

Reactivity of Carboranylacetylenes towards Cobalt Complexes

Avijit Goswami,^[a] Yong Nie,^[a] Thomas Oeser,^[b] and Walter Siebert*^[a]*Dedicated to Professor Herbert Schumann on the occasion of his 70th birthday***Keywords:** Carboranes / Carboranylacetylenes / Cobalt / (Cyclobutadiene)cobalt complexes / (Cyclopentadienone)cobalt complexes

The reaction of 1,6-diiodo- C_4B_2 *nido*-carborane derivative **1** with RC_2Li ($R = Me, SPh$) yields the corresponding carboranylacetylenes **2b,c**. Treatment of the PPh_2 -substituted *nido*-carborane **3a** with PhC_2ZnCl in the presence of a catalytic amount of $Pd(PPh_3)_4$ leads to the known basal-substituted *nido*-carboranylacetylene **2a**. The synthesis of apical-substituted compound **4b** is achieved by the substitution of **3b** by a Pd^0 -catalyzed Nigishi-type cross-coupling reaction; the basal boron atom is blocked by the *n*-butyl group. The 1,3-dicarboranyl-substituted (η^4 -cyclobutadiene)cobalt complexes **5a,c** are obtained from the reactions of **2a,c** with stoichiomet-

ric amounts of $CpCo(C_2H_4)_2$. The 1,6-dialkynyl carborane **6** reacts regioselectively at the basal acetylene group with a stoichiometric amount of $CpCo(CO)_2$ to give 1,3-dicarboranyl-substituted (cyclobutadiene)cobalt complex **7**. The dicarboranyl-substituted (cyclopentadienone)cobalt complex **8** is formed by the reaction of compound **4b** with $CpCo(CO)_2$. The new compounds are characterized by NMR spectroscopy, mass spectrometry, and by X-ray crystal structure analyses for **5a** and **8**.

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Introduction

Over the past decades numerous functionalized carboranes were synthesized,^[1] and their properties have been extensively investigated by both theoretical^[2] and experimental analyses.^[3] A large number of carborane derivatives are used in medicinal and pharmaceutical applications.^[4] The reactivity of carboranylacetylenes towards transition-metal complexes has received relatively little attention. In 1973, Hawthorne et al.^[5] reported the first generation of 1,2,4-tris(*closo*-1,2- $C_2B_{10}H_{11}$ -1-yl)benzene by the reaction of 1-ethynyl-1,2-carborane with a catalytic amount of bis(acrylonitrile)nickel(0). Michl et al.^[6] presented a convenient route to synthesize tris(1,12-carboranyl)-substituted benzene derivatives by a palladium-catalyzed cross-coupling of three 1,12-dicarba-*closo*-dodecaboranyl units to a 1,3,5-trihalobenzene. In 1982, a series of σ -1-*ortho*- and σ -1-*meta*-carboranylacetylenides of copper, silver, palladium, platinum, and iron were synthesized by Zakharkin and his co-workers.^[7] In 2003, Grimes^[8] published an account on cluster formation between a 1,3,5-tris(carboranylacetylene)benzene and $Co_2(CO)_8$. Very recently, we reported cobalt-mediated

dimerization reactions of apically alkynyl-substituted *closo*- C_2B_5 carboranes with cobalt complexes.^[9] While the inherent scope and reaction efficiencies are found to be limited, the study introduces the attractive prospect that small alkynyl-substituted carboranes might be utilized for metal-mediated dimerization reactions. Here we report the synthesis of functionalized *nido*- C_4B_2 carboranes and the reactions of some of the alkynyl-substituted derivatives with cobalt complexes.

Results and Discussion

Preparation and Characterization of C_4B_2 *nido*-Carboranylacetylenes **2b,c**

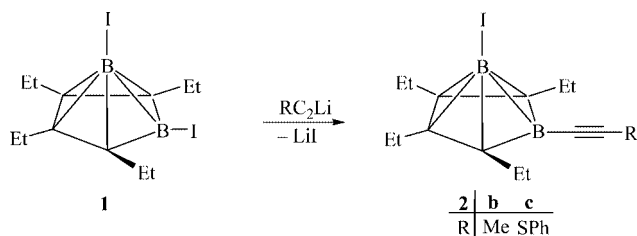
Because of the easy accessibility and high stability of the peralkylated 2,3,4,5-tetracarba-*nido*-hexaboranes(**6**)^[10] (in comparison with the parent $C_4B_2H_6$ ^[11]), their reactivity has drawn special attention.^[12,13] To investigate substitution reactions of C_4B_2 *nido*-carboranes, functional groups other than alkyl or aryl groups are needed at the boron atom(s). Wrackmeyer et al.^[12] and more recently our group^[14] noticed that nucleophilic substitutions proceeded smoothly at the basal boron atom to give the corresponding carboranes with organyl, stannyl, diphenylphosphanyl, N-bonded (μ -NS)Fe₂(CO)₆ groups, as well as with the [CpFe(CO)₂] group. However, even the presence of an excess of nucleo-

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

[b] Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
E-mail: oeser@uni-hd.de

phile was not enough to achieve substitution at the apical boron atom.^[12,14]

Analogously, nucleophilic substitution reactions of 2,3,4,5-tetraethyl-1,6-diiodo-2,3,4,5-tetracarba-*nido*-hexaborane(6) (**1**) with RC_2Li ($\text{R} = \text{Me}$, SPh) led to the corresponding basal-substituted carborane derivatives **2b,c** in high yields (Scheme 1). In agreement with the findings of Wrackmeyer et al.^[12] and our recent results,^[14] an excess of lithium acetylides did not effect additional substitution at the apical boron atom. Compounds **2b,c** (light yellow oils) were characterized by ^1H -, ^{13}C -, and ^{11}B NMR spectroscopy, as well as by mass spectrometry. The *nido*- C_4B_2 framework is retained, and little difference is found in the ^1H - and ^{13}C NMR spectra in comparison to that of compound **1**. In the ^{11}B NMR spectra of **2b,c** the basal boron atoms give signals at $\delta = 10$ – 12 ppm, which are only slightly shifted downfield from that of **1** ($\delta = 5.5$ ppm), while the shifts of the signals for the apical boron atoms are the same as that of the starting carborane **1** ($\delta = -52.7$ ppm).

