Synthesis and Reactivity of Boron-Functionalized C_2B_5-*closo*-Carboranes

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Dedicated to Dr. Karlheinz Schmidt on the occasion of his 60th birthday

Treatment of the *nido*-2,3-$Et_2C_2B_4H_4^{2-}$dianion (**1**) with monoboron reagents led to *closo*-C_2B_5 carborane derivatives with functional substituents at the inserted apical boron atom. The reactions of **1** with BX_3 (X = Br, I) afforded the corresponding *closo*-1-X-2,3-$Et_2C_2B_5H_4$ (**2a**,**b**), and with PhC≡CBcat (cat = $O_2C_6H_4$) produced the alkynyl-substituted *closo*-1-C≡CPh-2,3-$Et_2C_2B_5H_4$ (**2c**). Pd-catalyzed Negishi-type cross-coupling reactions of **2b** with RC≡CZnCl at room temperature gave the corresponding *closo*-1-C≡CR-2,3-$Et_2C_2B_5H_4$ derivatives **2d-f**, R = $SiMe_3$, Me, and *t*Bu, respectively. Compound **3** with two C_2B_5 moieties linked *via* a C=C unit was obtained by a similar boron incorporation reaction with *cis*-$Cl_2B(Et)C=C(Et)BCl_2$. The reactions of **2c**,**d** with $Co_2(CO)_8$ afforded the dicobaltatetrahedrane-substituted carboranes **4c** and **d**, in which the clusters C_2B_5 and Co_2C_2 are connected by a B-C bond. Compounds **4c**,**d** lost the apical boron on wet silica gel or sand to give the *nido*-C_2B_4-C_2Co_2 compounds **5c**,**d**. Formation of the carboranyl-substituted (η^5-C_5H_5)Co(cyclobutadiene) complex **6c** was observed in the reaction of **2c** with (η^5-C_5H_5)Co(C_2H_4)$_2$. The composition of the products follows from NMR and MS data.

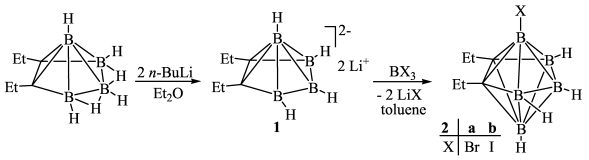
Key words: Boron, Carborane, Cross Coupling, Cobalt, Cluster Linkage

Introduction

Of the four possible isomers of the *closo*-$C_2B_5H_7$ carborane (1,2-, 1,7-, 2,3- and 2,4-), the 2,3- and 2,4-isomers are known, and studies of their chemistry have focused on the 2,4- compounds [1 – 3]. The much lower interest in the 2,3-isomer, which is predicted by calculations [4] to be 15 – 25 kcal/mol less stable than the 2,4-isomer, may be due to its difficult accessibility. The first C-alkyl derivative *closo*-2,3-$Me_2C_2B_5H_5$ was obtained in low yield by Schaeffer *et al.* [5] in the gas phase reaction of octaborane(12) with 2-butyne. Sneddon *et al.* [6] found a better way to *closo*-2,3-$Et_2C_2B_5H_5$ by a capping reaction (boron insertion) of *nido*-2,3-$Et_2C_2B_4H_6$ with $Et_3N{\cdot}BH_3$ at 140 °C in 50 – 60% yield. Alternatively, *closo*-2,3-$Et_2C_2B_5H_5$ is formed in the reaction of *nido*-2,3-$Et_2C_2B_4H_5^-Na^+$ and $Me_2S{\cdot}BH_3$ (44% yield), or from the *nido*-2,3-$Et_2C_2B_4H_4^{2-}Na^+Li^+$ and $Me_2S{\cdot}BHBr_2$ (49% yield) [6 – 9]. Sneddon and Beck also studied the reaction of *nido*-2,3-$Et_2C_2B_4H_4^{2-}Na^+Li^+$ with $PhBCl_2$ and $MeBBr_2$, respectively, and obtained *closo*-1-R-2,3-$Et_2C_2B_5H_4$ (R = Ph, Me) derivatives in moderate yields [7]. The parent *closo*-2,3-$C_2B_5H_7$ [10] has been isolated in *ca.* 65% yield by vacuum thermolysis of *nido*-4,5-$C_2B_6H_{10}$. More recently Grimes, Siebert *et al.* [11] reported the benzene-centered 1,3,5-(*closo*-$Et_2C_2B_5H_4)_3C_6H_3$ by reacting the *nido*-2,3-$Et_2C_2B_4H_4^{2-}$ dianion with tris(diiodoboryl)benzene, which gave the corresponding 1,3,5-tris-*nido*-C_2B_4 carborane on silica. We have described the formation of *closo*-2,3-$Et_2C_2B_5I_5$ [12] from the reaction of 3-hexyne, BI_3, and a $NaK_{2.8}$ alloy at room temperature. Herein we report on the synthesis of apically functionalized *closo*-C_2B_5 carboranes, and the reactions of some of the alkynyl- substituted derivatives with cobalt complexes.

