Hybrid Diborolyl/Dicarbaboranyl Triple-Deckers: [(μ^5-Cyclopentadienyl)cobalt][μ,η^5-1,3-diborolyl)cobalt]dicarba-heptacarboranyl and -nonacarboranyl Complexes☆

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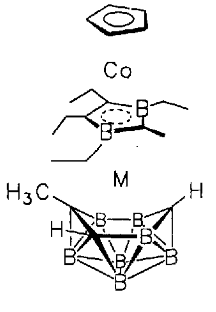
The three-component reactions of the sandwich anion $[(\eta^5\text{-}C_5H_5)Co(\eta^5\text{-}Et_4MeC_3B_2)]^-$ **(4-H)**$^-$ and various dicarbaborane anions with metal halides are described. Thus, **(4-H)**$^-$, *nido*-4,5-$C_2B_6H_9^-$ **(5)**, and $CoCl_2$ form the 30VE triple-decker $[(\eta^5\text{-}C_5H_5)Co(\mu,\eta^5\text{-}Et_4MeC_3B_2)Co(\eta^5\text{-}2,3\text{-}C_2B_5H_7)]$ **(6)**. An analogous three-component reaction of **(4-H)**$^-$, *arachno*-4,5-$C_2B_7H_{12}^-$ **(7)**, and $CoCl_2$ yields $[(\eta^5\text{-}C_5H_5)Co(\mu,\eta^5\text{-}Et_4MeC_3B_2)Co(\eta^5\text{-}6,9\text{-}C_2B_7H_9)]$ **(8)**, which rearranges on heating (57°C) to give the 1,6-isomer $[(\eta^5\text{-}C_5H_5)Co(\mu,\eta^5\text{-}Et_4MeC_3B_2)Co(\eta^5\text{-}1,6\text{-}C_2B_7H_9)]$ **(9)** with an activation energy of 127 ± 10 kJ/mol. The thermodynamically most stable 1,10-isomer $[(\eta^5\text{-}C_5H_5)Co(\mu,\eta^5\text{-}Et_4MeC_3B_2)Co(\eta^5\text{-}1,10\text{-}C_2B_7H_9)]$ **(10)** is formed by heating of **9** at 180°C. An alternative route to **9** is provided by the reaction of *arachno*-6,8-$C_2B_7H_{12}^-$ **(11)** with **(4-H)**$^-$ and $CoCl_2$. The analogous reaction with $RhCl_3$ leads to $[(\eta^5\text{-}C_5H_5)Co(\mu,\eta^5\text{-}Et_4MeC_3B_2)Rh(1,6\text{-}C_2B_7H_9)]$ **(15)** and unexpectedly to *closo*-2-$(\eta^5\text{-}C_5H_5)Co(1,6\text{-}C_2B_7H_9)$ **(12)**. The constitutions of the described compounds are derived from their ^1H-, ^{11}B-, ^{13}C-NMR data as well as mass spectral data. The X-ray structure analyses of **10** and **12** show the expected metal complexes with a $CoC_2B_7H_9$ framework. In **10** the carbon atoms occupy the capping positions of a bicapped square antiprism. The short Co–Co distance of 3.20 Å is in agreement with the 30VE configuration of **10**. In both **10** and **12**, the distance from the cobalt to the four-coordinate C4 is the shortest Co-to-cage atom distance.

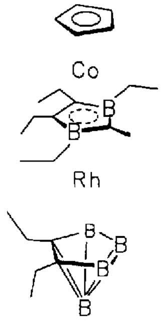
The independently developed complex chemistry of boron heterocycles and of metallaboranes was combined in hybrid triple-decker complexes with a bridging 1,3-diborolyl and a terminal carborane ligand[1]. Recently, the extension of this strategy to carbon-rich carboranes enabled the synthesis of the complexes **1a–c** with a terminal $CH_3C_3B_7H_9$ ligand, in which the electronic properties and the structure of the carborane ligand depend on the metal (M = Fe, Co, Ni)[2]. In the diamagnetic 30VE iron complex **1a** the carborane ligand and the iron atom form a *closo*-FeC_3B_7 cage fragment, whereas the 30VE nickel compound **1c** adopts a *nido*-NiC_3B_7 arrangement. The paramagnetic cobalt complex **1b** (31VE) has an intermediate structure.

