_{14}{}^1H_8{}^{16}O_2{}^{32}S_2{}^{11}B_2$: 294.0152]; Δmmu = 1.2.

1-[Bis(diisopropylamino)boryl]-2-(*tert*-butyl)acetylene (5a) and 1-[Bis(diisopropylamino)boryl]-2-(trimethylsilyl)acetylene (5b): *n*BuLi (2.5 M in hexane; 5.8 mL, 14.6 mmol) was added slowly at −78 °C to a solution of alkylacetylene [**5a**: 1.2 g of (*tert*-butyl)acetylene; **5b**: 1.44 g of (trimethylsilyl)acetylene; 14.6 mmol; in 40 mL of hexane]. The reaction mixture was allowed to warm to room temp. and stirred for 2 h. A solution of chlorobis(diisopropylamino)borane (3.6 g, 14.6 mmol) in 10 mL of hexane was added and the mixture stirred at room temp. overnight. The solid was separated, the solvent removed under vacuum, and a light-yellow liquid was distilled.

5a: Yield: 3.5 g (82%), b.p. 48 °C/0.01 mbar. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.21 [d, $^3J_{H,H}$ = 7.1 Hz, 24 H, $CH(CH_3)_2$], 1.23 [s, 9 H, $C(CH_3)_3$], 3.37 [sept, 4 H, $^3J_{H,H}$ = 7.1 Hz, $CH(CH_3)_2$] ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 26 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 24.00 [$CH(CH_3)_2$], 30.36 [$C(CH_3)_3$], 30.79 [$C(CH_3)_3$], 46.38 [$CH(CH_3)_2$], 90.89 (C_{sp}-C_{ipso}) ppm; C_{sp}-B signal not observed. MS (70 eV, EI): *m*/*z* (%) = 292 (25) [M^+], 277 (100) [M^+ − Me], 249 (95) [M^+ − *i*Pr]. MS (70 eV, HR-EI): *m*/*z* (%) = 292.3038 (30) [M^+; $^{12}C_{18}{}^1H_{37}{}^{14}N_2{}^{11}B$: 292.3049]; Δmmu = −1.1.

5b: Yield: 3.2 g (71%), b.p. 51 °C/0.03 mbar. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.13 (s, 9 H, $SiMe_3$), 1.21 [d, $^3J_{H,H}$ = 7.2 Hz, 24 H, $CH(CH_3)_2$], 3.36 [sept, $^3J_{H,H}$ = 7.1 Hz, 4 H, $CH(CH_3)_2$] ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 25 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = −0.19 ppm($SiMe_3$), 24.30 [$CH(CH_3)_2$], 46.87 [$CH(CH_3)_2$], 112.7 (C_{sp}-C_{ipso}) ppm; C_{sp}−B signal not observed. ^{29}Si NMR (39.8 MHz, $CDCl_3$): δ = −4.7 ppm. MS (70 eV, EI): *m*/*z* (%) = 308 (10) [M^+], 293 (100) [M^+ − Me], 265 (90) [M^+ − *i*Pr].

1-(1,3,2-Benzodioxaborol-2-yl)-2-(*tert*-butyl)acetylene (6a), 1-(*tert*-Butyl)-2-(5-methyl-1,3,2-benzodithiaborol-2-yl)acetylene (7a) and 1-(1,3,2-Benzooxathiaborol-2-yl)-2-(*tert*-butyl)acetylene (8a): $HCl{\cdot}OEt_2$ (2 M; 15.5 mL, 31 mmol) was added to a stirred solution of 1-bis(diisopropylamino)boryl-2-*tert*-butylacetylene (**5a**; 4.08 g, 14.0 mmol; in 40 mL of THF) at −78 °C within 15 min. Stirring was continued for 1 h and then 14.0 mmol of the corresponding aromatic diol (**6a**: 1.54 g of catechol; **7a**: 2.18 g of 4-methyldithiocatechol; **8a**: 1.76 g of 2-hydroxythiophenol; dissolved in 15 mL of THF) was added at room temp. The reaction mixture was stirred overnight. After filtration, the solvent was removed to yield **6a** and **8a** as colorless liquids and **7a** as a solid.