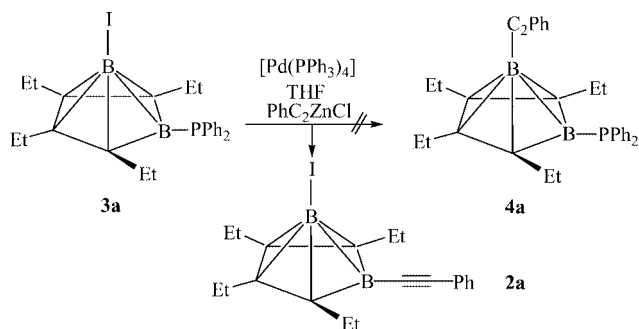


Scheme 1.

The ^1H NMR spectrum of **2b** exhibits the signals ($\delta = 1.2$ – 2.4 ppm) for the ethyl groups, in addition to the methyl resonance ($\delta = 1.98$ ppm). In the ^{13}C NMR spectrum, a signal ($\delta = 112.4$ ppm) is found for the skeletal carbon atoms nonadjacent to the basal boron atom, whereas the signals for the boron-bound carbon atoms and for the acetylene carbon atoms are not observed. Similarly, the ^1H NMR spectrum of **2c** shows the signals ($\delta = 1.3$ – 2.4 ppm) for the ethyl groups along with the multiplets ($\delta = 7.2$ – 7.6 ppm) for the aryl protons. The ^{13}C NMR spectrum features a signal at $\delta = 113.0$ ppm for the skeletal carbon atoms nonadjacent to the basal boron atom; however, the signals for the boron-bound carbon atoms and the acetylene carbon atoms are not detected. EI-MS data confirm the identity of carboranes **2b,c** through the appearance of the molecular ion peaks with the correct isotopic pattern.

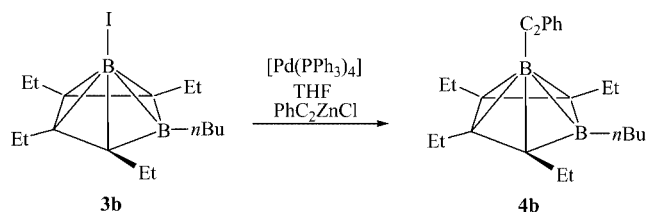
Substitution Reactions at the Apical Boron Atom of **3a**

In most of the cases, the apical boron–halogen bonds are found to be inert;^[12,14] however, substitution reactions can be achieved by Pd^0 -catalyzed Nigishi-type cross-coupling reactions.^[15] Analogously, an attempt to prepare the carborane **4a** by the reaction of **3a** with PhC_2ZnCl in the presence of a catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ was not successful, as the known carborane **2a**^[14] was obtained by the substitution of PPh_2 at the basal boron atom (Scheme 2).



Scheme 2.

On the other hand, treatment of compound **3b** with PhC_2ZnCl in the presence of a catalytic amount of $\text{Pd}(\text{PPh}_3)_4$ led to the expected carborane **4b** in moderate yield (Scheme 3). Compound **4b** (yellow oil) was characterized by ^1H -, ^{13}C -, and ^{11}B NMR spectroscopy, as well as by mass spectrometry. The ^{11}B NMR signal of the substituted apical boron atom is shifted only slightly downfield to $\delta = -50.5$ ppm, whereas the chemical shift for the basal boron atom remains the same as that for **3b** ($\delta = 19$ ppm). In the EI mass spectrum of **4b**, the molecular ion peak appears at $m/z = 344$ with the expected isotopic distribution.

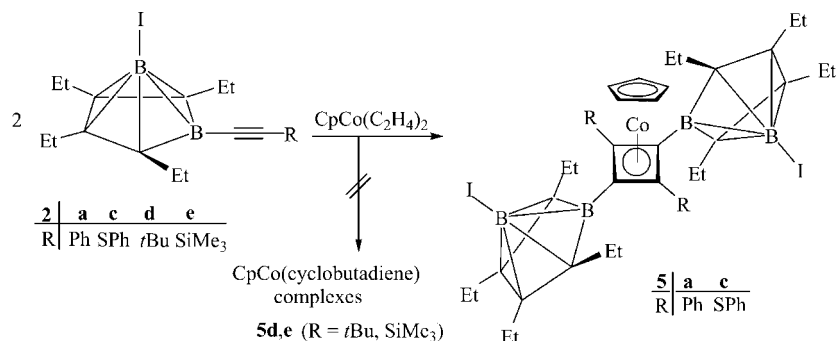


Scheme 3.

Formation of Bis(carboranyl)cyclobutadiene Cobalt Complexes **5** and **7**

No reaction was observed between carboranylacetylene derivatives **2** with catalytic and stoichiometric amounts of $\text{CpCo}(\text{CO})_2$ in refluxing toluene for several days, as monitored by ^{11}B NMR spectroscopy. However, adding $\text{CpCo}(\text{C}_2\text{H}_4)_2$ to the reaction mixture and refluxing for an additional two days, followed by column chromatography afforded the 1,3-dicarboranyl-substituted $\text{CpCo}(\eta^4\text{-cyclobutadiene})$ complexes **5a,c** (Scheme 4). No reaction was observed with **2d,e**.