An example with a smaller carborane ligand is the diamagnetic CoRh triple-decker **2** having 30 VE[1a]. The larger *nido*-C_2B_9 ligand[3] was incorporated in the triple-decker complexes **3a, b**[4]. Diamagnetic **3a** has 30 VE, the complex **3b** is paramagnetic.

To our knowledge no triple-decker complexes with a terminal dicarborane ligand having seven to ten vertices have previously been known. We describe here the first triple-decker metal complexes with a bridging 1,3-diborolyl heterocycle and a terminal $C_2B_5H_7$ or a $C_2B_7H_9$ ligand, respectively.



	1a	b	c
M	Fe	Co	Ni



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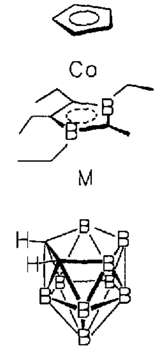

	3a	b
M	Co	Ni

Results and Discussion

Deprotonation of the 18VE complex $[(\eta^5\text{-}C_5H_5)Co\{\eta^5\text{-}(EtC)_2(EtB)_2CHMe\}]$ **(4)**[5] leads to the sandwich anion **(4-H)**$^-$, its reaction with $CoCl_2$ and the carboranyl anion *nido*-4,5-$C_2B_6H_9^-$ **(5)** gives unexpectedly the slightly air-sensitive triple-decker complex **6**. The brown, crystalline compound was obtained in 10% yield, its mass spectrum is consistent with the loss of one BH unit. This is in agreement with the ^{11}B-NMR data (see Experimental).

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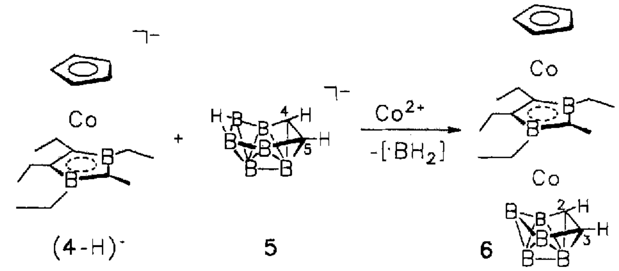
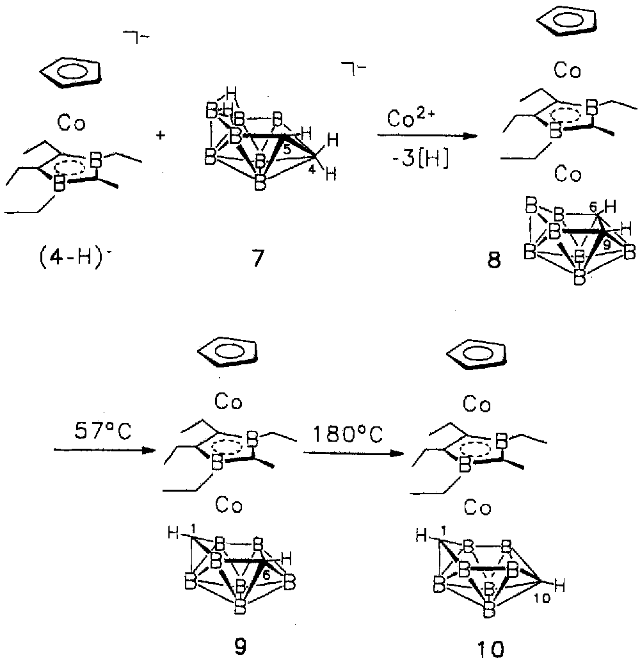
Scheme 1