6a:[8] Yield: 1.8 g (64%), b.p. 49 °C/0.1 mbar. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.33 [s, 9 H, $C(CH_3)_3$], 7.05, 7.18 (m, 4 H, C_6H_4) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 24 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.31 [$C(CH_3)_3$], 32.19 [$C(CH_3)_3$], 86.90 (C_{sp}-C_{ipso}), 112.2, 122.4, 148.2 (C_6H_4) ppm; C_{sp}−B signal not observed.

7a: Yield: 1.9 g (57%), m.p. 51 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.33 [s, 9 H, $C(CH_3)_3$], 2.34 (s, 3 H, CH_3), 6.86, 7.61 (m, 3 H, C_6H_3) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 48 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.86 [$C(CH_3)_3$], 31.58 [$C(CH_3)_3$], 125.9, 126.7, 126.9, 135.6, 137.5, 140.9 (C_6H_3) ppm; C_{sp}−B signal not observed. MS (70 eV, EI): *m*/*z* (%) = 246 (100) [M^+], 231 (90) [M^+ − Me]. MS (70 eV, HR-EI): *m*/*z* (%) = 246.0700 (100) [M^+; $^{12}C_{13}{}^1H_{15}{}^{32}S_2{}^{11}B$: 246.0708]; Δmmu = −0.8.

8a: Yield: 1.84 g (61%), b.p. 53 °C/0.1 mbar. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.34 [s, 9 H, $C(CH_3)_3$], 7.1−7.6 (m, 4 H, C_6H_4) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 38 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.40 [$C(CH_3)_3$], 30.88 [$C(CH_3)_3$], 114.6, 123.7, 125.3, 126.1, 126.9, 156.5 (C_6H_4) ppm; C_{sp}−B signal not observed. MS (70 eV, EI): *m*/*z* (%) = 216 (100) [M^+]. MS (70 eV, HR-EI): *m*/*z* (%) = 216.0788 (92) [M^+; $^{12}C_{12}{}^1H_{13}{}^{16}O^{32}S^{11}B$: 216.0781]; Δmmu = 0.7.

1-(1,3,2-Benzodioxaborol-2-yl)-2-(trimethylsilyl)acetylene (6b), 1-(5-Methyl-1,3,2-benzodithiaborol-2-yl)-2-(trimethylsilyl)acetylene (7b) and 1-(1,3,2-Benzooxathiaborol-2-yl)-2-(trimethylsilyl)acetylene (8b): $HCl{\cdot}OEt_2$ (2 M; 16 mL, 32 mmol) was added to a stirred solution of 1-[bis(diisopropylamino)boryl]-2-(trimethylsilyl)acetylene (**5b**; 4.62 g, 15.0 mmol; in 40 mL of THF) at −78 °C within 15 min. Stirring was continued for 1 h and then 15.0 mmol of the corresponding aromatic diol (**6b**: 1.65 g of catechol; **7b**: 2.34 g of 4-methyldithiocatechol; **8b**: 1.89 g of 2-hydroxythiophenol; dissolved in 15 mL of THF) was added at room temp. The reaction mixture was stirred overnight. After filtration, the solvent was removed to yield colorless liquids **6b** and **8b**, and solid **7b**.

6b: Yield: 2.16 g (67%), b.p. 63 °C/0.1 mbar. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.25 (s, 9 H, $SiMe_3$), 7.11, 7.19 (m, 4 H, C_6H_4) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 23 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = −0.28 ($SiMe_3$), 113.0, 123.5, 147.9 (C_6H_4) ppm; C_{sp}−B signal not observed. ^{29}Si NMR (39.7 MHz, $CDCl_3$): δ = −15.7 ppm. MS (70 eV, EI): *m*/*z* (%) = 216 (35) [M^+], 201 (100) [M^+ − Me]. MS (70 eV, HR-EI): *m*/*z* (%) = 216.0799 (39) [M^+; $^{12}C_{11}{}^1H_{13}{}^{16}O_2{}^{28}Si^{11}B$: 216.0778]; Δmmu = 2.1.