Results and Discussion

Boron insertion or capping reactions [13] are a convenient pathway to functionalized carborane products. To achieve apically B-halogenated *closo*-2,3-C_2B_5 carborane derivatives, we carried out reactions of the *nido*-2,3-$Et_2C_2B_4H_4^{2-}$ dianion (**1**, formed by deprotonation of *nido*-2,3-$Et_2C_2B_4H_6$ with 2 equiv. *n*-



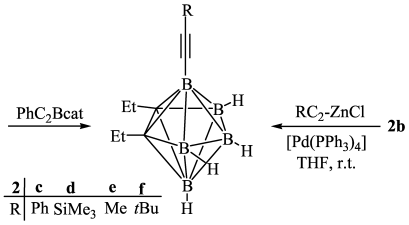
Scheme 1.

BuLi in diethylether, Scheme 1) and BX_3 (X = Br, I) in toluene, which led to **2a**,**b** as yellow oils, respectively. Their ^{11}B NMR spectra exhibit signals at 6.3 (B4,6), 1.2 (B5), −17.4 (B7), and −23.6 (B1) (**2a**), and 6.7 (B4,6), 1.9 (B5), −18.3 (B7), and −31.9 (B1) ppm (**2b**), in a ratio of 2:1:1:1, respectively. The mass spectra of **2a**,**b** give the corresponding molecular ion peaks with correct isotopic patterns.

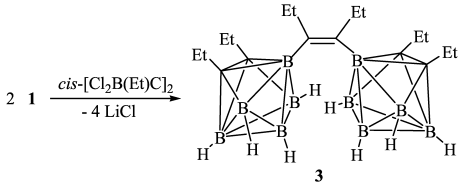
The formation of **2a**,**b** is of interest, as the bromination of *closo*-2,3-$Et_2C_2B_5H_5$ with Br_2 or $Br_2/AlBr_3$ occurs selectively at the B5 position, affording *closo*-5-Br-2,3-$Et_2C_2B_5H_4$ as the single product in moderate yield [7]. Wrackmeyer *et al.* [14] studied the reaction of *nido*-[2,4-$(EtC)_2(BEt)_4H]^-$ Na^+ with BBr_3 to give *closo*-1-Br-2,4-$(EtC)_2(BEt)_4B$ as a side product, the major product being *closo*-2,4-$(EtC)_2(BEt)_4BH$.

Similarly, the reaction of **1** with PhC≡CBcat (cat = $O_2C_6H_4$) produced the apically alkynyl-substituted *closo*-1-C≡CPh-2,3-$Et_2C_2B_5H_4$ (**2c**) (Scheme 2) as a yellow oil. A more efficient way to **2d-f** was found by the Pd-catalyzed Negishi-type cross-coupling reactions of **2b** (Scheme 2). The ^{11}B NMR spectrum of **2c** shows signals at 6.4 (B4,6), 1.8 (B5), −16.1 (B1), and −18.7 (B7) ppm in a ratio of 2:1:1:1, and similar shifts are observed for **2d-f**. There is no significant "anti-podal" effect [15] of the halogen atoms (in **2a,b**), or RC_2 groups (in **2c-f**) at B1 upon B7, as the ^{11}B NMR shifts for B7 in **2a-f** (−17.4 to −20.3 ppm in $CDCl_3$) are comparable to that of *closo*-2,3-$C_2B_5H_7$ (B7: −17.9 ppm) [10]. By contrast, the chemical shift for *closo*-1-butenyl-2,3-$C_2B_5H_6$ (B7: −25.0 ppm) differs considerably from that of *closo*-2,3-$C_2B_5H_7$ [10].

The Pd-catalyzed reactions could be easily monitored by the stepwise color change and by ^{11}B NMR:



Scheme 2.

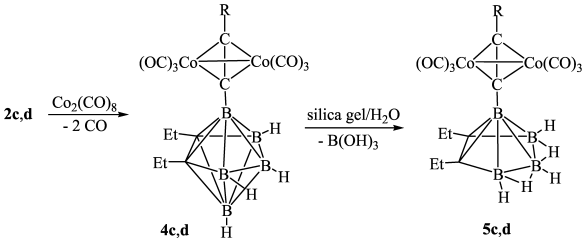


Scheme 3.