The *trans*-1,3-isomers are sterically favored, as confirmed by the solid-state structure of **5a**. However, several known complexes have *cis*-bis(trimethylsilyl)cyclobutadiene ligands.^[16] The stereochemistry problem was resolved unequivocally by the analysis of the major peaks in the mass spectra with respect to the degradation of the cyclobutadiene ring. In general, three different acetylene molecules are released from the molecular ion of the *cis* isomer, whereas only one acetylene molecule is released from the *trans* isomer.^[17] Here, in both of **5a** and **5c**, only a single acetylene molecule was released from the molecular ion. Therefore,



Scheme 4.

the mass spectra clearly provide evidence for *trans* isomers. The ^{11}B NMR signals of **5a,c** for the basal boron atoms are shifted downfield to $\delta = 18$ ppm, while the chemical shifts for the apical boron atoms remain the same as those for in the starting carboranes ($\delta = -52$ ppm). The ^1H NMR spectra of **5a,c** show the multiplets ($\delta = 7.1\text{--}7.6$ ppm) for the aryl hydrogen atoms in addition to the Cp resonances ($\delta = 4.95$ and 5.10 ppm). In the ^{13}C NMR spectra, the signals ($\delta = 84\text{--}86$ ppm) for the Cp–C are observed, but the signals for the four quaternary carbon atoms of the cyclobutadiene ring are not found.

The structure of **5a** was characterized by performing a single-crystal X-ray diffraction analysis. Two independent molecules were found in the asymmetric unit with very similar distances and angles; the structure of one molecule is shown in Figure 1. It reveals almost equal C–C bond lengths within the cyclobutadiene ring, and none of the phenyl groups lie in the C_4 plane. The conformation is highly influenced by the bulky C_4B_2 *nido*-carboranyl groups, which are oriented away from the metal center.

Regioselective reactivity of the carboranylacetylene derivative **6**^[14] towards cobalt complexes CpCoL_2 ($\text{L} = \text{CO}, \text{C}_2\text{H}_4$) was observed. In the reactions of CpCoL_2 with the C_4B_2 *nido*-carborane **6** containing two acetylene moieties at the boron atoms, only the basal boron-substituted acetylene unit undergoes cyclobutadiene ring formation to give **7** (Scheme 5). The ^{11}B NMR spectrum of complex **7** exhibits signals at $\delta = 15$ and -50.4 ppm; the latter value for the apical boron atom is shifted slightly downfield relative to that of the starting carborane **6**. The mass spectrum shows the molecular ion peak with the expected isotopic pattern.

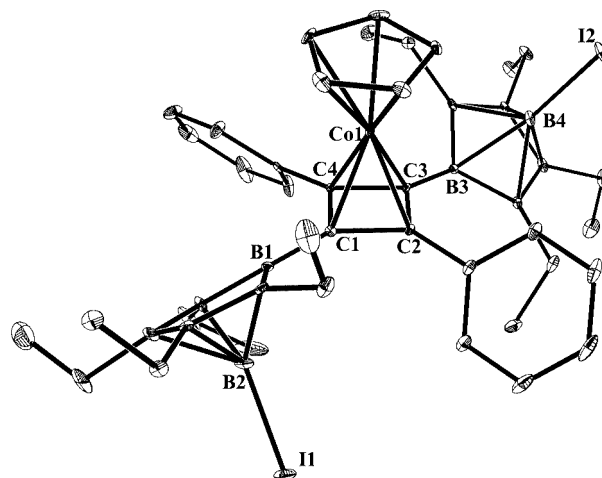
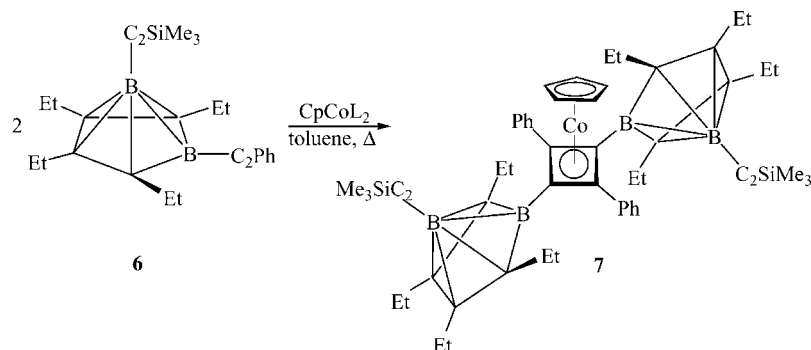


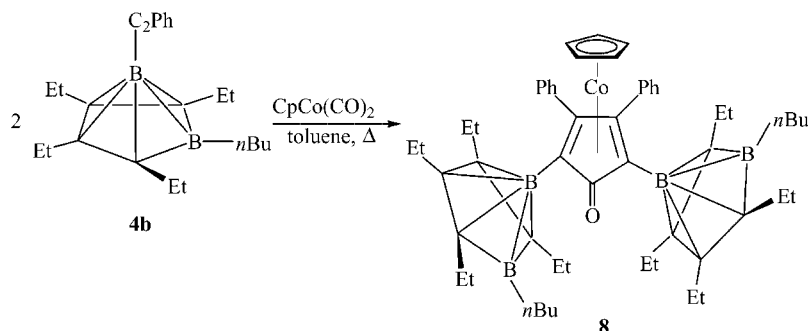
Figure 1. Molecular structure of **5a** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: C1–B1 1.559(6), C3–B3 1.549(6), C1–C2 1.471(5), C2–C3 1.480(5), C3–C4 1.465(5), C4–C1 1.466(5), B2–I1 2.131(5), B4–I2 2.114(5), B1–B2 1.943(6), B3–B4 1.820(6), C1–C2–C3 91.2(3), C2–C3–C4 88.2(3), C3–C4–C1 92.0(3), C4–C1–C2 88.5(3), B1–B2–I1 144.5(3), B3–B4–I2 141.6(3). Only one of the two independent molecules is shown to provide a better overview.