The elimination of one BH vertex from the ligand during the formation of the complex **6** leading to the CoC_2B_5 framework is consistent with other studies of the coordination chemistry of the *nido*-4,5-$C_2B_6H_9^-$ anion which have shown that, for example, the *closo*-(η^5-C_5H_5)Co-2,3-$C_2B_5H_7$ complex is the predominant product formed by reaction of *nido*-4,5-$C_2B_6H_9$ with $Na^+C_5H_5^-$ and $CoCl_2$[6a]. According to the isolobal analogy[7] the (η^5-C_5H_5)Co(μ,η^5-$Et_4MeC_3B_2$)Co fragment functions as a two-electron donor. Thus, the CoC_2B_5 framework of **6** contains the 18 skeletal electrons required for a *closo*-metallacarborane structure. The dinuclear **6** is an electronic and structural analog of *closo*-1-(η^5-C_5H_5)Co-2,3-$Et_2C_2B_5H_5$[6b,c].

The analogous three-component reaction with the larger *arachno*-4,5-$C_2B_7H_{12}^-$ anion (**7**)[8] leads to the expected triple-decker complex [(η^5-C_5H_5)Co(μ,η^5-$Et_4MeC_3B_2$)Co(η^5-6,9-$C_2B_7H_9$)] (**8**) in 14% yield. The mass spectra and the ^{11}B-NMR data of the brown air-stable product indicate that (**7**-3H) is present in **8**. The metallacarborane cage fragment has 22 skeletal electrons and adopts a 10 vertex *closo* structure.

Scheme 2



As evidenced by the NMR data, heating of a C_6D_6 solution of **8** at 57 °C results in the formation of the metalladicarborane **9**. The isomerization of **8** to **9** involves a rearrangement where the carbon atoms migrate from their adjacent 6,9-positions in **8** to the non-adjacent 1,6-positions in **9**. This isomerization is entirely consistent with the earlier studies of Hawthorne et al.[9] who showed that the [2-(η^5-C_5H_5)Co-6,9-$C_2B_7H_9$] complex readily isomerizes to [2-(η^5-C_5H_5)Co-1,6-$C_2B_7H_9$] upon heating.

The isomerization of **8** was monitored by NMR spectroscopy, which reveals a first-order reaction and a half-life time of 40.5 h at 57 °C. The half-life time of **8** decreases to 3.7 h by increasing the reaction temperature to 75 °C. The activation energy was calculated to be 127 ± 10 kJ/mol. A comparable value of 129 kJ/mol was found for the isomerization of [2-(C_5H_5)Co-6,9-$C_2B_7H_9$] (**11**) to [2-(C_5H_5)Co-1,6-$C_2B_7H_9$] (**12**)[9a,b]. Further isomerization occurs by heating **9** to 180 °C, resulting in the formation of the brown air-stable **10** in 72% yield, which is the triple-decker analog of [2-(C_5H_5)Co-1,10-$C_2B_7H_9$] (**13**)[9b]. These isomerizations follow established rules[10]. The metal is located in the position of highest connectivity, the carbon atoms increase their separation and migrate to positions with a lower or the same connectivity. The thermodynamically most favored arrangement of this metallacarborane is realized when both carbon atoms are located in the four-coordination capping positions.

The comparison of the ^{11}B-NMR data of the triple-decker compounds **8**–**10** with those of the isomeric sandwich complexes [(η^5-C_5H_5)Co($C_2B_7H_9$)] **11**–**13** reveals the electronic similarity between the (η^5-C_5H_5)Co organometallic fragment and the (η^5-C_5H_5)Co(μ,η^5-$Et_4MeC_3B_2$)Co complex fragment (Table 1).