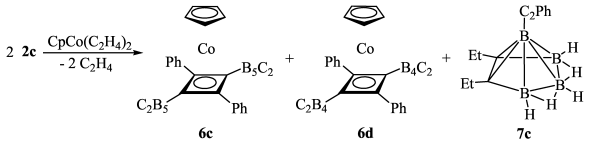
the yellow solution of **2b** in THF turned to red upon addition of a catalytic amount of $Pd(PPh_3)_4$, and again gradually to yellow after the corresponding zinc reagents were added. It is noteworthy that the Pd-catalyzed cross coupling in the present work was achieved at ambient temperature (48 – 72 h), whereas in most of the reported Pd-catalyzed coupling reactions involving halogenated borane or other carborane clusters, either heating or longer reaction time or both are needed [16 – 22]. The initial attempt to obtain **2d** by heating the THF solution at reflux led only to a mixture of **2d** and unidentified carborane species. The effort to obtain the proposed oxidative addition intermediate 2,3-$Et_2C_2B_5$-$Pd(PPh_3)_2I$ by reacting **2b** and $Pd(PPh_3)_4$ in THF at room temperature was not successful, instead red crystals of *trans*-$Pd(PPh_3)_2I_2$ [23] were observed, which was also formed in a trace amount in the preparation of **2d**. The desilylation reaction of **2d** with *n*-Bu_4NF in THF did not lead to a terminal carboranylacetylene, only degradation of the cluster occurred.

A similar reaction of **1** with *cis*-$Cl_2B(Et)C{=}C(Et)BCl_2$ produced compound **3** (Scheme 3), in which two *closo*-2,3-C_2B_5 clusters are linked *via* a C=C double bond unit. Its ^{11}B NMR spectrum exhibits broad signals at 6.2 (B4,6), 2.9 (B5), −4.7 (B1), and −21.5 (B7) ppm. The mass spectrum shows the molecular ion peak with correct isotopic envelope.

The reactions of **2c,d** with $Co_2(CO)_8$ afforded the dicobaltatetrahedrane derivatives **4c,d** as brown oils, each having the C_2B_5 and Co_2C_2 clusters connected by a B-C bond. As observed for the benzene-centered triscarboranyl compound 1,3,5-(*closo*-$Et_2C_2B_5H_4)_3C_6H_3$ [11], our attempt to purify



Scheme 4.



Scheme 5.

compounds **4c,d** by column chromatography on silica gel or sand led to mixtures of **4c,d** and the *nido*-C_2B_4-clusters **5c,d**, respectively, formed by elimination of a BH group [as $B(OH)_3$ in a "decapitation" reaction [24] of **4c,d** with H_2O and protonation to give **5c,d**].

The ^{11}B NMR spectrum of **4c** (in hexane, before column chromatography) exhibits signals at 7.2 (B4,6), 2.9 (B5), −5.6 (B7), and −20.5 (B1) ppm in a ratio of 2:1:1:1. After chromatography new signals appeared at −2.8 and −35.6 ppm, indicating the formation of **5c**. Additionally, the mass spectra of **4c**/**5c** exhibit the molecular ion peaks at $m/z = 527$ and $m/z = 517$, respectively, and the characteristic fragments of sequential loss of the six carbonyl ligands. The ^{11}B NMR and MS spectra of **4d**/**5d** provide similar information.

No reaction was observed between **2c** and CpCo-$(CO)_2$ (Cp = η^5-C_5H_5) in refluxing toluene (1 week) as monitored by ^{11}B NMR. However, adding [CpCo-$(C_2H_4)_2$] to this mixture and refluxing for additional 6 days led to a brown mixture (after filtration through a pad of sand), in which the C_2B_5-substituted CpCo(cyclobutadiene) complex **6c**, the C_2B_4-substituted analog **6d** (from partial decapitation of **6c**), and the partial degradation (of **2c**) product **7c** (Scheme 5) were detected, with the latter two being the minor species (^{11}B NMR: $\delta = 6.3$, 2.2, −4.0, −16.6, −19.6, −45.1 ppm; EI-MS: $m/z = 606$ for **6c**, 597 for **6d**, and 232 for **7c**, respectively). Compounds **6d** and **7c** may be formed in a way similar to **5c,d**. No evidence was found for cyclotrimerization in this case.

