# Synthesis and Bonding in Hybrid Diborolyl/Boranyl and Thiaboranyl Triple-Decker Compounds – Electronic Contribution of Heteroborane Cluster Ligands in Complexes☆

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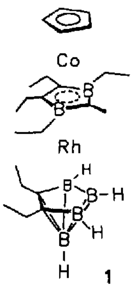
The three-component reaction of $[(\eta^5\text{-}C_5H_5)Co\{\eta^5\text{-}(CEt)_2(BEt)_2CMe\}]^-$ (**6**-H)$^-$, $CoCl_2$ and $B_9H_{14}^-$ (**7**) yields the triple-decker complex $[(\eta^5\text{-}C_5H_5)Co\{\mu,\eta^5\text{-}(CEt)_2(BEt)_2CMe\}\text{-}6\text{-}Co(B_9H_{13})]$ (**8**) with a terminal $B_9H_{13}$ ligand containing two cobalt–boron-bridging hydrogen atoms. Analogously, (**6**-H)$^-$, $CoCl_2$, and *arachno*-6-$SB_9H_{12}^-$ (**10**) react to give the triple-decker $[(\eta^5\text{-}C_5H_5)Co\{\mu,\eta^5\text{-}(CEt)_2(BEt)_2CMe\}\text{-}1\text{-}Co\text{-}2\text{-}(SB_9H_9)]$ (**11**). The analogous reaction with the heteroboranyl anion *arachno*-6,8-$S_2B_7H_8^-$ leads to the loss of one boron atom, forming the air-stable triple-decker complex $[(\eta^5\text{-}C_5H_5)Co\{\mu,\eta^5\text{-}(CEt)_2(BEt)_2CMe\}\text{-}7\text{-}Co\text{-}6,8\text{-}(S_2B_6H_8)]$ (**12**). The X-ray structure determination shows that the dithiacobaltaborane fragment in **12** has an *arachno* cluster geometry. The three-component reaction of (**6**-H)$^-$, $CoCl_2$, and *arachno*-2,3-$S_2B_9H_{10}^-$ yields the expected triple-decker $[(\eta^5\text{-}C_5H_5)Co\{\mu,\eta^5\text{-}(CEt)_2(BEt)CMe\}Co\text{-}6,8\text{-}(S_2B_9H_9)]$ (**15**), and surprisingly the sandwich complex $(\eta^5\text{-}C_5H_5)Co\text{-}6,8\text{-}(S_2B_9H_9)$ (**16**). The constitutions of the new compounds are based on NMR and MS data. A rule is described regarding the electron donation of heteroboranyl cluster ligands in metal complexes.

## Introduction

The complex chemistry of boron heterocycles and the chemistry of metallacarboranes has been combined in carboranyl triple-decker compounds with bridging $C_3B_2$ and $C_2B_3$ ligands[1]. In the "hybrid" complexes **1**–**5** the carborane clusters function as terminal ligands which supply four electrons in **1**, **2**, **3**, and **5**, five electrons in **4a**, **b**, and three electrons in **4c** for the bonding to the metal center. Alternatively, **1**–**5** can be viewed as metallacarboranes with seven to twelve cluster atoms[1–4].

The framework of the metallacarboranes in **1**, **2**, **3**, **4a**, and **5a** adopts a *closo* structure, and in **4c** a *nido* arrangement whereas **4b** and **5b** have structures between *closo* and *nido*. In order to further elucidate the donor capability of carboranes, boranes and heteroboranes as ligands to metal centers we have synthesized the new triple-decker complexes **8**, **11**, **12** and **15** with borane and thiaborane ligands. We present here a general electron-counting procedure to determine the electron contribution of heteroborane cluster ligands in metal complexes.



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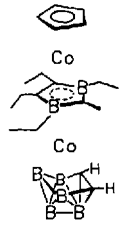

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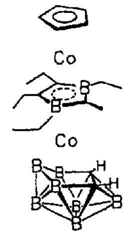