7b: Yield: 2.88 g (73%), m.p. 67 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.23 (s, 9 H, $SiMe_3$), 2.36 (s, 3 H, CH_3), 7.12, 7.67 (m, 3 H, C_6H_3) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 47 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = −0.46 ppm($SiMe_3$), 21.04 (CH_3), 126.1, 126.8, 127.1, 131.6, 135.9, 140.7 (C_6H_3) ppm; C_{sp}−B signal not observed. ^{29}Si NMR (39.7 MHz, $CDCl_3$): δ = −16.9 ppm. MS (70 eV, EI): *m*/*z* (%) = 262 (50) [M^+], 247 (100) [M^+ − Me]. MS (70 eV, HR-EI): *m*/*z* (%) = 262.0476 (54) [M^+; $^{12}C_{12}{}^1H_{15}{}^{32}S_2{}^{28}Si^{11}B$: 262.0477]; Δmmu = −0.1.

8b: Yield: 2.31 g (66%), b.p. 70 °C/0.1 mbar. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.26 (s, 9 H, $SiMe_3$), 7.1−7.6 (m, 4 H, C_6H_4) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 37 ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = −0.53 ppm($SiMe_3$), 114.8, 123.9, 125.4, 126.3, 126.7, 156.4 (C_6H_4) ppm; C_{sp}−B signal not observed. ^{29}Si NMR (39.7 MHz, $CDCl_3$): δ = −16.4 ppm. MS (70 eV, EI): *m*/*z* (%) =

232 (60) [M^+], 217 (100) [M^+ − Me]. MS (70 eV, HR-EI): *m/z* (%) = 232.0557 (31) [M^+; $^{12}C_{11}{}^{1}H_{13}{}^{16}O^{32}S^{28}Si^{11}B$: 232.0550]; Δmmu = 0.7.

[η⁴-Bis(4-methyldithiocatecholborol-2-yl)cyclobutadiene](η⁵-cyclopentadienyl)cobalt(I) (9/9′), [η⁴-Bis(1,3,2-benzooxathiaborol-2-yl)cyclobutadiene](η⁵-cyclopentadienyl)cobalt(I) (10/10′), (η⁵-Cyclopentadienyl)[η⁴-tetrakis(dithiocatecholborol-2-yl)cyclobutadiene]cobalt(I) (11) and (η⁵-Cyclopentadienyl)[η⁴-tetrakis(1,3,2-benzooxathiaborol-2-yl)cyclobutadiene]cobalt(I) (12): Borylalkyne (**1b**: 1.52 g; **2**: 1.28 g; **3**: 2.60 g; **4**: 2.32 g; 8 mmol) was added at room temp. to a solution of dicarbonyl(η⁵-cyclopentadienyl)cobalt (0.72 g, 4 mmol) in 30 mL of toluene. The reaction mixture was heated under reflux for 4 d. After cooling, the precipitate was collected by filtration, washed several times with hexane and dried in vacuo.

9/9′: Yield: 0.98 g (51%), brown solid, m.p. 170−174 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.44 (s, 2 H, CH), 4.75 (s, 5 H, H_{Cp}), 6.56, 7.07, 8.24 (m, 8 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 60 (br.) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 80.98 (C_{Cp}), 83.54 (C_{4ring}), 126.1, 126.8, 140.9 (dithiocatechol) ppm. MS (70 eV, EI): *m/z* (%) = 476 (100) [M^+], 300 (75) [$M^+ - C_6H_4S_2BC_2H$], 150 (3) [$M^+ - C_6H_4S_2BC{\equiv}CBS_2C_6H_4$]. MS (70 eV, HR-EI): *m/z* (%) = 475.9581 (100) [M^+; $^{12}C_{21}{}^{1}H_{15}{}^{32}S_4{}^{11}B_2{}^{59}Co$: 475.9574]; Δmmu = 0.7.