Conclusion

Apically functionallized *closo*-1-R-2,3-$Et_2C_2B_5H_4$ compounds (R = Br, I, C_2Ph) (**2a-c**) have been prepared either by treatment of the *nido*-2,3-$Et_2C_2B_4H_4^{2-}$ dianion (**1**) with BX_3 (X = Br, I) or PhC≡CBcat. A more efficient pathway to apically alkynyl-substituted derivatives was developed *via* Pd-catalyzed Negishi-type cross-coupling reactions of **2b** with R'C≡CZnCl at room temperature to give *closo*-1-C≡CR'-2,3-$Et_2C_2B_5H_4$ (**2d-f**, R' = $SiMe_3$, Me, *t*Bu). Compound **3** with two C_2B_5 moieties linked *via* a C=C unit was obtained by a similar boron insertion reaction with *cis*-$Cl_2B(Et)C{=}C(Et)BCl_2$. The reactions of carboranylacetylenes **2c,d** with $Co_2(CO)_8$ afforded **4c,d**, in which a *closo*-C_2B_5 and a *nido*-Co_2C_2 cluster are connected by a B-C bond. Compounds **4c,d** lost the apical boron atom on silica gel to give *nido*-C_2B_4-Co_2C_2 **5c,d**. The formation of the carboranyl-substituted CpCo(cyclobutadiene) complex **6c** was observed in the reaction of **2c** with CpCo$(C_2H_4)_2$.

Experimental Section

All reactions and manipulations were performed in dry glassware under argon or nitrogen using standard Schlenk techniques. Solvents were dried, distilled, and saturated with nitrogen. NMR specta were recorded on a Bruker DRX 200 spectrometer (^{1}H: 200.13 MHz, ^{11}B: 64.21 MHz, ^{13}C: 50.32 MHz) in $CDCl_3$ and C_6D_6 as solvents. $Et_2O{\bullet}BF_3$ was used as the external standard for ^{11}B NMR. As internal references for ^{1}H and ^{13}C NMR, the signals of the deuterated solvents were used and the shifts calculated relative to TMS. MS: ZAB-2F VH Micromass CTD spectrometer, and a JEOL MS Station JMS 700 spectrometer. *nido*-2,3-$Et_2C_2B_4H_6$ was kindly provided by Prof. R. N. Grimes (Charlottesville, USA).

*1-Bromo-2,3-diethyl-2,3-dicarbaheptaborane(7) (***2a***)*

2,3-$Et_2C_2B_4H_6$ (250 mg, 1.91 mmol) in diethyl ether (30 ml) was treated with *n*-BuLi (2.5 M in hexane, 1.55 ml, 3.8 mmol) at −65 °C. The solution was stirred for 4 h at r.t., then the solvent removed *in vacuo*, the residue dissolved in toluene (15 ml) and cooled to −20 °C. A solution of BBr_3 (550 mg, 2.2 mmol) in toluene (15 ml) was added dropwise. The reaction mixture was warmed to r.t. and stirred overnight. All volatiles were removed, the white residue was extracted with hexane (30 ml) and filtered to give a slight yellow filtrate, which was dried *in vacuo* to leave **2a** as a yellow oil (298 mg, 71%). – ^{1}H{^{11}B} NMR ($CDCl_3$): $\delta = 1.36$ (t, 6 H, $^3J_{H,H} = 7.6$ Hz, CH_3), 2.64 (q, 4 H, $^3J_{H,H} = 7.6$ Hz, CH_2), 3.4 (br., 1 H, B5-H), 4.2 (br., 2 H, B4,6-H), signal for B7-H n.o. – ^{11}B NMR ($CDCl_3$): $\delta = 6.3$ (d, $J_{B,H} = 170$ Hz, B4,6), 1.2 (d, $J_{B,H} = 170$ Hz, B5), −17.4 (s, B1), −23.6 (d, $J_{B,H} = 180$ Hz, B7). – ^{13}C NMR ($CDCl_3$): $\delta = 13.2$ (CH_3), 22.1 (CH_2), 113.5 (br., C_{cage}). – EI-MS: *m/z* (%) = 220 (100) [M^+], 205 (36) [$M^+ - Me$]. – HR-MS (EI): $m/z = 220.0751$ [M^+]; calcd. for $^{12}C_6{}^1H_{14}{}^{11}B_5{}^{79}Br$ 220.0744 ($\Delta m = 0.7$ mmu).