(η^5 -Cyclopentadienyl)(η^4 -2,5-bis-carboranyl)(cyclopentadienone)cobalt Complex **8**

To investigate the reactivity of the apical boron-bound acetylene group, the carboranylacetylene derivative **4b** was prepared (see earlier), in which the basal boron atom is blocked by the *n*-butyl group. Interestingly, the reaction of compound **4b** with a stoichiometric amount of CpCo –



Scheme 5.



Scheme 6.

(CO)₂ led to the 2,5-dicarboranyl-substituted (η^4 -cyclopentadienone)cobalt complex **8** in good yield (Scheme 6). It was characterized by ¹H-, ¹³C-, and ¹¹B NMR spectroscopy, mass spectrometry, and X-ray crystal structure analysis. As expected, the ¹¹B NMR signal of the apical boron atom is shifted downfield to $\delta = -44.4$ ppm. The ¹H NMR spectrum of **8** shows a singlet at $\delta = 4.95$ ppm for C₅H₅, in addition to the phenyl group resonances ($\delta = 6.90$ – 7.63 ppm). In the ¹³C NMR spectrum, the signals for the Cp–C and carbonyl groups are observed at $\delta = 81.7$ and 188.1 ppm, respectively, while the signals for the cyclopentadienone ring are not found. The IR spectrum of **8** shows a band at $\tilde{\nu} = 1593$ cm^{−1}, and the appearance of the molecular ion peak with the correct isotopic distribution in the EI-MS data confirms the identity.

The solid-state structure of **8** was characterized by performing a single-crystal X-ray diffraction analysis (Figure 2). Four molecules of **8** crystallized with one hexane molecule. As expected,^[18] the structure reveals that the bulky carboranyl groups are bound to α -carbon atoms of the cyclopentadienone ring to reduce the steric strain.

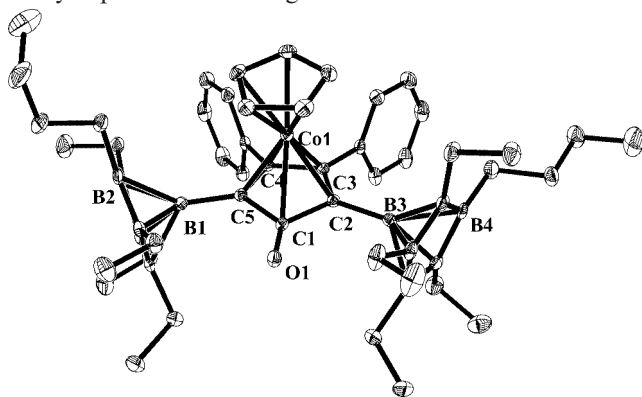


Figure 2. Molecular structure of **8** in the solid state; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and bond angles [°]: C5–B1 1.549(5), C2–B3 1.560(5), C1–C2 1.490(5), C2–C3 1.427(5), C3–C4 1.452(5), C4–C5 1.447(5), C5–C1 1.488(5), C1–O1 1.241(4), B1–B2 1.878(6), B3–B4 1.851(6), C1–C2–C3 108.0(3), C2–C3–C4 108.6(3), C3–C4–C5 109.3(3), C4–C5–C1 106.7(3), C5–C1–C2 106.3(3), O1–C1–C5 126.5(3), O1–C1–C2 126.9(3).

Conclusions

The reactions of carboranylacetylenes with catalytic and stoichiometric amounts of cobalt complexes CpCoL₂ (L =

CO, C₂H₄) have been studied. Reactions in the presence of catalytic amounts of [CpCoL₂] with carboranylacetylenes **2**, **4b**, and **6** do not lead to benzene derivatives, which can be explained on steric grounds. The (η^4 -1,3-dicarboranyl-cyclobutadiene)cobalt complexes **5a,c** are formed by the reactions of **2a,c** with stoichiometric amounts of CpCo(C₂H₄)₂. Regioselective reactions occur between CpCoL₂ and the C₄B₂ *nido*-carborane **6**. Only the basal-substituted borylacetylene moiety of compound **6** is involved in cyclobutadiene ring formation, whereas the apical-substituted borylacetylene unit remains unreacted. The reaction of carboranylacetylene **4b**, carrying an *n*-butyl group at the basal boron atom, with CpCo(CO)₂ leads to the (cyclopentadienone)cobalt complex **8**. The cobalt complexes **5**, **7**, and **8** are stable at room temperature and are resistant to light, oxygen, and moisture.

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-, ¹³C- and ¹¹B NMR spectra were recorded with a Bruker AC 200 spectrometer. ¹H- and ¹³C NMR spectra were referenced to (CH₃)₄Si, and ¹¹B NMR spectra were referenced to F₃B·OEt₂. IR spectra were recorded with a Bruker IFS 28 FT spectrometer. 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 that were filled under nitrogen and sealed. The *nido*-carboranes **1**,^[19] **2a,d,e**,^[14] **3a**,^[14] **6**,^[14] and CpCo(C₂H₄)₂^[20] were prepared according to literature procedures. CpCo(CO)₂ was purchased from Aldrich®.

General Procedure for Basal Boron-Substituted Carboranylacetylenes **2b,c**

An appropriate solution of lithium acetylide in hexane (30 mL) was cooled to -40 °C and added by syringe to a solution of the *nido*-carborane **1** in hexane (20 mL) at -78 °C. The mixture was warmed to room temp. and stirred for 2 d. After filtration, the light yellow solution was dried in vacuo to give a yellow oil.