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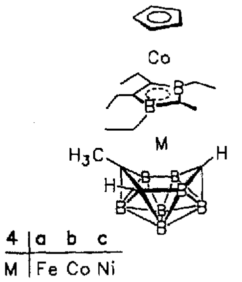
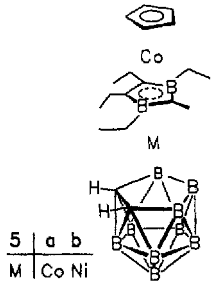
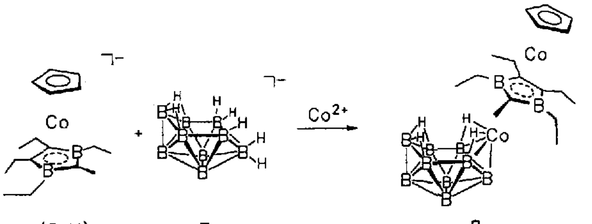




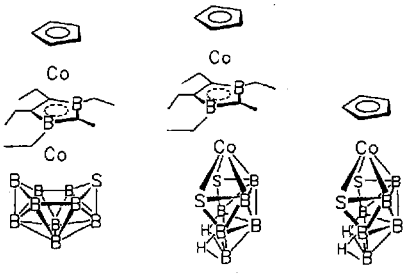
## Synthesis and Properties

The three-component reaction of the sandwich anion (**6**-H)$^-$ and the boranyl anion $B_9H_{14}^-$ (**7**) with $CoCl_2$ followed by oxidation in air leads to the brown triple-decker complex **8** in 24% yield. Its constitution is derived from NMR and MS data (see Experimental Section). The cluster electroncount for **8** (24 skeletal electrons and 10 vertices) predicts a *nido* structure akin to decaborane $B_{10}H_{14}$. Several isomers of the related cluster $(\eta^5\text{-}C_5H_5)Co(B_9H_{13})$ are known, the $^{11}B$-NMR spectrum of **8** is very similar to that of $[6\text{-}(\eta^5\text{-}C_5H_5)Co(B_9H_{13})]$ (**9**)[5]. The bridging B–H–Co hydrogen atoms appear only in the $^1H\{^{11}B\}$-NMR spectrum as a high-field signal at $\delta = -15.5$. In **9** the corresponding $^1H$-NMR signal is found at $\delta = -12.8$, which indicates that the isolobal fragments ($\eta^5$-$C_5H_5$)Co{$\mu$,$\eta^5$-$(CEt)_2(BEt)_2$-CMe}Co and ($\eta^5$-$C_5H_5$)Co have similar electronic properties.



(6-H)$^-$ 7 8

An analogous reaction of *arachno*-$Cs^+SB_9H_{12}^-$ (**10**), (**6**-H)$^-$, and $CoCl_2$ results in a 14% yield of **11**, the first triple-decker with a terminal thiaborane ligand. The air-sensitive green complex is diamagnetic; its constitution follows from the NMR data. The thiacobaltaborane framework $B_9CoS$ in **11** adopts with its 24 skeletal electrons and 11 vertices a *closo* arrangement.

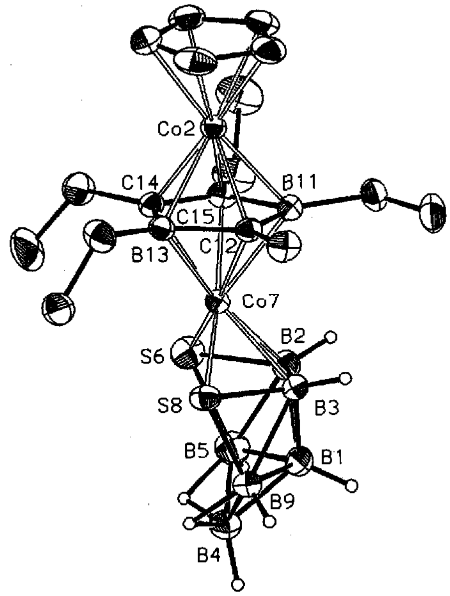


11 12 13

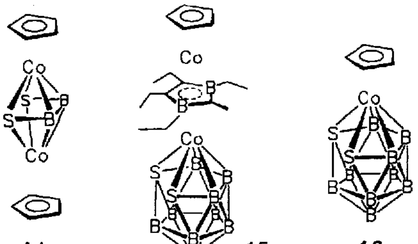
The comparable three-component reaction of the *arachno*-6,8-$S_2B_7H_8^-$ anion with $CoCl_2$ and the sandwich anion (**6**-H)$^-$ results in the air-stable triple-decker complex **12**. Its MS data indicate that the reaction occurred with extrusion of a BH unit. In agreement, **12** shows four signals in its $^{11}$B-NMR spectrum in a ratio of 2:2:1:1. The observed intensities and chemical shifts of these resonances are consistent with the $^{11}$B-NMR data of the electronically related complex *arachno*-7-($C_5H_5$)Co-6,8-$S_2B_6H_8$ (**13**)[6], which suggests similar structures for the $B_6CoS_2$ frameworks in **12** and **13**.