*1-Iodo-2,3-diethyl-2,3-dicarbaheptaborane(7) (***2b***)*

Similar procedure as described for **2a**. 2,3-$Et_2C_2B_4H_6$ (165 mg, 1.26 mmol), *n*-BuLi (2.5 M in hexane, 1 ml, 2.5 mmol), BI_3 (498 mg, 1.27 mmol). **2b** was obtained as a yellow oil (320 mg, 95%). – ^{1}H NMR ($CDCl_3$): $\delta = 1.38$ (t, 6 H, $^3J_{H,H} = 7.8$ Hz, CH_3), 2.61 (q, 4 H, $^3J_{H,H} = 7.8$ Hz,

CH_2). – ^{11}B NMR ($CDCl_3$): $\delta = 6.7$ (d, $J_{B,H} = 173$ Hz, B4,6), 1.9 (d, $J_{B,H} = 173$ Hz, B5), −18.3 (d, $J_{B,H} = 180$ Hz, B7), −31.9 (s, B1). – ^{13}C NMR ($CDCl_3$): $\delta = 13.3$ (CH_3), 22.4 (CH_2), 113.9 (br., C_{cage}). – EI-MS: *m/z* (%) = 267 (100) [M^+], 112 (28) [$M^+ - I - C_2H_4$].

*1-Phenylethynyl-2,3-diethyl-2,3-dicarbaheptaborane(7) (***2c***)*

Similar procedure as described for **2a**. 2,3-$Et_2C_2B_4H_6$ (340 mg, 2.6 mmol), *n*-BuLi (2.5 M in hexane, 2.1 ml, 5.25 mmol), PhC≡CBcat (570 mg, 2.6 mmol). **2c** was obtained as an orange red oil (393 mg, 63%). – ^{1}H NMR ($CDCl_3$): $\delta = 1.48$ (t, 6 H, $^3J_{H,H} = 7.6$ Hz, CH_3), 2.82 (q, 2 H, $^3J_{H,H} = 7.6$ Hz, CH_2), 2.82 (q, 2 H, $^3J_{H,H} = 7.4$ Hz, CH_2), 7.37 (m, 5 H, Ph). – ^{11}B NMR ($CDCl_3$): $\delta = 6.4$ (br., B4,6), 1.8 (br., B5), −16.1 (s, B1), −18.7 (br., B7). – ^{13}C NMR ($CDCl_3$): $\delta = 13.6$ (CH_3), 22.5 (CH_2), 94.1 (PhC≡), 115.1 (br., C_{cage}), 122.5, 128.2, 128.7, 132.0 (Ph), signal for B-C≡ n.o.. – EI-MS: *m/z* (%) = 241 (100) [M^+], 226 (34) [$M^+ - Me$]. – HR-MS (EI): *m/z* = 242.1986 [M^+]; calcd. for $^{12}C_{14}{}^1H_{19}{}^{11}B_5$ 242.1952 (Δm = 3.4 mmu).

*1-Trimethylsilylethynyl-2,3-diethyl-2,3-dicarbaheptaborane(7) (***2d***)*

The zinc reagent was prepared by treatment of $Me_3SiC{\equiv}CLi$ (preformed from $Me_3SiC{\equiv}CH$ and *n*-BuLi, 218 mg, 2.1 mmol) with a solution of $ZnCl_2$ (286 mg, 2.1 mmol) in THF (6.5 ml) at −10 °C, and stirred at r. t. for 2 h. In another flask, a solution of **2b** (534 mg, 2 mmol) in THF (10 ml) was added to a solution of $Pd(PPh_3)_4$ (75 mg, 0.065 mmol) in THF (10 ml). To the resulting red solution the zinc reagent was added at r. t. The reaction mixture became yellow during 1 h. After completion all volatiles were removed *in vacuo*, the brown residue was extracted with hexane (40 ml) and filtered. The yellow filtrate was dried to give **2d** as an orange red oil (340 mg, 72%). After NMR measurement in $CDCl_3$, pieces of red crystals were formed, which were identified by X-ray analysis to be *trans*-$Pd(PPh_3)_2I_2$. – ^{1}H{^{11}B} NMR ($CDCl_3$): $\delta = 0.02$ (s, 9 H, $SiMe_3$), 1.36 (t, 6 H, $^3J_{H,H} = 7.6$ Hz, CH_3), 2.71 (q, 4 H, $^3J_{H,H} = 7.6$ Hz, CH_2), 3.7 (br., 1 H, B5-H), 4.2 (br., 2 H, B4,6-H), −1.7 (br., 1 H, B7-H). – ^{11}B NMR ($CDCl_3$): $\delta = 6.3$ (br., B4,6), 1.5 (br., B5), −17.4 (s, B1), −19.1 (br., B7). – ^{13}C NMR ($CDCl_3$): $\delta = -0.39$ ($SiMe_3$), 13.4 (CH_3), 22.4 (CH_2), 102.4 ($Me_3SiC{\equiv}$), 114.8 (br., C_{cage}), signal for B-C≡n.o. – ^{29}Si NMR ($CDCl_3$): $\delta = -19.4$. – EI-MS: *m/z* (%) = 237 (16) [M^+], 222 (100) [$M^+ - Me$]. – HR-MS (EI): *m/z* = 238.2050 [M^+]; calcd. for $^{12}C_{11}{}^1H_{23}{}^{11}B_5{}^{28}Si$ 238.2035 (Δm = 1.5 mmu).

