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Electrophilic substitution in eleven-vertex metallacarborane 1,2,4-$CpCoC_2B_8H_{10}$

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Bromination and mercuration of cobaltacarborane 1,2,4-$CpCoC_2B_8H_{10}$ were investigated. Mercuration under mild conditions ($Hg(OCOCF_3)_2$ in CH_2Cl_2) afforded the only monomercurated complex containing the mercury atom at position 6. Bromination gave rise to 3-mono-, 6-mono-, or 6,9-disubstituted derivatives depending on the reaction conditions. The mercurated derivative was studied by the X-ray diffraction method.

Key words: cobaltacarboranes, mercuration, bromination, X-ray diffraction analysis.

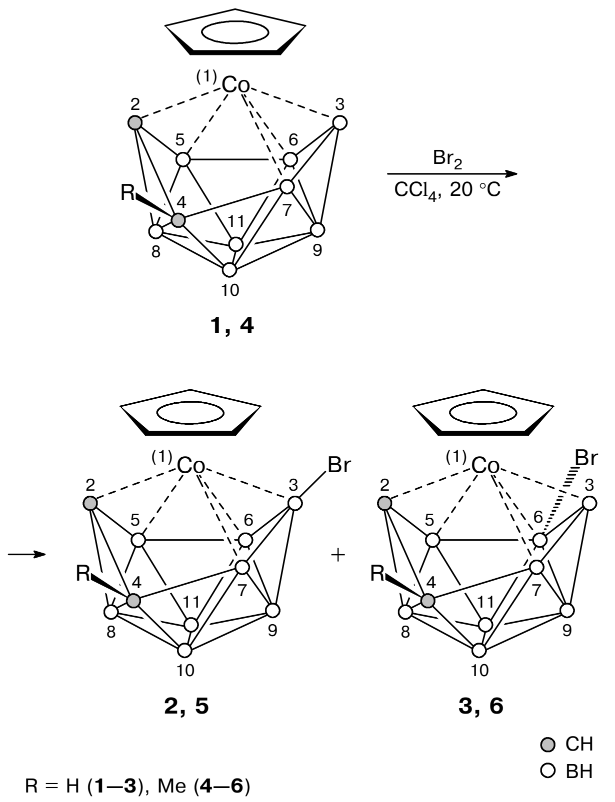
Previously,[1,2] we have studied the electrophilic substitution in a series of various icosahedral metallacarboranes and revealed some its characteristic features. The electrophilic substitution in non-icosahedral metallacarboranes containing a nonplanar open face of the π-carborane ligand is studied to a lesser extent.

Earlier, 2,1,6-$CpCoC_2B_7H_9$ has been brominated to give a dibromo derivative in which the positions of the Br atoms remained unknown.[3] Acylation of 2,1,6-$CpCoC_2B_7H_9$ gave rise to 2,1,6-$CpCoC_2B_7H_8$(8-COMe).[3] Bromination of another non-icosahedral cobaltacarborane, *viz.*, 1,2,3-$CpCoC_2B_8H_{10}$, was also investigated.[4] Two isomers containing Br atoms at the B(10) and B(4) atoms were isolated. The pentabromo derivative 4,5,6,10,11-Br_5-1,2,3-$CpCoC_2B_8H_5$ was prepared[4] by the reaction with an excess of bromine in the presence of $AlCl_3$. As part of our continuing studies on metallacarboranes, in the present work we examined the electrophilic substitution in eleven-vertex cobaltacarborane 1,2,4-$CpCoC_2B_8H_{10}$ (**1**) isomeric to the compound studied previously.[4]

Results and Discussion

The reaction of cobaltacarborane **1** with 1 equiv. of bromine in CCl_4 afforded two isomeric monobromides, *viz.*, 3-bromo-1-cyclopentadienyl-1-cobalta-2,4-dicarba-*closo*-octaborane(9) (**2**) and 6-bromo-1-cyclopentadienyl-1-cobalta-2,4-dicarba-*closo*-octaborane(9) (**3**) (Scheme 1).