Table 1. ^{11}B-NMR shifts of **8**–**13**

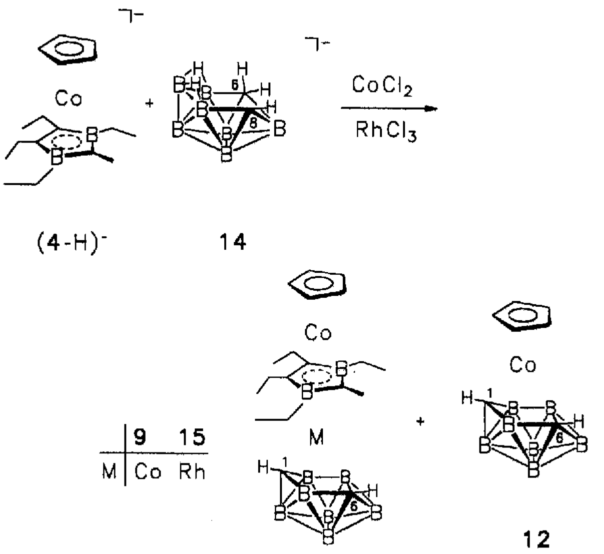
compound	^{11}B NMR data δ						ref.
(C_5H_5)Co($Et_4MeC_3B_2$)-Co-6,9-($C_2B_7H_9$) (**8**)	81.1	18.2(2B)*	1.0	-11.1 (2B)	-23.0	-28.1 (2B)	this work
(C_5H_5)Co-6,9-($C_2B_7H_9$) (**11**)	79.3	--	-3.0	-11.7(2B)	-24.8	-29.3(2B)	[9a]
(C_5H_5)Co($Et_4MeC_3B_2$)-Co-1,6-($C_2B_7H_9$) (**9**)	21.0	16.5(2B)*	-4.0(2B)	-18.1	-24.1(2B)	-32.2	this work
(C_5H_5)Co-1,6-($C_2B_7H_9$) (**12**)	20.2	--	-4.3 -6.8	-20.2	-24.2 -25.4	-33.0	[9b]
(C_5H_5)Co($Et_4MeC_3B_2$)-Co-1,10-($C_2B_7H_9$) (**10**)		17.1(2B)*	4.0(3B)	-17.2(2B)	-20.1(2B)		this work
(C_5H_5)Co-1,10-($C_2B_7H_9$) (**13**)			5.2(1B) 1.6(2B)	-18.0(2B)	-19,2(2B)		[9a]
(C_5H_5)Co($Et_4MeC_3B_2$)-Rh-1,10-($C_2B_7H_9$) (**15**)		14.5(2B)*	1,3(3B)	-17.2(2B)	-20.8(2B)		this work

* These signals are assigned to the boron atoms of the diborolyl ring.

When the carborane *arachno*-6,8-$C_2B_7H_{12}^-$ (**14**)[8], an isomer of **7**, is treated with the sandwich anion (**4**-H)$^-$ and $CoCl_2$ the triple-decker complex **9** is formed in 9% yield, which is the same compound obtained by rearrangement of **8** at 57 °C. When $RhCl_3$ is used the analogous reaction affords the 30VE triple-decker complex **15**. Surprisingly, in the latter reaction the sandwich complex **12**[9b] is formed in low yield. Presumably, it occurs via exchange of the 1,3-

diborolyl ligand in (**4**-H)$^-$ by **14**. Similar exchange reactions were observed when (**4**-H)$^-$ was allowed to react with $CH_3C_3B_7H_9^-$ as well as with $S_2B_9H_{10}^-$[11].

Scheme 3



X-ray Crystal-Structure Analyses

The quality of the crystal of **10** was not very good. Only 1/3 of the measured reflections up to $\Theta = 22°$ was observed [$I > 2\sigma(I)$]. The Co atoms were refined anisotropically, all other non-hydrogen atoms isotropically. The results of the refinement confirm the molecular topology derived from the NMR data, but do not allow any detailed discussion of bond lengths and angles. Compound **10** shows a triple-decker arrangement with the terminal carborane ligand $1,10\text{-}C_2B_7H_9$ (Figure 1). The best planes through the cyclopentadienyl and the diborolyl ligands exhibit an interplanar angle of 6.1°. The cobalt-cobalt distance (3.20 Å) is significantly shorter than in the 31VE complex **1b** (3.32 Å), which is explained by the difference in the electronic contribution of the *nido*-$C_2B_7H_9$ and the *nido*-$C_3B_7H_{10}$ carborane ligands. In contrast to **1b**, in **10** (30VE) no antibonding orbital is occupied. In the metallacarborane **10** the CoC_2B_7 fragment adopts a *closo* structure of a bicapped square antiprism, in which the capping positions are occupied with carbon atoms.