The X-ray crystal structure analysis of **12** confirms the triple-decker arrangement with the bridging 1,3-diborolyl ring and the terminal thiaborane ligand (Figure 1). As in **13** and the $\mu$-dithiadicobalta triple-decker **14**[7] the thiaborane is $\eta^4$-coordinated via the $S_2B_2$ face to the cobalt atom. The Co−B and Co−S bond lengths (Table 1) in **12**, **13**, and **14** are comparable, which indicates a similar bonding of the thiaboranes to the cobalt atom. As predicted based on its skeletal electron count (9 cluster atoms, 24 skeletal electrons) the $CoS_2B_6$ fragment has, like in **13**, an *arachno*-type geometry based on an octadecahedron missing two vertices. In contrast, the $B_2Co_2S_2$ framework of **14** with 16 skeletal electrons adopts a *nido* structure.

Figure 1. Molecular structure of **12**[a]



[a] Selected bond lengths [Å] and angles [°]: Co7−S6 2.245(1), Co7−S8 2.241(1), Co7−B2 2.148(4), Co7−B3 2.124(4), Co7−B11 2.128(3), Co7−B13 2.148(4), Co7−C12 2.084(3), Co7−C14 2.109(3), Co7−C15 2.069(3), B−S 1.886−1.920(4), B2−B3 1.782(6); S6−B2−B3 116.1(2), S8−B3−B2 116.9(3).



14 15 16

Table 1. Selected bond lengths in the thiacobaltaboranes **12**, **13**, and **14**

| | Co−S6 | Co−B2 | Co−B3 | Co−S8 |
|---|---|---|---|---|
| **12** | 2.245(1) | 2.148(4) | 2.124(4) | 2.241(1) |
| **13** | 2.231(1) | 2.112(4) | 2.109(4) | 2.235(1) |
| **14** | 2.244(2) | 2.138(6) | 2.181(7) | 2.232(2) |
| | 2.239(2) | 2.148(6) | 2.181(6) | 2.237(2) |

The spectroscopic and X-ray data reveal again that the ($\eta^5$-$C_5H_5$)Co{$\mu$,$\eta^5$-$(CEt)_2(BEt)_2$CMe}Co and ($C_5H_5$)Co fragments have similar electronic properties. Obviously, the electronic contribution of the $S_2B_6H_8$ part in the complexes **12** and **13** is the same for the ($\eta^5$-$C_5H_5$)Co{$\mu$,$\eta^5$-$(CEt)_2$-$(BEt)_2$CMe}Co and the ($\eta^5$-$C_5H_5$)Co fragment. The cobalt−cobalt distance (3.22 Å) of **12** is similar to that of the related 30-VE triple-decker [($\eta^5$-$C_5H_5$)Co{$\mu$,$\eta^5$-$(CEt)_2$-$(BEt)_2$CMe}Co(1,10-$C_2B_7H_9$)][2] with the cobalt atoms 3.20 Å apart, whereas the Co−Co distances in the 31-VE complexes [($\eta^5$-$C_5H_5$)Co{$\mu$,$\eta^5$-$(CEt)_2(BEt)_2$CMe}Co(2-$CH_3$-2,3,5-$C_3B_7H_9$)] (3.32 Å)[3] and [($\eta^5$-$C_5H_5$)Co{$\mu$,$\eta^5$-$(CR^1)_2$-