Scheme 1



The isomers were separated by chromatography. Compounds **2** and **3** were obtained in 7.7 and 89% yields, respectively. The reaction of compound **1** with *N*-bromosuccinimide also gave rise to monobromides **2** and **3**; however, the yields were lower.

Compounds **2** and **3** were obtained as air-stable dark-violet crystalline substances. When kept in benzene for 2 days, both monobromides underwent rear-

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Table 1. Parameters of the ^{11}B NMR spectra of compounds **1**—**8**

Compound	δ	J_{B-H}/Hz	B atom in the cage
1	78.47	163.6	3
	14.09	147.6	9
	4.88	127.8	6
	3.10	138.3	5
	−7.84	157.6	10
	−20.11	173.7	8, 11
	−40.21	156.1	7
2	76.04	0	3
	15.80	151.6	9
	4.53	170.5	6
	2.05	156.4	5
	−8.38	159.4	10
	−21.70	160.5	8, 11
	−38.16	157.3	7
3	72.94	157.1	3
	14.80	152.1	9
	7.63	0	6
	2.99	155.9	5
	−9.69	158.4	10
	−19.85	157.6	8, 11
	42.60	157.8	7
4	74.38	160.1	3
	11.53	147.4	9
	0.81	102.2	6
	0.20	93.6	5
	−6.76	158.2	10
	−18.06	178.2	8
	−21.29	145.5	11
	−36.77	155.5	7
5	71.16	158.2	3
	12.81	152.4	9
	4.19	0	6
	1.31	148.3	5
	−8.30	161.1	10
	−18.74	195.9	8
	−20.51	160.1	11
	−38.68	159.2	7
7	71.01	163.8	3
	12.75	0	9
	8.91	0	6
	0.30	153.6	5
	−9.05	167.8	10
	−18.52	119.5	8
	−20.30	136.8	11
	−39.95	157.7	7
8	75.49	145.0	3
	14.34	130.0	9
	8.78	2288.8*	6
	3.01	153.0	5
	−8.18	150.0	10
	−19.88	137.0	8, 11
	−39.79	153.0	7

Note. The spectra of compounds **1**—**3**, **6** and **7** were measured in C_6H_6; the spectrum of **8** was measured in CH_2Cl_2, the spectra of **4** and **5** were measured in $CDCl_3$.

* J_{B-Hg}/Hz.

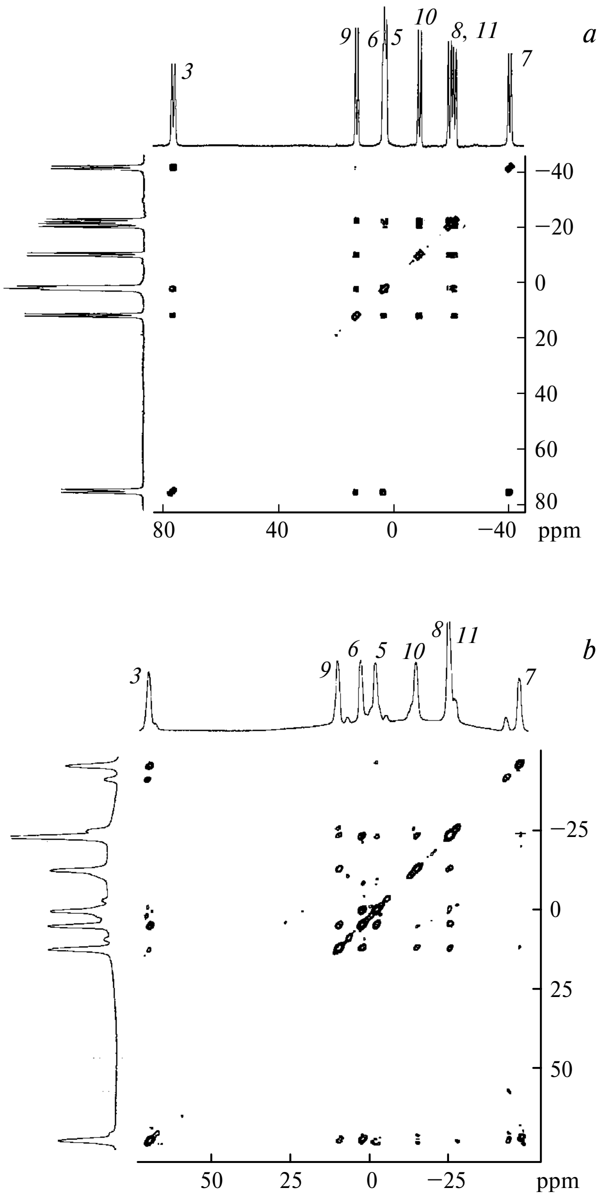
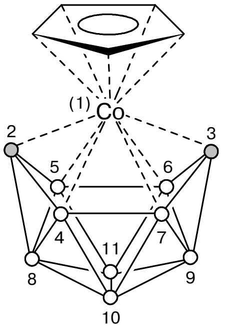