For **12** all non-hydrogen atoms were refined anisotropically, hydrogen atoms were localized in a difference Fourier synthesis and refined isotropically. The cobaltacarborane **12** contains 22 skeletal electrons and 10 vertices for which a *closo* arrangement is expected. The X-ray structure analysis confirms the bicapped square antiprism with one carbon and one boron atom in the capping positions (Figure 2). The structural data reveal similarities to the isoelectronic ferracarborane $[\eta^6\text{-}C_6(CH_3)_3H_3]Fe\text{-}(1,6\text{-}C_2B_7H_9)]$[12]. The complexed face (C1–B3–C6–B9–B5) in **12** is planar with the exception of C1 which juts out by 0.43 Å. The plane through the cyclopentadienyl ligand and the best plane through C1–B3–C6–B9–B5 enclose an interplanar angle of 7°. The shortest distance of the cobalt to a cage atom is Co2–C1 [1.913(3) Å].

Figure 1. Molecular structure of **10**. Selected bond lengths [Å]: Co2–C1 1.95(3), Co2–B3 2.19(3), Co2–B5 2.12(3), Co2–B6 2.05(3), Co2–B9 2.07(2), Co2–B11 2.14(2), Co2–B13 2.09(3), Co2–C12 2.07(2), Co2–C14(15) 2.09, 2.08(2), Co1–B11(13) 2.07, 2.08(3), Co1–C12 1.98(2), Co1–C14(15) 2.00, 2.02 (2)

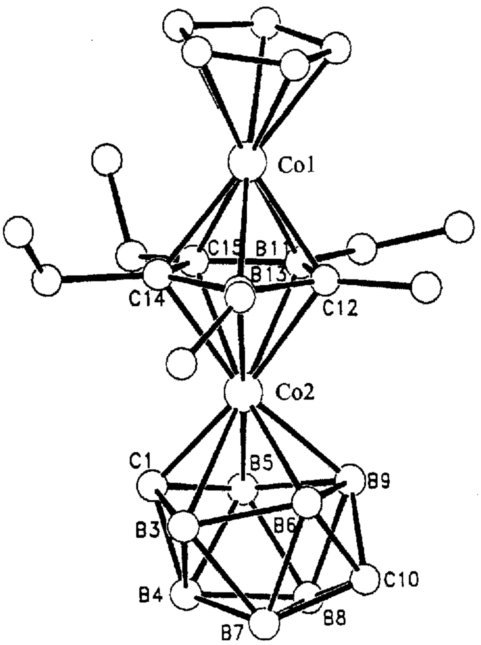
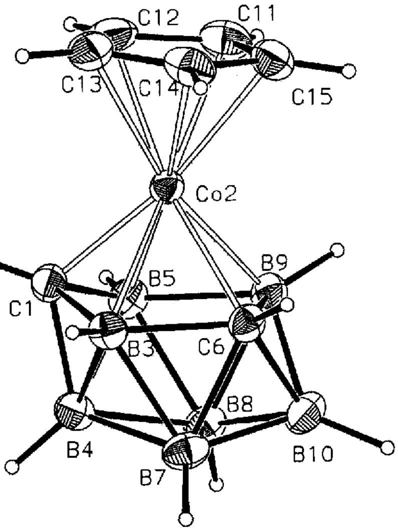


Figure 2. Molecular structure of **12**. Selected bond lengths [Å]: Co2–C1 1.913(3), Co2–B3 2.125(4), Co2–B5 2.156(4), Co2–C6 2.070(3), Co2–B9 2.069(4), Co2–C(Cp) 2.024–2.059(4), C1–B 1.591–1.613(5), C6–B 1.622–1.777(5), B10–B 1.678–1.704(6), B4–B7 1.764(6), all other B–B 1.800–1.853(6)



Conclusion

Reactions of the sandwich anion (**4**-H)$^-$ and various dicarbaborane anions with $CoCl_2$ lead to dinuclear species with triple-decker structures. The products have electronic properties similar to those of analogous C_5H_5Co complexes. Thus, the elimination of BH_2 from the *nido*-4,5-

$C_2B_6H_9^-$ carboranyl anion during the synthesis of **6** indicates that the fragments Co(**4**-H) and Co(C_5H_5) impose similar electronic requirements on the carboranyl ligand. The thermal rearrangement of **8** to **9** and then **10** parallels that of the analogous Co(C_5H_5) complex. These findings are further proof for the isolobal relationship between (**4**-H^-) and $C_5H_5^-$.