$(BR^2)_2CR^3\}$-Co($\eta^5$-$C_5H_5$)] (3.28–3.32 Å)[8] are increased due to the additional electron in an antibonding MO. The reaction of the anions $S_2B_9H_{10}^-$[9] and (**6**-H)$^-$ with $Co^{2+}$ leads to the triple-decker complex **15**. In addition, the sandwich complex **16** is formed, which indicates either an exchange of the boron heterocycle in (**6**-H)$^-$ for the thiaborane ligand or an elimination of $C_5H_5^-$ from (**6**-H)$^-$ had occurred. Todd et al.[10] reported the synthesis and structure of the related diselena complex [($C_5H_5$)Co($Se_2B_9H_9$)] (**17**) with a *nido* 12-atom arrangement for the $CoSe_2B_9$ cluster. The $^{11}$B-NMR spectrum shows six signals (δ = 27.8, 14.0, 0.0, −2.1, −4.5, −22.4) in the ratio 1:2:2:1:1:2, indicating a higher symmetry than that found in the solid-state structure. This difference was attributed to either an accidental overlap of resonances or a fluxional process[10]. The thiacobaltaborane **16** exhibits five signals (δ = 23, 8, −1, −3, and −22) in the ratio 1:2:3:1:2, indicating that [($C_5H_5$)Co($Se_2B_9H_9$)] and **16** have similar structures in solution. The apparent properties of **15** contrast with that of the recently reported[11] isoelectronic complex [$(PPh_2)_2HIrS_2B_9H_9$] which appears to have a static structure in solution.

### Electronic Contribution of Heteroboranes as Ligands in Metal Complexes

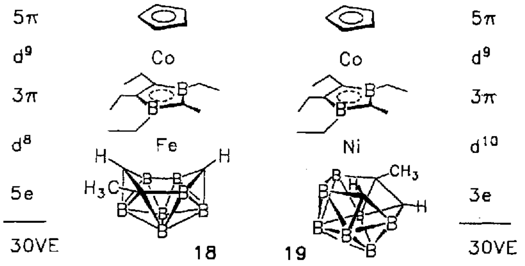
The cluster electron-counting rules[12] for *closo*, *nido*, and *arachno* compounds and the isolobal relationship[13] between atoms and metal complex fragments as building blocks for polyhedral compounds are valuable tools to predict the structure of clusters. While the electron contribution of an organic ligand can be predicted in a straightforward manner, the electron-donating properties of a heteroborane ligand are sometimes confusing.

The electron-donation of a heteroborane to a metal center depends on two factors: (I) the geometry of the heteroborane framework in the metallaborane and (II) the electron donation of the heteroatoms in the heteroborane framework. Let us first consider the electronic influence of the geometry of the borane frameworks to metals. We notice that any borane ligand with a *nido* framework geometry supplies two electrons to a metal center in a *closo* $MB_n$ cluster, any borane ligand with an *arachno* framework geometry does not donate any electron to a metal center in a *nido* $MB_n$ cluster, whereas a borane ligand with a *hypho* framework geometry functions as a two-electron acceptor (a minus-2e donor) in an *arachno*-$MB_n$ cluster. This is summarized in Table 2.

Table 2. Electrons donated by borane ligands

| *Geometry* of borane complex | *Geometry* of borane ligand | Electrons donated by borane ligands |
|---|---|---|
| *closo*-borane-$ML_n$ | *nido*-borane | +2e |
| *nido*-borane-$ML_n$ | *arachno*-borane | 0e |
| *arachno*-borane-$ML_n$ | *hypho*-borane | −2e |

The electronic contribution of the individual heteroatom(s) of a heteroborane ligand to a metal center is a follows: Of the four valence electrons of a carbon atom, one is used for bonding to the exopolyhedral substituent, e.g. a hydrogen atom, and two are involved in the framework bonding of the heteroborane, which leaves one electron of a CH or CR unit to interact with the metal center in the complexes. A sulfur atom in a thiametallaborane contributes two electrons to the heteroborane framework and two electrons are located in an exopolyhedral lone-pair orbital, thus two electrons may interact with the metal center. A BeR unit counts as minus-one-electron donor to a metal center. To illustrate this relationship let us compare the diamagnetic triple-decker complexes **18** and **19**[3]. Both carry the terminal $CH_3C_3B_7H_9$ ligand, which exhibits in **18** a *nido* framework, in **19** an *arachno* arrangement. This causes different electronic contributions of the $CH_3C_3B_7H_9$ carborane ligand: In **18** the *nido* carborane ligand supplies a total of 5 electrons (3e from 3 CH groups and 2e from the *nido* framework) for the bonding to the iron center, whereas the *arachno* carborane ligand in **19** donates only 3e to the nickel center (3e from 3 CH groups and no electron from the arachno framework).