Fig. 1. The ^{11}B—^{11}B NMR correlation spectra of compounds **1** (*a*) and **3** (*b*).

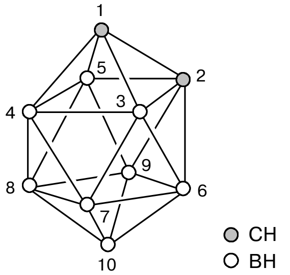
rangements to form identical mixtures of **2** and **3** in a ratio of 1 : 1.2 (according to the ^{11}B NMR spectroscopic data). On subsequent storage, the isomer ratio remained unchanged.

The positions at which the substitution occurred were determined based on comparison of the ^{11}B NMR spectra of compounds **1**, **2**, and **3** (Table 1). The signals were assigned based on the ^{11}B—^{11}B NMR correlation spectra of compounds **1** (Fig. 1, *a*) and **3** (Fig. 1, *b*) using a standard procedure.[5]

With the aim of investigating the effect of additional substituents in the open face of the carborane ligand on the rearrangement of bromo derivatives, the *C*-methyl derivative of the starting cobaltacarborane, *viz.*, 4-Me-1,2,4-Cp-$CoC_2B_8H_9$ (**4**), was synthesized by a procedure analogous to that used previously[6] for the preparation of complex **1**. The position of the methyl group in **4** was determined based on comparative analysis of the ^1H NMR spectra of complexes **1** and **4**, cobaltacarborane 1,2,3-Cp-$CoC_2B_8H_{10}$,[7] and carborane *closo*-1,2-$C_2B_8H_{10}$.[8]



1,2,3-Cp-$CoC_2B_8H_{10}$



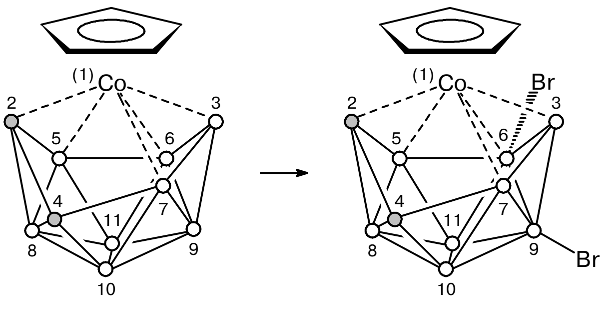
closo-1,2-$C_2B_8H_{10}$

The ^1H NMR spectrum of compound **4** cotains one singlet of the CH group at δ 5.82 corresponding to the proton at the C(2) atom and a signal at δ 1.92 corresponding to the Me group at the C(4) atom.