2,3,4,5-Tetraethyl-1-iodo-6-methylethynyl-2,3,4,5-tetracarba-*nido*-hexaborane(6) (2b): Starting materials: compound **1** (0.9 g, 2.05 mmol) and MeC₂Li (0.23 g, 5.0 mmol). Yield: 0.5 g (69%), yellow oil. ¹H NMR (200.1 MHz, CDCl₃): $\delta = 1.25$ (t, ³J_{H,H} = 7.6 Hz, 12 H, CH₂CH₃), 1.98 (s, 3 H, Me), 2.22 (m, 8 H, CH₂CH₃) ppm. ¹³C NMR (50.3 MHz, CDCl₃): $\delta = 13.4$, 14.3 (CH₂CH₃), 18.2

(Me), 18.1, 19.6 (CH₂CH₃), 112.4 (skeletal carbon atoms nonadjacent to the basal boron) ppm; skeletal carbon atoms adjacent to the basal boron and alkynyl carbon atoms were not observed. ¹¹B NMR (64.2 MHz, CDCl₃): δ = 10 (br., B_{basal}), 52.7 (s, B_{apical}) ppm. MS (EI, 70 eV): *m/z* (%) = 352 (100) [M⁺], 225 (20) [M⁺ – I]. MS (HR-EI, 70 eV): *m/z* (%) = 352.1031 (100) [M⁺], ¹²C₁₅¹H₂₃¹¹B₂¹²⁷I: 352.1030; Δ_{mmu} = 0.1.

2,3,4,5-Tetraethyl-1-iodo-6-phenylthioethynyl-2,3,4,5-tetracarba-nido-hexaborane(6) (2c): Starting materials: compound **1** (0.9 g, 2.05 mmol) and PhSC₂Li (0.7 g, 5.0 mmol). Yield: 0.65 g (71%), yellow oil. ¹H NMR (200.1 MHz, CDCl₃): δ = 1.29, 1.31 (t, ³J_{H,H} = 7.5 Hz, 2 × 6 H, CH₃), 2.05, 2.38 (m, 2 × 4 H, CH₂), 7.22–7.61 (m, 5 H, SPh) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 13.5, 14.6 (CH₃), 18.5, 19.9 (CH₂), 113.0 (skeletal carbon atoms nonadjacent to the basal boron), 127.6, 128.1, 131.7 (SPh) ppm; skeletal carbon atoms adjacent to the basal boron and alkynyl carbon atoms were not observed. ¹¹B NMR (64.2 MHz, CDCl₃): δ = 12 (br., B_{basal}), –52.7 (s, B_{apical}) ppm. MS (EI, 70 eV): *m/z* (%) = 446 (100) [M⁺], 319 (10) [M⁺ – I]. MS (HR-EI, 70 eV): *m/z* (%) = 446.0922 (58) [M⁺], ¹²C₂₀¹H₂₅¹¹B₂¹²⁷I³²S: 446.0908; Δ_{mmu} = 1.4.

6-Butyl-2,3,4,5-tetraethyl-1-iodo-2,3,4,5-tetracarba-nido-hexaborane(6) (3b): A solution of *n*BuLi (1.7 mL, 4.2 mmol) was very slowly added to a solution of *nido*-carborane **1** (0.92 g, 2.1 mmol) in hexane (50 mL) at –78 °C. The mixture was warmed to room temp. and was stirred for 20 h. After filtration, the slightly yellow filtrate was dried in vacuo and distilled at 43 °C/0.04 mbar to give a yellow oil. Yield: 0.70 g (90%). ¹H NMR (200.1 MHz, CDCl₃): δ = 0.89, 1.45, 1.95 (m, 9 H, *n*Bu), 1.19, 1.40 (t, 2 × 6 H, CH₂CH₃), 2.08, 2.36 (m, 2 × 4 H, CH₂CH₃) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 13.7, 14.2 (CH₃), 18.5, 19.0 (CH₂), 16.0, 17.6, 25.9, 26.6 (*n*Bu), 112.9 (skeletal carbon atoms nonadjacent to the basal boron) ppm. ¹¹B NMR (64.2 MHz, CDCl₃): δ = 19 (br., B_{basal}), –52.6 (s, B_{apical}) ppm. MS (EI, 70 eV): *m/z* (%) = 370 (100) [M⁺], 243 (10) [M⁺ – I].

Attempt to Prepare 2,3,4,5-Tetraethyl-1-phenylethynyl-6-diphenyl-phosphanyl-nido-carborane (4a): To lithium phenylacetylide (0.54 g, 5.0 mmol) in THF (15 mL) at room temp. was added ZnCl₂ (0.68 g, 5.0 mmol), and the solution was stirred for 3 h. The solution was then added to a mixture of **3a** (1.24 g, 2.5 mmol) and Pd(PPh₃)₄ (0.04 g, 0.034 mmol), and the resulting yellow mixture was heated at reflux for 10 d. The solvent was removed under high vacuum, the black residue was extracted with hexane (2 × 20 mL) and filtered. The yellow filtrate was dried in vacuo to give a yellow viscous oil. Yield: 0.51 g (49%) **2a**. NMR and mass spectroscopic data were in agreement with the previously reported result.^[19]