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Experimental

All reactions and manipulations were performed in dry glassware under nitrogen by using standard Schlenk techniques. Solvents were distilled from appropriate drying agents under nitrogen before use. (η^5-C_5H_5)Co(η^5-$MeEt_4C_3B_2H$) (**4**)[5], $Na^+C_2B_6H_9^-$ (**5**)[13], Na^+*arachno*-4,5-$C_2B_7H_{12}^-$ (**7**)[8], Na^+*arachno*-6,8-$C_2B_7H_{12}^-$[14] were prepared by previously described methods. $CoCl_2$ was dried for 15 h at 120 °C in vacuo and stored under nitrogen until used. – NMR: C_6D_6 solutions, Bruker AM 200 and AM 500.

(η^5-C_5H_5)Co(μ,η^5-$Et_4MeC_3B_2$)Co(η^5-2,3-$C_2B_5H_7$) (**6**): 191 mg (0.61 mmol) of **4** was deprotonated with a solution of 0.38 ml of 1.6 M *n*BuLi in 10 ml of THF. 195 mg (1.60 mmol) of Na^+ $C_2B_6H_9^-$ (**5**) and 118 mg (0.91 mmol) of $CoCl_2$ were added, and the reaction mixture was warmed to room temp. The volatile components were evaporated, and the residue was adsorbed on Al_2O_3. The product was eluted with CH_2Cl_2 and separated by preparative TLC on silica gel plates (CH_2Cl_2/C_5H_{12}, 1:1; 500 μm). Crystallization from a hexane solution gave 29 mg (10%) of brown **6**, m.p. 101 °C. – ^1H NMR (C_6D_6, 200 MHz): $\delta = 5.35$ (br, CH, 2H), 3.84 (s, C_5H_5, 5H), 2.34 (q, CH_2CH_3, 2H), 2.33 (q, CH_2CH_3, 2H), 2.29 (s, CCH_3, 3H), 1.2–1.7 (m, BCH_2CH_3, 10H), 1.13 (t, CH_2CH_3, 6H). – ^{11}B NMR (C_6D_6, 64.2 MHz): $\delta = 72$, 22, 14 (2 B), 1, −5, −8. – MS (CI), *m/z* (%): 457 [M^+] (35), 372 [$M^+ - C_2B_5H_7$] (25). Highly resolved mass for $^{12}C_{19}{}^1H_{35}{}^{11}B_7{}^{59}Co_2$: calcd. 458.2054; found 458.2040.

Table 2. Crystallographic data collection and structural refinement information[a]

	10	12
formula	$C_{19}H_{35}B_9Co_2$	$C_7H_{14}B_7Co$
fw	478.6	228.3
space group	Pcab	$P2_1/n$
Z	16	4
a [Å]	17.45 (1)	7.177 (5)
b [Å]	18.29 (1)	12.280 (7)
c [Å]	30.95 (2)	13.098 (8)
β [deg]		104.79 (5)
V [$Å^3$]	9878 (10)	1116 (1)
μ [cm^{-1}]	13.5	14.9
cryst.size [mm]	0.15x0.20x0.57	0.05x0.30x0.55
D_{calcd} [gcm^{-3}]	1.29	1.39
temperature	ambient	203 K
2Θmax [deg]	44	60
hkl collected	17, 19, 32	±10, 17, 18
no.of rflns measured	6030	3224
no.of unique rflns	6030	3224
no.of obsd rflns [$I > 2\sigma(I)$]	2264	2175
no of parameters	284	193
R1	0.106	0.043
wR2	0.329	0.113