Bromination of compound **4** (see Scheme 1) also afforded a mixture of monobromides, which are analogs of compounds **2** and **3**. However, the reaction of compound **4** gave rise to B(6)-substituted isomer **6** as the major product, while the second isomer was obtained only in trace amounts. Prolonged storage (for more than one month) of a solution of bromide **6** in benzene also afforded complex **5**; however, the yield was substantially lower (according to the ^{11}B NMR spectroscopic data, the ratio **6** : **5** = 10 : 1). The ^1H NMR spectrum of the resulting mixture cotains a signal at δ 1.83 assigned to the C—CH_3 group of compound **6** as well as a signal at δ 1.57 corresponding to the analogous group in compound **5**. Therefore, the introduction of a substituent hinders the rearrangement. This rearrangement can, in principle, proceed according to two different mechanisms, *viz.*, through the migration of the Br atom between the B(3) and B(6) positions and through the skeletal rearrangement of the carborane cage analogous to that described previously.[9] The results obtained did not allow us to make an unambiguous choice between the mechanisms of the monobromide rearrangement.

The reaction of complex **1** with a 10-fold excess of bromine with afforded 6,9-dibromo-1-cyclopentadienyl-1-cobalta-2,4-dicarba-*closo*-octaborane(8) (**7**) containing the Br atoms at positions 6 and 9 of the carborane cage (Scheme 2).

Scheme 2



1 **7**

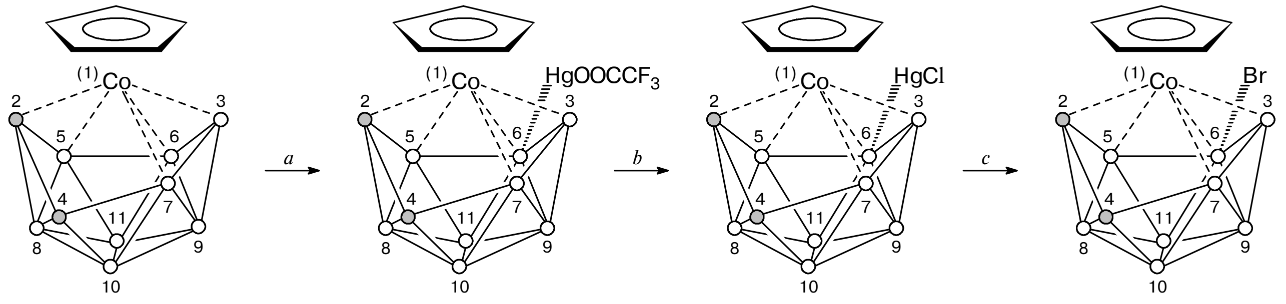
Reagents and conditions: Br_2 (excess), CH_2Cl_2, 20 °C.

No formation of the dibromide containing the Br atoms at positions 3 and 6 was observed.

Mercuration of compound **1** with mercuric trifluoroacetate in CH_2Cl_2 followed by treatment with NaCl in aqueous acetone gave rise to chloromercurio derivative **8**. The reaction of complex **8** with bromine in CH_2Cl_2 at 20 °C afforded monobromide **3** (Scheme 3), which is additional evidence for the proposed structure of **3**.

Complexes **4—8** are air-stable dark-violet crystalline compounds, which are soluble in most of organic sol-

Scheme 3



1 **8** **3**

Reagents and conditions: *a*. $Hg(OOCCF_3)_2$, CH_2Cl_2, 20 °C; *b*. NaCl, $Me_2CO—H_2O$; *c*. Br_2, CH_2Cl_2.

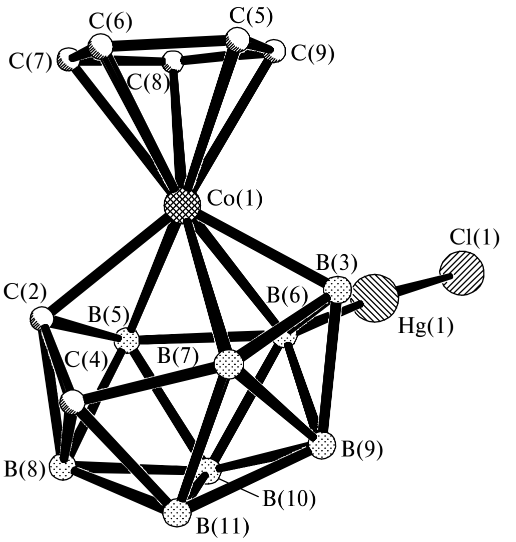


Fig. 2. Structure of molecule **8** (the hydrogen atoms are omitted).

vents and insoluble in saturated hydrocarbons and water. The compounds obtained were characterized by the ^{1}H and ^{11}B NMR spectra and the data from elemental analysis. Complex **8** was studied by X-ray diffraction analysis.