10/10′: Yield: 0.80 g (45%), red-brown solid, m.p. 160−163 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 3.75 (s, 2 H, CH), 5.45 (s, 5 H, H_{Cp}), 6.90, 7.18, 7.88 (m, 8 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 50 (br.) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 81.34 (C_{Cp}), 83.97 (C_{4ring}), 115.1, 120.9, 124.2, 125.8, 126.7, 156.5 (2-hydroxythiophenol) ppm. MS (70 eV, EI): *m/z* (%) = 444 (100) [M^+], 284 (80) [$M^+ - C_6H_4OSBC_2H$], 150 (5) [$M^+ - C_6H_4OSBC{\equiv}CBOSC_6H_4$], 124 [CpCo]. MS (70 eV, HR-EI): *m/z* (%) = 444.0042 (100) [M^+; $^{12}C_{21}{}^{1}H_{15}{}^{16}O_2{}^{32}S_2{}^{11}B_2{}^{59}Co$: 444.0031]; Δmmu = 1.1.

11: Yield: 1.48 g (47%), red solid, m.p. 232 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 4.87 (s, 5 H, H_{Cp}), 7.32, 7.79, 8.09 (m, 16 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 63 (br.) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 79.90 (C_{Cp}), 84.38 (C_{4ring}), 125.4, 126.4, 141.4 (dithiocatechol) ppm. MS (70 eV, EI): *m/z* (%) = 776 (50) [M^+], 450 (70) [$M^+ - C_6H_4S_2BC{\equiv}CBS_2C_6H_4$]. MS (70 eV, HR-EI): *m/z* (%) = 775.9119 (80) [M^+; $^{12}C_{33}{}^{1}H_{21}{}^{32}S_8{}^{11}B_4{}^{59}Co$: 775.9113]; Δmmu = 0.6.

12: Yield: 1.30 g (45%), brown solid, m.p. 213 °C (dec.). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 5.37 (s, 5 H, H_{Cp}), 7.2−7.6 (m, 16 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 50 (br.) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 83.47 (C_{Cp}), 86.07 (C_{4ring}), 115.1, 121.0, 124.2, 125.5, 126.6, 127.9, 156.5 (2-hydroxythiophenol) ppm. MS (70 eV, EI): *m/z* (%) = 712 (50) [M^+], 418 (100) [$M^+ - C_6H_4OSBC{\equiv}CBOSC_6H_4$]. MS (70 eV, HR-EI): *m/z* (%) = 712.0046 (100) [M^+; $^{12}C_{33}{}^{1}H_{21}{}^{16}O_4{}^{32}S_4{}^{11}B_4{}^{59}Co$: 712.0026]; Δmmu = 2.0.

[η⁴-Bis(*tert*-butyl)bis(catecholborol-2-yl)cyclobutadiene](η⁵-cyclopentadienyl)cobalt(I) (13a/13a′), [η⁴-Bis(*tert*-butyl)bis(4-methyldithiocatecholborol-2-yl)cyclobutadiene](η⁵-cyclopentadienyl)cobalt(I) (14a/14a′) and [η⁴-Bis(1,3,2-benzooxathiaborol-2-yl)bis(*tert*-butyl)cyclobutadiene](η⁵-cyclopentadienyl)cobalt(I) (15a/15a′): Borylacetylene (**6a**: 0.80 g; **7a**: 0.98 g; **8a**: 0.86 g; 4 mmol) was added at −20 °C to a solution of (η⁵-cyclopentadienyl)bis(ethene)cobalt (0.36 g, 2 mmol) in 40 mL of hexane. The reaction mixture was stirred at room temp. for 2 d. After filtration, the solvent was evaporated almost to dryness. The resulting orange-yellow solid was crystallized from toluene.