6-Butyl-2,3,4,5-tetraethyl-1-phenylethynyl-2,3,4,5-tetracarba-nido-hexaborane(6) (4b): To lithium phenylacetylide (0.54 g, 5.0 mmol) in THF (30 mL) at room temp. was added ZnCl₂ (0.68 g, 5.0 mmol), and the solution was stirred for 3 h. The solution was then added to a mixture of **3b** (0.85 g, 2.3 mmol) and Pd(PPh₃)₄ (0.04 g, 0.034 mmol) in THF (30 mL). The resulting yellow mixture was heated at reflux for 6 d. After evaporation of the solvent, the black residue was extracted with hexane (2 × 20 mL) and filtered. The yellow filtrate was dried in vacuo to give a yellow oil. Yield: 0.5 g (63%). ¹H NMR (200.1 MHz, CDCl₃): δ = 0.95, 1.52, 2.02 (m, 9 H, *n*Bu), 1.19, 1.25 (t, 2 × 6 H, CH₂CH₃), 2.10, 2.45 (m, 2 × 4 H, CH₂CH₃), 7.22–7.35 (m, 5 H, Ph) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 14.1, 15.4, 22.6, 26.3 (*n*Bu), 17.4, 18.5 (CH₃), 29.7, 30.5 (CH₂), 112.1 (skeletal carbon atoms nonadjacent to the basal boron), 127.7, 128.0, 131.9 (Ph) ppm. ¹¹B NMR (64.2 MHz, CDCl₃): δ = 20 (br., B_{basal}), –50.5 (s, B_{apical}) ppm. MS (EI, 70 eV): *m/z* (%) = 344 (100) [M⁺].

General Procedure for Cobalt Complexes 5a,c

To an appropriate solution of carboranylacetylene in toluene was added a portion of CpCo(CO)₂ at room temp. The deep-red mixture was heated at reflux and monitored by ¹¹B NMR spectroscopy, indicating that no reaction took place. After 4 d, one portion of CpCo(C₂H₄)₂ was added, and the resulting mixture was again heated at 120 °C for another 2 d. After completion of the reaction, the solvent was removed to dryness, and the crude product was purified by column chromatography on silica gel to give two fractions. Using hexane as the eluant, unreacted CpCo(CO)₂ and CpCo(C₂H₄)₂ were obtained. The second fraction (toluene) contained the corresponding (cyclobutadiene)cobalt complex.

{η⁴-Bis[2,3,4,5-tetraethyl-1-iodo-2,3,4,5-tetracarba-nido-hexaboranyl]diphenyl(cyclobutadiene)}(η⁵-cyclopentadienyl)cobalt(I) (5a): Starting materials: compound **2a** (0.50 g, 1.2 mmol), CpCo(CO)₂ (0.10 g, 0.6 mmol), and CpCo(C₂H₄)₂ (0.10 g, 0.6 mmol). Yield: 0.40 g (76%), yellow crystals, m.p. 124–125 °C. Compound **5a** was recrystallized from a solution of toluene at –20 °C. ¹H NMR (200.1 MHz, CDCl₃): δ = 1.3 (m, 24 H, CH₃), 2.3 (m, 16 H, CH₂), 5.10 (s, 5 H, Cp–H), 7.25, 7.55 (m, 10 H, Ph) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 13.4, 14.3 (CH₃), 18.4, 19.8 (CH₂), 84.5 (Cp–C), 113.0 (skeletal carbon atoms nonadjacent to the basal boron), 127.6, 128.0, 131.7 (Ph) ppm; quaternary carbon atoms were not found. ¹¹B NMR (64.2 MHz, CDCl₃): δ = 18 (br., B_{basal}), –52.0 (s, B_{apical}) ppm. MS (EI, 70 eV): *m/z* (%) = 952 (100) [M⁺], 538 (10) [M⁺ – Et₄C₄B₂I(C₂Ph)]. MS (HR-EI, 70 eV): *m/z* (%) = 952.2087 [M⁺], ¹²C₄₅¹H₅₅¹¹B₄⁵⁹Co¹²⁷I₂: 952.2097; Δ_{mmu} = –1.0.

{η⁴-Bis[2,3,4,5-tetraethyl-1-iodo-2,3,4,5-tetracarba-nido-hexaboranyl]diphenylthio(cyclobutadiene)}(η⁵-cyclopentadienyl)cobalt(I) (5c): Starting materials: compound **2c** (0.40 g, 1.2 mmol), CpCo(CO)₂ (0.10 g, 0.6 mmol), and CpCo(C₂H₄)₂ (0.10 g, 0.6 mmol). Yield: 0.25 g (54%), brown-red oil. ¹H NMR (200.1 MHz, CDCl₃): δ = 1.26, 1.35 (t, 2 × 12 H, CH₃), 2.10, 2.35 (m, 2 × 8 H, CH₂), 4.95 (s, 5 H, Cp–H), 7.15–7.55 (m, 10 H, SPh) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 13.6, 15.7 (CH₃), 19.1, 19.7 (CH₂), 85.4 (Cp–C), 115.5 (skeletal carbon atoms nonadjacent to the basal boron), 125.0, 128.8, 131.0 (SPh) ppm; skeletal carbon atoms adjacent to the basal boron and quaternary carbon atoms were not found. ¹¹B NMR (64.2 MHz, CDCl₃): δ = 18 (br., B_{basal}), –52.1 (s, B_{apical}) ppm. MS (EI, 70 eV): *m/z* (%) = 1016 (70) [M⁺], 570 (5) [M⁺ – Et₄C₄B₂I(C₂SPh)]. MS (HR-EI, 70 eV): *m/z* (%) = 1016.1550 [M⁺], ¹²C₄₅¹H₅₅¹¹B₄⁵⁹Co¹²⁷I₂³²S₂: 1016.1538; Δ_{mmu} = 1.2.

CpCo[Bis(carboranyl)cyclobutadiene] (7): To a solution of **6** (0.053 g, 0.14 mmol) in toluene (8 mL) was added a portion of CpCo(CO)₂ (0.04 g, 0.22 mmol) at room temp. The deep-red reaction mixture was heated at reflux for 9 d. The brown reaction mixture was cooled and filtered through a pad of sea sand; the yellow-brown filtrate was dried in vacuo to give a brown oil. Yield: 0.056 g (89%). ¹¹B NMR (64.2 MHz, CDCl₃): δ = 15 (br, B_{basal}), –50.4 (s, B_{apical}) ppm. MS (EI, 70 eV): *m/z* (%) = 892 (100) [M⁺]. MS (HR-EI, 70 eV): *m/z* (%) = 892.4999 [M⁺], ¹²C₅₅¹H₇₃¹¹B₄⁵⁹Co²⁸Si₂: 892.4955; Δ_{mmu} = 4.4.