The structure of molecule **8** is shown in Fig. 2.

In the molecule of chloromercurio derivative **8**, the eleven-vertex *isocloso*-metalladicarbaborane cage has an "open" deltahedral structure with one open Co(1)—C(2)—C(4)—B(7) tetragonal face. The C(4) atom of the six-atom C(2)—C(4)—B(7)—B(3)—B(6)—B(5) face of the dicarbaborane cage is not involved in coordination to the Co atom. This face adopts a distorted boat-like conformation.

In compound **8**, the Co(1)—C(2) and Co(1)—B(3) bond lengths as well as the Co(1)—B(5) and Co(1)—B(6) bond lengths have close values (the average bond lengths are 1.97 and 2.165 Å, respectively). The Co(1)—B(7) bond is the longest one (2.27 Å); the Co(1)...C(4) distance is 2.606 Å. An analogous structure of the metalladicarbaborane fragment was found for [1,1-$(PPh_3)_2$-1-H-1,2,4-$IrC_2B_8H_{10}$] (**9**)[10] and [2,4-Me_2-1-(MeC_6H_4-*n*-Pr^i)-1,2,4-$RuC_2B_8H_8$] (**10**).[11] However, all M—B(5), M—B(6), and M—B(7) bonds in molecule **9**, unlike those in **8** and **10**, are equalized. In all structures, the open C(2)—C(4)—B(7)—M face is planar. The geometry of the coordinated $\{C_2B_4\}$ face in compounds **8—10** is characterized by the unusually short C—C bond (1.48 Å) compared to the standard bond lengths in dicarbaboranes (1.60—1.65 Å). Other interatomic bonds in the coordinated face bear similarities to the character of bonding with the M atom. Thus in compounds **8** and **10** in which the M—B(5) and M—B(6) bonds are shorter than the M—B(7) bond, the B(5)—B(6) bond is elongated (1.83—1.85 Å) with respect to two other B—B bonds (1.72—1.73 Å), whereas in compound **9** characterized by identical Ir—B bond lengths, the B—B bonds of the face are more equalized (1.76, 1.79, and 1.81 Å). As a whole, the $\{C_2B_8\}$ dicarbaborane cage in compounds **8—10** is substantially distorted. For example, the B—B bond lengths vary from 1.71 Å (B(3)—B(9)) to 1.89 Å (B(7)—B(9)), these distortions being identical in all three molecules irrespective of the substituents.

It should be noted that a different mode of coordination of the carborane ligand was observed in the complex 10-Br-1-(C_5H_5)-1,2,3-$CoC_2B_8H_9$ (**11**)[4] isomeric to compounds **2** and **3**. The Co atom in compound **11** is coordinated by all six atoms of the open six-atom face of the dicarbaborane cage. Unlike complex **8**, the resulting eleven-vertex metalladicarbaborane cage has a "closed" deltahedral structure. The coordinated $\{C_2B_4\}$ face adopts a slightly distorted boat conformation (both C atoms deviate from the planar B_4 fragment by 0.49 Å). However, the Co—B bond lengths in compound **11** have different values, *e.g.*, the Co—B bonds involving atoms of one edge of the coordinated face (B(5)—B(6)) are shorter (2.22(1) and 2.24(1) Å) than the Co—B bonds involving atoms of the parallel edge (B(4)—B(7); the Co—B(4) and Co—B(7) bond lengths are equal to 2.27(1) Å). A distinguishing feature of compound **11** is substantial weakening of the B—B bonds (1.85 and 1.89 Å) lying in the boat bottom of the six-atom coordinated face of the carborane cage. The remaining B—B bond lengths in the core are, on the average, 1.77 and 1.79 Å. It should be noted that the M atom in compounds **8—11** is coordinated by the six-atom open face of the dicarbaborane cage. Even in the structures in which the M atom is coordinated by all six atoms[4] of the boat-like open face of the carborane cage, the bonds involving the B atoms that form the bottom of the boat have different lengths, *e.g.*, two of these bonds are weaker, which leads to distortion of the geometry of the boat. As a result, the M atom in some compounds is coordinated only by four atoms of the carborane ligand.[12,13]