13a/13a′: Yield: 0.73 g (70%), orange-yellow solid, m.p. 145−150 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.36 [s, 18 H, $C(CH_3)_3$], 5.02 (s, 5 H, H_{Cp}), 7.09, 7.23 (m, 8 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 36 (br.) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.83 [$C(CH_3)_3$], 32.20 [$C(CH_3)_3$], 80.15 (C_{Cp}), 101.8 (C_{4ring}), 112.2, 122.3, 148.5 (catechol) ppm. MS (70 eV, EI): *m/z* (%) = 524 (100) [M^+], 509 (90) [M^+ − Me], 467 (10) [M^+ − *t*Bu], 387 (35) [$M^+ - t$BuC≡C*t*Bu + 1], 324 (38) [$M^+ - H_4C_6O_2BC{=}Ct$Bu], 124 (75) [CpCo]. MS (70 eV, HR-EI): *m/z* (%) = 524.1727 (100) [M^+; $^{12}C_{29}{}^{1}H_{31}{}^{16}O_4{}^{11}B_2{}^{59}Co$: 524.1740]; Δmmu = −1.3.

14a/14a′: Yield: 0.80 g (65%), orange-yellow solid, m.p. 162−165 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.16 [s, 18 H, $C(CH_3)_3$], 2.43 (s, 6 H, CH_3), 5.18 (s, 5 H, H_{Cp}), 7.14, 7.65 (m, 6 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 63 (br.) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.49 (CH_3), 31.41 [$C(CH_3)_3$], 32.25 [$C(CH_3)_3$], 79.95 (C_{4ring}), 80.66 (C_{Cp}), 125.3, 125.8, 126.3, 126.6, 129.0, 131.6 (4-methyldithiocatechol) ppm. MS (70 eV, EI): *m/z* (%) = 616 (10) [M^+], 370 (9) [$M^+ - H_3CH_3C_6S_2BC{\equiv}Ct$Bu], 124 (85) [CpCo]. MS (70 eV, HR-EI): *m/z* (%) = 616.1163 (100) [M^+; $^{12}C_{31}{}^{1}H_{35}{}^{32}S_4{}^{11}B_2{}^{59}Co$: 616.1139]; Δmmu = 2.4.

15a/15a′: Yield: 0.72 g (64%), orange-yellow solid, m.p. 154−159 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.20 [s, 18 H, $C(CH_3)_3$], 5.07 (s, 5 H, H_{Cp}), 7.02−7.55 (m, 8 H, H_{aryl}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 31.58 [$C(CH_3)_3$], 32.63 [$C(CH_3)_3$], 80.67 (C_{Cp}), 85.20 (C_{4ring}) 114.3, 123.2, 124.9, 125.6, 128.3, 156.8 (2-hydroxythiophenol) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 50 (br.) ppm. MS (70 eV, EI): *m/z* (%) = 556 (70) [M^+], 541 (15) [M^+ − Me], 499 (10) [M^+ − *t*Bu], 419 (10) [$M^+ - t$BuC≡C*t*Bu + 1], 340 (38) [$M^+ - H_4C_6OSBC{\equiv}Ct$Bu], 124 (100) [CpCo]. MS (70 eV, HR-EI): *m/z* (%) = 556.1312 (100) [M^+; $^{12}C_{29}{}^{1}H_{31}{}^{16}O_2{}^{32}S_2{}^{11}B_2{}^{59}Co$: 556.1284]; Δmmu = 2.8.