(η^5-(C_5H_5)Co(Et_4Me-1,3-C_3B_2)Co(6,9-$C_2B_7H_9$) (**8**): 163 mg (1.21 mmol) of Na^+4,5-$C_2B_7H_{12}^-$ (**7**) and 181 mg (1.40 mmol) of $CoCl_2$ were added at −78 °C to a solution of 332 mg (1.06 mmol) of (**4**-H)$^-$ in 15 ml of THF. The work-up was similar to **6**. Crystallization from a hexane solution gave 74 mg (14%) of brown, air-stable **8**, m.p. 82 °C. – ^1H NMR (C_6D_6, 500 MHz): $\delta = 4.35$ (br, CH, 1H), 4.04 (C_5H_5, s, 5H), 3.62 (br, CH, 1H), 2.63 (m, CH_2CH_3, 2H), 2.42 (m, CH_2CH_3, 2H), 2.02 (m, CH_2CH_3, 2H), 1.88 (m, CH_2CH_3, 2H), 1.72 (s, CCH_3, 3H), 1.61 (t, CH_2CH_3, 3H), 1.55 (t, CH_2CH_3, 3H), 1.12 (t, CH_2CH_3, 3H), 1.04 (t, CH_2CH_3, 3H). – ^{11}B NMR (C_6D_6, 64.2 MHz): $\delta = 81.1$, 18.2 (2 B), 1.0, −11.1 (2 B), −23.0, −28.1 (2 B). – ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 96$ (br), 81.2, 58 (br), 39 (br), 25.1, 24.8, 17.7, 13.8, 13.6, 12 (br). – MS (EI), *m/z* (%): 481 [M^+] (100), 372 [$M^+ - C_2B_7H_9$] (65). Highly resolved mass for $^{12}C_{19}{}^1H_{37}{}^{11}B_9{}^{59}Co_2$: calcd. 482.2397; found 482.2401.

(η^5-C_5H_5)Co(μ,η^5-$Et_4MeC_3B_2$)Co(η^5-1,6-$C_2B_7H_9$) (**9**): a) 152 mg (0.49 mmol) of (**4-H**)$^-$ was treated with 86 mg (0.63 mmol) of *arachno*-Na^+6,8-$C_2B_7H_{12}^-$ and 98 mg (0.74 mmol) of $CoCl_2$ as in the previous experiment. The work-up furnished 23 mg (9%) of brown **9**, m.p. 82 °C.

b) A sealed NMR sample of **8** in C_6D_6 was heated at 57 °C. The isomerization of **8** to **9** was followed by integration of the C_5H_5 signals in the NMR spectroscopy. The same experiment was repeated at 75 °C. Kinetic data: $k_{57\,°C} = 4.75 \cdot 10^{-6}$/s, $k_{75\,°C} = 5.27 \cdot 10^{-5}$/s (yield quantitative). – ^1H NMR (C_6D_6, 200 MHz): $\delta = 4.18$ (br, CH, 1H), 4.01 (s, C_5H_5, 5H), 2.76 (m, CH_2CH_3, 2H), 2.28 (m, CH_2CH_3, 2H), 1.85 (s, CCH_3, 3H), 1.78 (q, CH_2CH_3, 4H), 1.43 (t, CH_2CH_3, 6H), 1.08 (t, CH_2CH_3, 6H), 0.95 (br, CH, 1H). – ^{11}B NMR (C_6D_6, 64.2 MHz): $\delta = 21.0$ (2 B), 16.5 (2 B), −4.0 (2 B), −18.1 (2 B), −32.2. – ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 80.8$, 40 (br), 19.6, 17.7, 13.5, 11 (br). – MS (EI), *m/z* (%): 481 [M^+] (100), Highly resolved mass for $^{12}C_{19}{}^1H_{37}{}^{11}B_9{}^{59}Co_2$: calcd. 482.2397; found 482.2401.