**18** **19**

One can regard **18** and **19** as clusters, in which the [($C_5H_5$)Co(CEt)$_2$(BEt)$_2$CMe]Fe and [($C_5H_5$)Co(CEt)$_2$(BEt)$_2$CMe]Ni units supply 1e and 3e, respectively. The eleven-vertex $FeC_3B_7$ cluster of **18** has a total of 24 skeletal electrons, the expected *closo* geometry is found. In **19** the eleven-vertex $NiC_3B_7$ cluster has 26 framework electrons and the calculated *nido* structure of the tricarbanickelaundecaborane is realized. If the $C_3B_7$ ligand would act in **18** as a 3e donor to give **18′** with 28 valence electrons, we would expect a diamagnetic complex and an *arachno*-$C_3B_7$ ligand. In **19** the carborane could function as a 5e ligand, leading to a paramagnetic 32e triple-decker, which, however, is energetically unfavorable.

An alternative way of calculating the donor capabilities of heteroborane ligands to metal centers in diamagnetic complexes having 18 or 30 VE works as follows: Addition of all donor electrons of the other ligand(s) and the d electrons of the metal center(s), and then subtraction of this sum from 18 (for mononuclear complexes) or from 30 (for triple-decker complexes) results in the number of donor electrons of the heteroborane ligand.

Let us now consider **12**. The electronic contribution of the heteroborane ligand $S_2B_6H_8$ to the metal center is counted as follows: 4e from 2 S, 2e from 2 H, and minus-2e (*hypho* framework) give a total of 4e donated by the *hypho* ligand to the cobalt atom. The number of 30 VE is given by: 5π ($C_5H_5$), d$^9$ (Co), 3π ($C_3B_2$), d$^9$ (Co), 4e ($S_2B_6H_8$).

This is consistent with the observed diamagnetic behavior of **12**.

The diamagnetic dicobalt complex **15** has a total of 30 VE: the *arachno* ligand with its framework $B_9S_2$ supplies 2 × 2e from the two sulfur atoms and 0e from the *arachno* framework in the *nido* cluster for the bonding to the cobalt atom.

## Conclusion

In this work we report the synthesis and the structure of new triple-decker complexes with the terminal ligands $B_9H_{13}$, $SB_9H_9$, $S_2B_6H_8$, and $S_2B_9H_9$. A rule was found, which allows the electron book-keeping in heteroborane metal complexes on the basis of the structure of the heteroborane ligand and of the kind of its heteroatoms. Thus, a *nido* ligand in a *closo* metallaborane donates 2 electrons, an *arachno* ligand in a *nido* metallaborane donates zero electrons, and a *hypho* ligand in an *arachno* metallaborane functions as a minus-2e donor. The heteroatoms of the heteroboranes supply additional electrons as listed in Table 3.

Table 3. Individual electronic contributions of atoms or units

| Atom group | Number of valence electrons | Exopolyhedral electrons | Framework electrons | Valence electrons donated to metal |
|---|---|---|---|---|
| CH | 5 | 2 | 2 | 1 |
| BH | 4 | 2 | 2 | 0 |
| BeH | 3 | 2 | 2 | −1 |
| S | 6 | 2 | 2 | 2 |
| NH | 6 | 2 | 2 | 2 |

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## Experimental Section

*General Procedures:* Unless otherwise noted, all reactions and manipulations were performed in dry glassware under $N_2$ using standard Schlenk or vacuum-line techniques. Solvents were distilled from appropriate drying agents under $N_2$ before use. The compounds $Na^+$(*nido*-$B_9H_{14}^-$)[13], $Cs^+$(*nido*-6-$SB_9H_{12}$)$^-$[14], $Na^+$(*arachno*-6,8-$S_2B_7H_9^-$)[15], $C_{14}H_{18}N_2^+$(*arachno*-2,3-$S_2B_9H_{10}^-$)[9], and $Li^+[(\eta^5\text{-}C_5H_5)Co\{\eta^5\text{-}(CEt)_2(BEt)_2CMe\}]^-$[16] were prepared by previously described methods. $CoCl_2$ was dried for 15 h at 120 °C in vacuo and stored under $N_2$ until use. The NMR spectra were recorded in $C_6D_6$ solution with a Bruker AF 200. Mass spectra were obtained with a V6-Fisons ZAB-H using a V6 11-250-J unit.