(η⁵-Cyclopentadienyl)[η⁴-tris(catecholborol-2-yl)tris(trimethylsilyl)cyclohexatriene]cobalt(I) (13b/13b′), (η⁵-Cyclopentadienyl)[η⁴-tris(4-methyldithiocatecholborol-2-yl)tris(trimethylsilyl)cyclohexatriene]cobalt(I) (14b/14b′) and (η⁵-Cyclopentadienyl)[η⁴-tris(1,3,2-benzooxathiaborol-2-yl)tris(trimethylsilyl)cyclohexatriene]cobalt(I) (15b/15b′): 1-Boryl-2-silylacetylene (**6b**: 1.29 g; **7b**: 1.48 g; **8b**: 1.39 g; 6 mmol) was added at room temp. to a solution of (η⁵-cyclopentadienyl)bis(ethene)cobalt (0.36 g, 2 mmol) in 40 mL of hexane. The reaction mixture was stirred at room temp. for 3 d. The solution was concentrated and a brown-red residue was obtained. Purification by column chromatography (Florosil/hexane) with hexane/toluene (2:1) afforded an air-sensitive red oil.

13b/13b′: Yield: 0.65 g (42%). ^{1}H NMR (200.1 MHz, C_6D_6): δ = 0.18, 0.20 (s, 27 H, $SiMe_3$), 5.05 (s, 5 H, H_{Cp}), 6.35, 6.75, 6.82 (m, 12 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, C_6D_6): δ = 33 (br.) ppm. ^{13}C NMR (50.3 MHz, C_6D_6): δ = −0.51, −0.04, 0.40, 0.56 ($SiMe_3$), 82.61 (C_{Cp}), 112.0, 122.1, 148.7 (catechol), 122.0, 122.5, 146.4, 149.9 (central C_{6ring}) ppm. ^{29}Si NMR (39.7 MHz, C_6D_6): δ = −21.8, −18.1, −0.7, 20.3 ppm. MS (70 eV, EI): *m/z* (%) = 772 (100) [M^+], 699 (7) [M^+ − Me]. MS (70 eV, HR-EI): *m/z* (%) = 772.2056 (100) [M^+; $^{12}C_{38}{}^{1}H_{44}{}^{16}O_6{}^{28}Si_3{}^{11}B_3{}^{59}Co$: 772.2057]; Δmmu = −0.1.

14b/14b′: Yield: 0.73 g (40%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.20 (s, 27 H, $SiMe_3$), 2.28 (s, 9 H, CH_3), 5.45 (s, 5 H, H_{Cp}), 7.01−7.90 (m, 12 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 60 (br.) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 0.29 ($SiMe_3$), 20.98 (CH_3), 79.76 (C_{Cp}), 124.5, 126.6, 130.1, 132.8, 140.2 (4-

methyldithiocatechol), 126.4 (central C_{6ring}) ppm. ^{29}Si NMR (39.7 MHz, $CDCl_3$): $\delta = -21.9$ ppm. MS (70 eV, EI): *m/z* (%) = 910 (25) [M^+], 895 (10) [$M^+ - Me$], 837 (10) [$M^+ - SiMe_3$], 745 (20) [$M^+ - H_3CC_6H_3S_2B$]. MS (70 eV, HR-EI): *m/z* (%) = 910.1175 (100) [M^+; $^{12}C_{41}{}^1H_{50}{}^{32}S_6{}^{28}Si_3{}^{11}B_3{}^{59}Co$: 910.1155]; Δmmu = 2.0.

15b/15b′: Yield: 0.62 g (38%). ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.21 (s, 27 H, $SiMe_3$), 4.96 (s, 5 H, H_{Cp}), 6.20−6.99 (m, 12 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 49 (br.) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = -0.34$ ($SiMe_3$), 81.24 (C_{Cp}), 115.0, 124.1, 125.6, 126.5, 126.8, 156.6 (2-hydroxythiophenol), 132.2 (central C_{6ring}) ppm. ^{29}Si NMR (39.7 MHz, $CDCl_3$): $\delta = -20.2$ ppm. MS (70 eV, EI): *m/z* (%) = 820 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 820.1392 (30) [M^+; $^{12}C_{38}{}^1H_{44}{}^{16}O_3{}^{32}S_3{}^{28}Si_3{}^{11}B_3{}^{59}Co$: 820.1371]; Δmmu = 2.1.