(η⁵-Cyclopentadienyl)(η⁴-2,5-bis-carboranyl-3,4-diphenylcyclopentadienone)cobalt(I) (8): Carboranylacetylene **4b** (0.45 g, 1.3 mmol) and (η⁵-cyclopentadienyl)(dicarbonyl)cobalt(I) (0.11 g, 0.65 mmol) were dissolved in toluene (30 mL). The resulting dark-red mixture was stirred at 120 °C for 3 d. After cooling, the solvent was removed under high vacuum, and the black residue was purified by column chromatography (SiO₂, hexane). Cobalt complex **8** was recrystallized from a solution of hexane at –20 °C. Yield: 0.4 g (73%), brown solid, m.p. 133–136 °C. ¹H NMR (200.1 MHz, CDCl₃): δ = 1.20 (m, 2 × 12 H, CH₂CH₃), 0.90, 1.85, 2.12 (m, 2 × 9

Table 1. Crystal data and structure refinement for **5a** and **8**.

	5a	8
Empirical formula	C ₄₅ H ₅₅ B ₄ CoI ₂	C ₅₅ C ₅₄ H ₇₃ B ₄ CoO + ¼ C ₆ H ₁₄
Formula weight	951.86	861.84
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	18.045(1)	11.0954(2)
<i>b</i> [Å]	27.847(2)	13.7519(3)
<i>c</i> [Å]	17.133(1)	18.9481(4)
α [°]	90	108.757(1)
β [°]	93.395(2)	103.617(1)
γ [°]	90	94.669(1)
Volume [Å ³]	8594(1)	2621.6(1)
<i>Z</i>	8	2
Calcd. density [g/cm ³]	1.47	1.09
μ [mm ⁻¹]	1.87	0.36
<i>F</i> (000)	3824	929
Crystal size [mm]	0.29 × 0.09 × 0.08	0.3 × 0.16 × 0.06
$\theta_{\max}$ [°]	28.3	22.0
Index ranges	−24/24, −36/37, 22/22	−11/11, −14/14, −19/19
Reflections:		
Collected	87065	17190
Independent (<i>R</i> _{int})	21131 (0.051)	6392 (0.042)
Observed [<i>I</i> > 2 σ <i>I</i>]	18167	4865
Parameters	953	574
Goodness-of-fit on <i>F</i> ²	1.24	1.02
<i>R</i> ₁ [<i>I</i> > 2 σ <i>I</i>]	0.064	0.048
<i>wR</i> ₂ [<i>I</i> > 2 σ <i>I</i>]	0.101	0.129
<i>T</i> [K]	100(2)	200(2)
Residual electron density [e/Å ³]	2.42/−2.17	0.76/−0.29

H, *n*Bu), 2.10, 2.35 (m, 2 × 8 H, CH₂), 4.95 (s, 5 H, Cp-H), 6.90, 7.45, 7.63 (m, 2 × 5 H, Ph) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 14.1, 14.9 (CH₃), 19.3, 19.9 (CH₂), 17.1, 19.5, 21.2, 25.3 (*n*Bu), 81.7 (Cp-C), 113.5 (skeletal carbon atoms nonadjacent to the basal boron), 126.9, 128.8, 132.0 (Ph), 188.1 (CO) ppm; skeletal carbon atoms adjacent to the basal boron and quaternary carbon atoms were not found. ¹¹B NMR (64.2 MHz, CDCl₃): δ = 18 (br., B_{basal}), −44.4 (s, B_{apical}) ppm. IR (hexane): $\tilde{\nu}$ = 1593 (s) cm⁻¹. MS (EI, 70 eV): *m/z* (%) = 840 (50) [M⁺], 812 (100) [M⁺ − CO]. MS (HR-EI, 70 eV): *m/z* = 840.5334 [M⁺], ¹²C₅₄¹H₇₃¹¹B₄⁵⁹Co¹⁶O: 840.5365; Δ mmu = −3.1.

X-ray Crystal Structure Determinations of **5a and **8**:** Crystal data and details of the structure determinations are listed in Table 1. Reflections were collected with Bruker SMART APEX (**5a**) and Bruker-AXS SMART 1000 (**8**) diffractometers (Mo-*K*_α radiation, λ = 0.71073 Å, graphite monochromator, ω -scan). Empirical absorption corrections were applied. The structure was solved by direct methods and refined by least-square methods based on *F*² with all measured reflections (SHELXTL 6.12).^[21] All non-hydrogen atoms were refined anisotropically. CCDC-276980 (**5a**) and CCDC-276981 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) D. S. Matteson, *J. Organomet. Chem.* **1973**, 58, 1–48; b) R. N. Grimes, *Pure Appl. Chem.* **1974**, 39, 455–474; c) M. S.