*$[(\eta^5\text{-}C_5H_5)Co\{\mu,\eta^5\text{-}(CEt)_2(BEt)_2CMe\}\text{-}6\text{-}Co(B_9H_{13})]$* (**8**): In a 100-ml Schlenk flask under $N_2$, a suspension of $CoCl_2$ (0.78 g, 0.61 mmol) in 10 ml of THF was added dropwise to a stirred mixture of $Li^+[(\eta^5\text{-}C_5H_5)Co\{\eta^6\text{-}(CEt)_2(BEt)_2CMe\}]^-$ (0.132 g, 0.42 mmol) and $Cs^+(B_9H_{14})^-$ (0.151 g, 0.62 mmol) in 20 ml of THF at −78 °C. The mixture was warmed to room temperature and stirred for 4 h. The solvent was evaporated to give an oily brown residue which was adsorbed on $Al_2O_3$. The alumina was extracted with $CH_2Cl_2$, and the solvent was evaporated. The resulting brown oil was chromatographed on an $SiO_2$ plate (500 μ, Merck) with $C_5H_{12}$/$CH_2Cl_2$ (3:1) to yield 0.48 g (24%) of brown **8**, m.p. 88 °C. – $^1H$ NMR $\delta$ = 3.78 (s, 5H), 2.52 (m, 2H), 2.28 (m, 2H), 2.11 (q, 4H), 1.81 (s, 3H), 1.57 (t, 6H), 0.82 (t, 6H), −3.4 (br., 2H), −15.5 (br., 2H). – $^{11}B$ NMR (64.2 MHz): $\delta$ = 21 (2B), 19 (2B), 17 (2B), 7, −2 (2B), −17, −27. – $^{13}C$ NMR (50.3 MHz): $\delta$ = 93 (br.), 81.5, 25.3, 20.9, 17.7, 14.5, 13 (br.). – $C_{17}H_{41}B_{11}Co_2$: calcd. 484.2896, found 484.2890 (HRMS).

*$[(\eta^5\text{-}C_5H_5)Co\{\mu,\eta^5\text{-}(CEt)_2(BEt)_2CMe\}Co(SB_9H_9)]$* (**11**): In a procedure similar to that used for **8**, a suspension of $CoCl_2$ (0.095 g, 0.73 mmol) in 10 ml THF was added dropwise at −78 °C to a stirred mixture of $Li^+[(\eta^5\text{-}C_5H_5)Co\{\eta^5\text{-}(CEt)_2(BEt)_2CMe\}]^-$ (0.170 g, 0.54 mmol) and $Cs^+$ 6-$SB_6H_{12}^-$ (0.145 g, 0.54 mmol) in THF (20 ml). The mixture was warmed to room temperature and stirred for 4 h. The product was separated using $C_5H_{12}$/$CH_2Cl_2$ (1:1) as the eluating solvent for the TLC to give 0.044 g (16%) of air-sensitive dark green **11**. – $^1H$ NMR (200 MHz): $\delta$ = 3.90 (s, 5H), 2.35–2.75 (m, 2H), 1.85–2.25 (m, 6H), 1.78 (s, 3H), 1.61 (t, 3H), 1.47 (t, 3H), 1.17 (t, 3H), 0.84 (t, 3H). – $^{11}B$ NMR (64.2 MHz): $\delta$ = 19 (2B), 12, 7, −2 (2B), −11 (2B), −17 (2B), −20. – MS (CI); *m/z* (%): 510 (100) [$M^+$], 372 (8) [$M^+ - SB_9H_9$], 313 (14) [$M^+ - CoSB_9H_9$].

*$(\eta^5\text{-}C_5H_5)Co\{\mu,\eta^5\text{-}(CEt)_2(BEt)_2CMe\}Co\text{-}6,8\text{-}(S_2B_6H_8)$* (**12**): In a procedure similar to that used for **8** and **11** $CoCl_2$ (0.085 g, 0.65 mmol), $Li^+[(\eta^5\text{-}C_5H_5)Co\{\eta^6\text{-}(CEt)_2(BEt)_2CMe\}]^-$ (0.130 g, 0.41 mmol) and $Na^+$(*arachno*-6,8-$S_2B_7H_8^-$) (0.112 g, 0.65 mmol) were allowed to react in 20 ml of THF at −78 °C. The mixture was stirred for 4 h and worked up by preparative TLC using $SiO_2$ plates and pentane/toluene (2:1) yielding 0.045 g (34%) of **12**, m.p. 88 °C. – $^1H$ NMR (200 MHz): $\delta$ = 3.92 (s, 5H), 3.2 (br., 2H), 3.12 (br., 2H), 2.62 (m, 2H), 2.15–2.40 (m, 6H), 1.65 (t, 6H), 1.48 (s, 3H), 1.18 (t, 3H), −1.7 (br., 2H). – $^{11}B$ NMR (64.2 MHz): $\delta$ = 19 (2B), 3 (2B), −9 (2B), −33, −41. – $^{13}C$ NMR (50.3 MHz): $\delta$ = 93 (br.), 81.1, 24.1, 17.4, 15.7, 13.9, 11.8 (br.). – $^{12}C_{17}{}^1H_{36}{}^{11}B_8{}^{59}Co_2{}^{32}S_2$: calcd. 510.1667, found 510.1646 (HRMS).