*1-Methylethynyl-2,3-diethyl-2,3-dicarbaheptaborane(7) (***2e***)*

Similar procedure as described for **2d**. $MeC{\equiv}CLi$ (115 mg, 2.5 mmol), $ZnCl_2$ (240 mg, 2.5 mmol), **2b** (534 mg, 2 mmol), $Pd(PPh_3)_4$ (40 mg, 0.035 mmol). **2e** was obtained as a yellow oil (297 mg, 85%). – ^{1}H{^{11}B} NMR ($CDCl_3$): $\delta = 1.37$ (t, 6 H, $^3J_{H,H} = 7.7$ Hz, CH_3), 1.63 (s, 3 H, Me), 2.70 (q, 2 H, $^3J_{H,H} = 7.7$ Hz, CH_2), 2.71 (q, 2 H, $^3J_{H,H} = 7.7$ Hz, CH_2), 3.7 (br., 1 H, B5-H), 4.2 (br., 2 H, B4,6-H), −1.5 (br., 1 H, B7-H). – ^{11}B NMR ($CDCl_3$): $\delta = 6.3$ (d, $J_{B,H} = 165$ Hz, B4,6), 2.2 (d, $J_{B,H} = 170$ Hz, B5), −16.3 (s, B1), −20.3 (d, $J_{B,H} = 168$ Hz, B7). – ^{13}C NMR ($CDCl_3$): $\delta = 4.2$ (Me), 13.5 (CH_3), 22.3 (CH_2), 102.4 (Me*C* ≡), 114.7 (br., C_{cage}), signal for B-C≡ n.o.. – EI-MS: *m/z* (%) = 179 (100) [M^+], 164 (82) [$M^+ - Me$]. – HR-MS (EI): $m/z = 180.1801$ [M^+]; calcd. for $^{12}C_9{}^1H_{17}{}^{11}B_5$ 180.1796 (Δm = 0.5 mmu).

*1-tert-Butylethynyl-2,3-diethyl-2,3-dicarbaheptaborane(7) (***2f***)*

Similar procedure as described for **2d**. *t*BuC≡CH (175 mg, 2.1 mmol), *n*BuLi (2.5 M in hexane, 0.9 ml, 22 mmol), $ZnCl_2$ (299 mg, 2.5 mmol), **2b** (534 mg, 2 mmol), $Pd(PPh_3)_4$ (75 mg, 0.065 mmol). **2f** was obtained as a yellow oil (292 mg, 66%). – ^{1}H{^{11}B} NMR ($CDCl_3$): $\delta = 1.05$ (s, 9 H, *t*Bu), 1.36 (t, 6 H, $^3J_{H,H} = 7.6$ Hz, CH_3), 2.71 (q, 4 H, $^3J_{H,H} = 7.6$ Hz, CH_2), 3.74 (br., 1 H, B5-H), 4.22 (br., 2 H, B4,6-H), −1.5 (br., 1 H, B7-H). – ^{11}B NMR ($CDCl_3$): $\delta = 6.4$ (d, $J_{B,H} = 159$ Hz, B4,6), 1.3 (d, $J_{B,H} = 199$ Hz, B5), −15.9 (s, B1), −20.2 (d, $J_{B,H} = 169$ Hz, B7). – ^{13}C NMR ($CDCl_3$): $\delta = 13.3$ (CH_3), 22.3 (CH_2), 29.7, 30.6 (*t*Bu), 104.2 (*t*Bu*C* ≡), 114.6 (br., C_{cage}), signal for B-C≡ n. o.. – EI-MS: *m/z* (%) = 221 (39) [M^+], 206 (100) [$M^+ - Me$]. – HR-MS (EI): $m/z = 222.2273$ [M^+]; calcd. for $^{12}C_{12}{}^1H_{23}{}^{11}B_5$ 222.2265 (Δm = 0.8 mmu).