[η^4-Bis(*tert*-butyl)cyclobutadiene](η^5-cyclopentadienyl)cobalt(I) (16): In attempts to purify **13a**, **14a** or **15a** by column chromatography on Florosil, the crude products were eluted with hexane; only hydrolysis to **16** was observed. Yellow solid, m.p. 68 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.03 [s, 18 H, $C(CH_3)_3$], 3.56 (s, 2 H, CH), 4.82 (s, 5 H, H_{Cp}) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 29.65 [$C(CH_3)_3$], 29.81 [$C(CH_3)_3$], 78.81 (CCp), 50.88, 90.36 (C_{4ring}) ppm. MS (70 eV, EI): *m/z* (%) = 288 (100) [M^+], 273 (80) [$M^+ - Me$], 124 (10) [CpCo]. MS (70 eV, HR-EI): *m/z* (%) = 288.1283 (100) [M^+; $^{12}C_{17}{}^1H_{25}{}^{59}Co$: 288.1289]; Δmmu = −0.6.

Tris(1,3,2-benzodithiaborol-2-yl)benzene (17/17′), Tris(1,3,2-benzooxathiaborol-2-yl)benzene (18/18′), Hexakis(1,3,2-benzodithiaborol-2-yl)benzene (19) and Hexakis(1,3,2-benzooxathiaborol-2-yl)benzene (20): Borylalkyne (**1a**: 0.52 g; **2**: 0.48 g; **3**: 0.98 g; **4**: 0.88 g; 3 mmol) and octacarbonyldicobalt (0.05 g, 0.15 mmol, 5 mol-%) were heated under reflux in 20 mL of toluene for 4 d. The solid was separated, washed several times with small amounts of solvents (**17/17′** and **18/18′**: hexane and toluene; **19** and **20**: toluene and CH_2Cl_2) and dried in vacuo.

17/17′: Yield: 0.40 g (77%), colorless solid, m.p. 192−194 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 7.34, 7.89, 8.42 (m, 15 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 61 (br.) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 126.8, 131.1, 140.1 (dithiocatechol) ppm; owing to low solubility,the signals of the central benzene ring carbon atoms were not observed. MS (70 eV, EI): *m/z* (%) = 528 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 527.9781 (100) [M^+; $^{12}C_{24}{}^1H_{15}{}^{32}S_6{}^{11}B_3$: 527.9777]; Δmmu = 0.4.

18/18′: Yield: 0.30 g (62%), colorless solid, m.p. 176−179 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 6.9−8.7 (m, 15 H, H_{aryl}) ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 51 (br.) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 111.8, 115.1, 121.1, 130.5, 135.5, 156.2 (2-hydroxythiophenol) ppm; the signals of the central benzene ring carbon atoms were not found. MS (70 eV, EI): *m/z* (%) = 480 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 480.0489 (100) [M^+; $^{12}C_{24}{}^1H_{15}{}^{16}O_3{}^{32}S_3{}^{11}B_3$: 480.0462]; Δmmu = 2.7.

19: Yield: 0.70 g (71%), colorless solid, m.p. > 300 °C. MS (70 eV, EI): *m/z* (%) = 978 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 977.9128 (20) [M^+; $^{12}C_{42}{}^1H_{24}{}^{32}S_{12}{}^{11}B_6$: 977.9085]; Δmmu = 4.3.

20: 0.69 g (78%), colorless solid, m.p. > 300 °C. MS (70 eV, EI): *m/z* (%) = 882 (100) [M^+]. MS (70 eV, HR-EI): *m/z* (%) = 882.0461 (100) [M^+; $^{12}C_{42}{}^1H_{24}{}^{16}O_6{}^{32}S_6{}^{11}B_6$: 882.0455]; Δmmu = 0.6.