- Gaunt, A. G. Massey, *Educ. Chem.* **1974**, 11, 118–121; d) E. V. Leonova, *Uspekhi Khimii* **1980**, 283–326; e) V. V. Korshak, S. A. Pavlova, P. N. Gribkova, T. N. Balykova, *Acta Polymerica* **1981**, 32, 61–74; f) K. Wade, H. M. Colquhoun, M. G. Davidson, M. A. Fox, W. R. Gill, P. L. Herbertson, T. G. Hibbert, J. A. H. Macbride, R. J. Peace, G. P. Rivers, *Royal Soc., Chem.* **1997**, 201, 289–296; g) R. N. Grimes, *Pure Appl. Chem.* **2003**, 75, 1211–1218; h) W. Siebert, C.-J. Maier, A. Maier, P. Greiwe, M. J. Bayer, M. Hoffmann, H. Pritzkow, *Pure Appl. Chem.* **2003**, 75, 1277–1286; i) Z. Xie, *Pure Appl. Chem.* **2003**, 75, 1335–1341; j) P. A. Jelliss, *Organomet. Chem.* **2004**, 31, 112–129; k) G.-X. Jin, *Coord. Chem. Rev.* **2004**, 248, 587–602.
- [2] A. Berndt, M. Hoffmann, W. Siebert, B. Wrackmeyer in *Molecular Clusters of the Main Group Elements* (Eds.: D. Driess, H. Nöth), Wiley, **2004**, pp. 267–309.
- [3] a) A. R. Oki, H. Zhang, N. S. Hosmane, H. Ro, W. E. Hatfield, *J. Am. Chem. Soc.* **1991**, 113, 8531–8532; b) W. Haubold, W. Keller, G. Sawitzki, *Angew. Chem.* **1988**, 100, 958–959; *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 925; c) A. E. Goeta, J. A. K. Howard, A. K. Hughes, A. L. Johnson, K. Wade, *Chem. Commun.* **1998**, 1713–1714; d) J. M. Russell, H. Sabat, R. N. Grimes, *Organometallics* **2002**, 21, 4113–4128; e) N. S. Hosmane, J. A. Maguier, *Eur. J. Inorg. Chem.* **2003**, 3989–3999; f) R. N. Grimes, *J. Chem. Educ.* **2004**, 81, 657–672.
- [4] a) J. F. Valliant, K. J. Guenther, A. S. King, P. Morel, P. Schaffer, O. O. Sogbein, K. A. Stephenson, *Coord. Chem. Rev.* **2002**, 232, 173–230; b) V. Tolmachev, S. Sjöberg, *Collect. Czech. Chem. Commun.* **2002**, 67, 913–915.
- [5] K. P. Callahan, M. F. Hawthorne, *J. Am. Chem. Soc.* **1973**, 95, 4574–4580.
- [6] U. Schöberl, T. F. Magnera, R. M. Harrison, F. Fleischer, J. L. Pflug, P. F. H. Schwab, X. Meng, D. Lipiak, B. C. Noll, V. S. Allured, T. Rudalevige, S. Lee, J. Michl, *J. Am. Chem. Soc.* **1997**, 119, 3907–3917.
- [7] L. I. Zakharkin, A. I. Kovredov, V. A. Ol'shevskaya, *Seriya Khim.* **1982**, 3, 673–675.

- [8] H. Yao, M. Sabat, R. N. Grimes, *Organometallics* **2003**, *22*, 2581–2593.
- [9] Y. Nie, A. Goswami, W. Siebert, *Z. Naturforsch.* **2005**, *60b*, 1–6.
- [10] a) P. Binger, *Tetrahedron Lett.* **1966**, *7*, 2675–2680; b) P. Binger, *Angew. Chem.* **1968**, *80*, 288–289; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 286; c) R. Köster, M. A. Grassberger, *Angew. Chem.* **1967**, *79*, 197–252; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 218–240; d) L. Killian, B. Wrackmeyer, *J. Organomet. Chem.* **1977**, *132*, 213–221; e) H. O. Berger, H. Nöth, B. Wrackmeyer, *Chem. Ber.* **1979**, *112*, 2884–2893.
- [11] a) T. P. Onak, G. T. F. Wong, *J. Am. Chem. Soc.* **1970**, *92*, 5226; b) V. R. Miller, R. N. Grimes, *Inorg. Chem.* **1972**, *11*, 862–865.
- [12] a) B. Wrackmeyer, G. Kehr, *J. Organomet. Chem.* **1995**, *501*, 87–93; b) B. Wrackmeyer, A. Glöckle, *Z. Naturforsch.* **1996**, *51b*, 859–864; c) B. Wrackmeyer, A. Glöckle, *Main Group Metal Chem.* **1997**, *20*, 181–189; d) B. Wrackmeyer, G. Kehr, A. Glöckle, *Phosphorus, Sulfur Silicon Relat. Elem.* **1997**, *131*, 25–35; e) M. Herberhold, U. Bertholdt, W. Milius, A. Glöckle, B. Wrackmeyer, *Chem. Commun.* **1996**, 1219–1220.
- [13] C. Balzereit, H. J. Winkler, W. Massa, A. Berndt, *Angew. Chem.* **1994**, *106*, 1579–1581; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1487–1489.
- [14] Y. Nie, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **2004**, 2425–2433.
- [15] E.-I. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979–2017.
- [16] a) E. R. F. Gesing, K. P. C. Vollhardt, *J. Organomet. Chem.* **1981**, *217*, 105–118; b) J. R. Fritch, K. P. C. Vollhardt, *J. Am. Chem. Soc.* **1978**, *100*, 3643–3644.
- [17] H. Sakurai, J. Hayashi, *J. Organomet. Chem.* **1972**, *39*, 365–370.
- [18] J. H. Hardesty, J. B. Koerner, T. A. Albright, G. Y. Lee, *J. Am. Chem. Soc.* **1999**, *121*, 6055–6067.
- [19] Y. Nie, S. Schwiegk, H. Pritzkow, W. Siebert, *Eur. J. Inorg. Chem.* **2004**, 1630–1638.
- [20] a) K. Jonas, E. Deffense, D. Habermann, *Angew. Chem.* **1983**, *95*, 729; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 716; b) J. K. Cammack, S. Jalisatgi, A. J. Matzger, A. Negron, K. P. C. Vollhardt, *J. Org. Chem.* **1996**, *61*, 4798–4800.
- [21] *SHELXTL 6.12*, Bruker AXS, Madison, WI, USA, **2001**.

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