*3,4-Bis[2',3'-diethyl-2',3'-dicarbaheptaboranyl(7)-1']-3-hexene (***3***)*

Similar procedure as described for **2a**. 2,3-$Et_2C_2B_4H_6$ (241 mg, 1.84 mmol), *n*-BuLi (2.5 M in hexane, 1.5 ml, 3.75 mmol), *cis*-3,4-bis(dichloroboryl)-3-hexene (227 mg, 0.92 mmol). **3** was obtained as a yellow oil (300 mg, 90%). – ^{1}H NMR ($CDCl_3$): $\delta = 0.61$ (t, 6 H, $^3J_{H,H} = 7.5$ Hz, Et-CH_3), 1.23 (t, 6 H, $^3J_{H,H} = 7.5$ Hz, cage-CH_3), 1.47 (q, 4 H, $^3J_{H,H} = 7.5$ Hz, Et-CH_2), 2.63 (q, 2 H, $^3J_{H,H} = 7.5$ Hz, cage-CH_2), 2.67 (q, 2 H, $^3J_{H,H} = 7.6$ Hz, cage-CH_2). – ^{11}B NMR ($CDCl_3$): $\delta = 6.2$ (br., B4,6), 2.9 (br., B5), −4.7 (s, B1), −21.5 (br., Hz, B7). – ^{13}C NMR ($CDCl_3$): $\delta = 13.9$, 14.1 (CH_3), 22.9, 26.5 (CH_2), 114.6 (br., C_{cage}), 144 (br., C=C). – EI-MS: *m/z* (%) = 362 (100) [M^+], 333 (680) [$M^+ - Et$]. – HR-MS (EI): $m/z = 364.3893$ [M^+]; calcd. for $^{12}C_{18}{}^1H_{38}{}^{11}B_{10}$ 364.3904 (Δm = −1.1 mmu).

Dicobaltatetrahedrane-substituted closo-C_2B_5 and nido-C_2B_4 carboranes **4c**, **5c**

A solution of **2c** (196 mg, 0.81 mmol) in hexane (15 ml) was added to a solution of $Co_2(CO)_8$ (276 mg, 0.81 mmol)

in hexane (15 ml) at −40 °C. The reaction mixture was warmed up to r.t. and stirred for 5 days to give a deep red solution. The transformation was complete as monitored by ^{11}B NMR. The solvent was removed, the dark brown residue was taken up with CH_2Cl_2 (2 ml) and chromatographed (Florisil®, hexane). A brown fraction was obtained and dried to give a brown oil (302 mg), which was identified to be a mixture of **4c** and **5c** (*ca.* 4 : 1). **4c**: ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (br., 6 H, CH_3), 2.75 (br., 4 H, CH_2), 7.33 (br., 5 H, Ph). – ^{11}B{^{1}H} NMR (hexane): $\delta = 7.2$ (B4,6), 2.9 (B5), −5.6 (B1), −20.5 (B7); – ^{11}B NMR ($CDCl_3$): $\delta =$ 6.7 (br., B4,6), 2.1 (br., B5), −6.3 (B1), −21.1 (d, $J_{B,H} =$ 150 Hz, B7). – ^{13}C NMR ($CDCl_3$): $\delta = 14.0$ (CH_3), 22.2 (CH_2), 115.5 (br., C_{cage}), 128.0, 128.8, 129.4, 137.7 (Ph), 199.2 (CO). – EI-MS: *m/z* (%) = 527 (2) [M^+], 499 (5) [$M^+ - CO$], 471 (3) [$M^+ - 2CO$], 443 (12) [$M^+ - 3CO$], 415 (42) [$M^+ - 4CO$], 387 (28) [$M^+ - 5CO$], 359 (37) [$M^+ - 6CO$], 241 (100) [$M^+ - 6CO - 2Co$]. – HR-MS (EI): $m/z =$ 528.0262 [M^+]; calcd. for $^{12}C_{20}{}^1H_{19}{}^{11}B_5Co_2O_6$ 528.0311 (Δm = −4.9 mmu); **5c**: ^{1}H NMR ($CDCl_3$): $\delta =$ −1.22 (br., 2 H, BHB), 0.88 (br., 6 H, CH_3), 2.40 (br., 4 H, CH_2), 7.42 (br., 5 H, Ph). – ^{11}B NMR ($CDCl_3$): $\delta = 6.7$ (br.), −2.8 (br.), −35.6 (apical boron). – ^{13}C NMR ($CDCl_3$): $\delta = 14.9$ (CH_3), 24.5 (CH_2), signals for the other carbon atoms are weak. – EI-MS: *m/z* (%) = 517 (2) [M^+], 489 (5) [$M^+ - CO$], 461 (5) [$M^+ - 2CO$], 434 (12) [$M^+ - 3CO$], 406 (10) [$M^+ - 4CO$], 378 (15) [$M^+ - 5CO$], 350 (18) [$M^+ - 6CO$], 231 (100) [$M^+ - 6CO - 2Co$].