X-ray Crystal-Structure Determinations of 1b, 5b, 6b, 14a, 15a and 16: Crystal data and details of the structure determinations are listed in Table 1. Reflections covering a whole sphere in the reciprocal space were collected with a Bruker-AXS SMART 1000 diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite mono-

Table 1. Crystal data and structure refinement for **1b**, **5b**, **6b**, **14a**, **15a** and **16**

	1b	**5b**	**6b**	**14a**	**15a**	**16**
Empirical formula	$C_{15}H_{23}BClNS_2$	$C_{17}H_{37}BN_2Si$	$C_{11}H_{13}BO_2Si$	$C_{31}H_{35}B_2CoS_4$	$C_{29}H_{31}B_2CoO_2S_2$	$C_{17}H_{25}Co$
Formula mass	327.72	308.39	216.11	616.38	556.21	288.30
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	orthorhombic	orthorhombic
Space group	$P2_1/c$	*Pbca*	$P2_1/c$	$P\bar{1}$	*Pbcn*	$Pna2_1$
a [Å]	16.2143(9)	18.6824(9)	18.282(2)	9.2159(1)	20.2951(4)	35.667(2)
b [Å]	7.5937(4)	11.8851(6)	5.4417(6)	9.2834(1)	8.9817(2)	5.9534(3)
c [Å]	15.5136(9)	19.0239(10)	11.7267(13)	18.0504(3)	30.1865(3)	14.3418(6)
α [°]	90	90	90	89.922(1)	90	90
β [°]	106.953(1)	90	95.612(2)	84.980(1)	90	90
γ [°]	90	90	90	88.738(1)	90	90
V [Å^3]	1827.1(2)	4224.1(4)	1161.1(2)	1538.0(3)	5502.5(2)	3045.4(2)
Z	4	8	4	2	8	8
$D_{calcd.}$ [g·cm^{-3}]	1.191	0.970	1.236	1.33	1.343	1.258
μ [mm^{-1}]	0.428	0.109	0.178	0.85	0.80	1.109
F(000)	696	1376	456	644	2320	1232
Crystal size [mm]	0.40 × 0.32 × 0.16	0.57 × 0.20 × 0.14	0.50 × 0.50 × 0.30	0.40 × 0.08 × 0.08	0.16 × 0.14 × 0.06	0.35 × 0.18 × 0.10
θ_{max} [°]	32.06	32.04	32.03	27.5	22.3	32.03
Index ranges	−24/22, 0/11, 0/23	0/27, 0/17, 0/28	−26/26, 0/ 7, 0/17	−11/11, −12/12, −23/23	−21/21, −9/9, −32/32	0/53, 0/8, −21/16
Reflections collected	32418	48978	19854	16166	34030	27277
Reflections independent (R_{int})	6329 (0.0341)	7305 (0.0449)	3961 (0.0399)	6996 (0.0363)	3477 (0.0740)	9051(0.0426)
Parameters	335	338	188	362	331	524
Goodness-of-fit on F^2	1.069	1.041	1.058	1.03	1.02	1.051
*R*1 [$I > 2\sigma(I)$]	0.0376	0.0417	0.0361	0.0360	0.0345	0.0392
*wR*2 (all reflections)	0.1042	0.1128	0.0994	0.0852	0.0814	0.0899
T [K]	103(2)	103(2)	103(2)	200(2)	200(2)	103(2)
Residual electron density [e/Å^3]	0.37/−0.24	0.48/−0.19	0.48/−0.23	0.36/−0.29	0.21/−0.28	0.67/−0.64

chromator, ω-scan). Empirical absorption corrections were applied. The structures were solved by direct methods (SHELXS-86)[17] and refined by least-squares methods based on F^2 with all measured reflections (SHELXL-97).[18] All non-hydrogen atoms were refined anisotropically. In **1b** the dithiocatechol is disordered and the cell contains one diisopropylamino hydrochloride. CCDC-238364 (**1b**), -238365 (**5b**), -238366 (**6b**), -238367 (**15a**), -238368 (**16**) and -238369 (**14a**) 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: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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