(η^5-C_5H_5)Co(μ,η^5-Et_4Me-1,3-C_3B_2)Co(η^5-1,10-$C_2B_7H_9$) (**10**): 25 mg (51 mmol) of **9** was dissolved in [D_8]toluene and the solution sealed in an NMR tube. The sample was heated for 3 h at 182 °C (NMR spectroscopic yield 85%). The reaction mixture was separated by TLC. Crystallization from CH_2Cl_2/C_5H_{12} (1:5) afforded 18 mg (72%) of brown **10**, m.p. 85 °C. – ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.85$ (br, CH, 1H), 6.30 (br, CH, 1H), 4.01 (s, C_5H_5, 5H), 2.81 (m, CH_2CH_3, 2H), 2.34 (m, CH_2CH_3, 2H), 1.93 (s, CCH_3, 3H), 1.85 (q, CH_2CH_3, 4H), 1.56 (t, CH_2CH_3, 6H), 1.18 (br, CH_2CH_3, 6H). – ^{11}B NMR (C_6D_6, 64.2 MHz): $\delta = 17.1$ (2 B), 4.0 (3 B), −17.2 (2 B), −20.1 (2 B). – MS (EI), *m/z* (%): 481 [M^+] (100). Highly resolved mass for $^{12}C_{19}{}^1H_{37}{}^{11}B_9{}^{59}Co_2$: calcd. 482.2397; found 482.2375.

(η^5-C_5H_5)Co(μ,η^5-Et_4Me-1,3-C_3B_2)Rh(η^5-1,6-$C_2B_7H_9$) (**15**) *and (η^5-C_5H_5)Co(η^5-1,6-$C_2B_7H_9$)* (**12**): 180 mg (0.57 mmol) of **4** was deprotonated with 0.38 ml of 1.5 M MeLi in 10 ml of THF. To this solution 68.0 mg (0.6 mmol) of *arachno*-Na-6,8-$C_2B_7H_{12}^-$ and 190.6 mg (0.57 mmol) of $RhCl_3 \cdot 3\,H_3CCN$ were added. The stirred reaction mixture was warmed up to room temp. After 1 h the vol-

[a] 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 numbers CSD-404508 (**12**) and -404509 (**10**), the names of the authors, and the journal citation.

atile components were evaporated, the residue was dissolved in $\mathrm{CH_2Cl_2}$ and the solution filtered through $\mathrm{SiO_2}$. The products were eluted with $\mathrm{CH_2Cl_2}$ and separated by preparative TLC on silica gel plates ($\mathrm{CH_2Cl_2/C_5H_{12}}$, 1:1; 500 μm). Crystallization from $\mathrm{C_6H_{14}/CH_2Cl_2}$ solution yielded 17 mg (12%) of red **12**, m.p. 157°C, and 14 mg (4.4%) of brown **15**. – ^{1}H NMR ($\mathrm{C_6D_6}$, 200 MHz): $\delta = 4.6$ (br., CH, 1H), 3.89 (s, $\mathrm{C_5H_5}$, 5H), 2.33 (m, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, 2H), 2.20 (m, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$, 2H), 1.82 (s, $\mathrm{CCH_3}$, 3H), 1.51–1.27 (m, $\mathrm{BC_2H_5}$, 10H), 1.26 (t, $\mathrm{CH_2C}\mathit{H}_3$, 6H), 0.95 (br., CH, 1H). – ^{11}B NMR ($\mathrm{C_6D_6}$, 64.2 MHz): $\delta = 14.5$ (2 B), 1.3 (3 B), –17.2 (2 B), –20.8 (2 B). – MS (EI), *m/z* (%): 525 [M$^+$] (100).

X-ray Crystal-Structure Analyses of **10** *and* **12**: The intensity data were collected with a Siemens-Stoe AED2 diffractometer (Mo-K_α radiation, graphite monochromator, ω scan) and corrected for Lp and absorption effects (empirical). The structures were solved by direct methods using the SHELXS86 and refined by full-matrix least-squares techniques based on F^2 of all reflections (SHELXL93).

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* Dedicated to Prof. *H. Roesky* on the occasion of his 60th birthday.

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