Dicobaltatetrahedrane-substituted closo-C_2B_5 and nido-C_2B_4 carboranes **4d**, **5d**

Similar procedures as described for **4c/5c**. **2d** (196 mg, 0.81 mmol), $Co_2(CO)_8$ (324 mg, 0.95 mmol). A brown oil was obtained which was identified to be a mixture of **4d/5d** (*ca.* 7 : 1) (300 mg, *ca.* 57%) after the reaction mixture was filtered on a pad of sand. **4d**: ^{1}H NMR (C_6D_6): $\delta = 0.2$ (br., $SiMe_3$), 1.3 (br., CH_3), 2.2 − 2.4 (br., CH_2). – ^{11}B{^{1}H} NMR (hexane): $\delta = 7.2$ (B4,6), 2.5 (B5), −6.4 (B1), −20.9 (B7); – ^{11}B NMR (C_6D_6): $\delta = 6.8$ (br. d, $J_{B,H} = 135$ Hz, B4,6), 1.2 (br., B5), −6.9 (B1), −21.4 (br. d, $J_{B,H} = 179$ Hz, B7). – ^{13}C NMR (C_6D_6): $\delta = -0.30$ ($SiMe_3$), 13.6 (CH_3), 21.8 (CH_2), 115.5 (br., C_{cage}), 200.3 (CO). – ^{29}Si NMR (C_6D_6): $\delta = 38.3$. – EI-MS: *m/z* (%) = 523 (2) [M^+], 495 (12) [$M^+ - CO$], 467 (6) [$M^+ - 2CO$], 439 (20) [$M^+ - 3CO$], 411 (51) [$M^+ - 4CO$], 383 (41) [$M^+ - 5CO$], 355 (46) [$M^+ - 6CO$]. – HR-MS (EI): $m/z = 524.0362$ [M^+]; calcd. for $^{12}C_{17}{}^1H_{23}{}^{11}B_5Co_2O_6{}^{28}Si$ 524.0393 (Δm = −3.1 mmu); **5d**: ^{11}B NMR (C_6D_6): $\delta = 6.8$ (br.), −2.9 (br.), −36.5 (apical boron). – ^{13}C NMR (C_6D_6): $\delta = 13.9$ (CH_3), 21.9 (CH_2), signals for the other carbon atoms are weak. – EI-MS: *m/z* (%) = 514 (1) [M^+], 486 (15) [$M^+ - CO$], 458 (9) [$M^+ - 2CO$], 430 (16) [$M^+ - 3CO$], 402 (6) [$M^+ - 4CO$], 374 (13) [$M^+ - 5CO$], 346 (15) [$M^+ - 6CO$]. – HR-MS (EI): $m/z = 514.0335$ [M^+]; calcd. for $^{12}C_{17}{}^1H_{24}{}^{11}B_4Co_2O_6{}^{28}Si$ 514.0378 (Δm = −4.3 mmu).

(Cyclopentadienyl)[1,3-bisdicarbaheptaboranyl(7)-2,4-diphenylcyclobutadiene] cobalt complex **6c**

To a solution of **2c** (195 mg, 0.81 mmol) in toluene (20 ml) was added a portion of $CpCo(CO)_2$ (81 mg, 0.45 mmol) at r. t.. The deep red mixture was heated at reflux and monitored by ^{11}B NMR. After one week, $CpCo(C_2H_4)_2$ (100 mg, 0.55 mmol) was added and the resulting mixture was again heated at 70 °C (oil bath) for 6 days. After cooling the brown mixture was dried to give a brown residue, which was extracted with hexane and filtered through a pad of sand. The filtrate was dried *in vacuo*, leaving a dark brown oil, which was identified to be a mixture of **6c**, **6d** and **7c**. – ^{11}B NMR (toluene): $\delta = 6.3$, 2.2, −4.0, −16.6, −19.6, −45.1(w) ppm. – EI-MS: *m/z* (%) = 606 (10) [**6c**$^+$], 597 (100) [**6d**$^+$], 365 (27) [**6c**$^+ -$ **2c**], 232 (32) [**7c**$^+$]. – HR-MS (EI): $m/z = 608.3672$ [**6c**$^+$]; calcd. for $^{12}C_{33}{}^1H_{43}{}^{11}B_{10}Co$ 608.3627 (Δm = 4.5 mmu); $m/z = 232.1932$ [**7c**$^+$]; calcd. for $^{12}C_{14}{}^1H_{20}{}^{11}B_4$ 232.1932 (Δm = −0.5 mmu).

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