*$(\eta^5\text{-}C_5H_5)Co\{\mu,\eta^5\text{-}(CEt)_2(BEt)_2CMe\}Co\text{-}6,8\text{-}(S_2B_9H_9)$* (**15**): 0.102 g of $CoCl_2$ (0.78 mmol) was added to a stirred mixture of $Li^+[(\eta^5\text{-}C_5H_5)Co\{\eta^5\text{-}(CEt)_2(BEt)_2CMe\}]^-$ (0.155 g, 0.49 mmol) and $C_{14}H_{18}N_2^+$(*arachno*-2,3-$S_2B_9H_{10}^-$) (0.183 g, 0.51 mmol) in 20 ml of THF at −78 °C. After warming up to room temperature and stirring for 3 h, the solvent was evaporated to give a brown residue which was dissolved in $CH_2Cl_2$ and filtered through $Al_2O_3$. The following separation by PTLC with $C_5H_{12}$/$CH_2Cl_2$ (2:1) as the eluating solvent yielded 0.021 mg of brown **15** (8%) and 0.015 g (10%) of brown **16**.

**15**: M.p. 143 °C. – $^1H$ NMR (200 MHz): $\delta$ = 3.87 (s, 5H), 2.76 (m, 2H), 2.42 (m, 2H), 2.19 (s, 3H), 1.91 (m, 2H), 1.74 (m, 2H), 1.41 (t, 6H), 0.95 (t, 6H). – $^{11}B$ NMR (64.2 MHz): $\delta$ = 21, 19 (2B), 11 (2B), −1 (3B), −4, −24 (2B). – $^{12}C_{17}{}^1H_{37}{}^{11}B_{11}{}^{59}Co_2{}^{32}S_2$: calcd. 544.2024, found 544.1998 (HRMS).

**16**: M.p. 104 °C. – $^1H$ NMR (200 MHz): $\delta$ = 4.09 (s). – $^{11}B$ NMR (28.75 MHz): $\delta$ = 23, 8 (2B), −1 (3B), −3, −22 (2B). – $^{12}C_5{}^1H_{14}{}^{11}B_9{}^{59}Co_1{}^{32}S_2$: calcd. 296.0706, found 296.0717 (HRMS).

*Crystal-Structure Analysis of* **12**: Crystal data: $M$ = 508.9; orthorhombic, space group *Pbca*, $a$ = 13.552(7), $b$ = 18.524(9), $c$ = 19.097(9) Å, $Z$ = 8, $V$ = 4794 Å$^3$, $d_{calcd.}$ = 1.41 g cm$^{-3}$. Data collection: Siemens-Stoe AED2 four circle diffractometer (Mo-$K_\alpha$ radiation, graphite monochromator) ambient temperature, ω-scan, 3° < 2Θ < 54°, *hkl* range 0–17, 0–23, 0–24, 5235 measured unique reflections, 3842 observed [$I > 2\sigma(I)$], empirical absorption correction (crystal size 0.5 × 0.5 × 0.6 mm, μ = 15.6 cm$^{-1}$, 0.881 < $T$ < 1.000). Structure solution by direct methods, refinement by full-matrix least squares on $F^2$ with all reflections, non-hydrogen atom anisotropic, the hydrogen atoms of the thiaborane ligand were located in a difference Fourier synthesis and refined isotropic, all other hydrogen atoms (methyl, ethyl, cyclopentadienyl) were inserted in calculated positions, only common isotropic temperature factors were refined, $R1 = 0.038$ (only observed reflection), $wR2 = 0.100$ all reflections, 310 parameters, electron density 0.3/−0.3 e Å$^3$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-406171, the names of the authors, and the journal citation.

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[☆] Dedicated to Professor *Rolf Gleiter* on the occasion of his 60th birthday.

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