To summarize, the electrophilic substitution in eleven-vertex cobaltacarboranes **1** and **4** was studied for the first time. Direct mercuration of **1** proceeded regiospecifically at position 6. Bromination of complexes **1** and **4** afforded compounds containing the Br atoms at positions 6 and 3 of the carborane cage. The reaction of complex **1** with an excess of bromine gave rise to 6,9-dibromide.

Experimental

All reactions were carried out in an inert atmosphere using anhydrous solvents prepared according to standard procedures. The reaction products were isolated in air. The starting complex **1** and complex **4** were prepared according to a known procedure.[6]

The ^{1}H and ^{11}B NMR spectra were recorded on Bruker WP 200 SY (200 MHz for ^{1}H and 64.2 MHz for ^{11}B) and

Bruker AMX-400 spectrometers (400 MHz for ^{1}H and 128.3 MHz for ^{11}B). The ^{11}B—^{11}B NMR correlation spectra were measured on a Bruker AMX-400 instrument (128.3 MHz). The mass spectra were obtained on a Kratos MS890 mass spectrometer; the energy of ionizing electrons was 70 eV; the temperature of the ionization chamber was 250 °C.

Bromination of 1. *A.* A solution of Br_2 (0.1 mL, 0.3 g, 2 mmol) in CCl_4 (10 mL) was added to a solution of compound **1** (0.5 g, 2 mmol) in CCl_4 (15 mL) at ~20 °C and the reaction mixture was stirred for 2 h. The solvent was removed *in vacuo*. The residue was chromatographed on a column with SiO_2 (a 1 : 2 benzene—hexane mixture as the eluent) and rapidly concentrated. Products **2** and **3** were isolated in yields of 0.05 g (7.7%) and 0.58 g (89%), respectively. ^{1}H NMR of product **2** (C_6D_6), δ: 9.34 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 163 Hz); 4.80 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 148 Hz); 4.58 (s, 1 H, C(2)H); 4.35 (s, 5 H, Cp); 3.64 (s, 1 H, C(4)H); 2.10 (m, 3 H, BH); −1.67 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 153 Hz). ^{1}H NMR of product **3** (C_6D_6), δ: 9.36 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 165 Hz); 4.92 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 156 Hz); 4.45 (s, 1 H, C(2)H); 4.36 (s, 5 H, Cp); 3.35 (s, 1 H, C(4)H); 2.14 (br.q (1 : 1 : 1 : 1), 3 H, BH, *J* = 158 Hz); −1.68 (q (1 : 1 : 1 : 1), 1 H, BH *J* = 162 Hz).

B. N-Bromosuccinimide (0.36 g, 2 mmol) was added to a solution of compound **1** (0.5 g, 2 mmol) in CCl_4 (15 mL) at ~20 °C. The reaction mixture was refluxed with stirring for 4 h and the solvent was removed *in vacuo*. The residue was chromatographed on a column with SiO_2 (a 1 : 1 benzene—hexane mixture as the eluent) and rapidly concentrated. Compounds **1**, **2**, and **3** were isolated in yields of 0.1 g (10%), 0.03 g (4.6%), and 0.49 g (76.5%), respectively.

C. A solution of Br_2 (1 mL, 3 g, 20 mmol) in CH_2Cl_2 (10 mL) was added to a solution of compound **1** (0.5 g, 2 mmol) in CH_2Cl_2 (15 mL) at ~20 °C. The reaction mixture was stirred for 2 h and the solvent was removed *in vacuo*. The residue was chromatographed on a column with SiO_2 (a 1 : 1 CH_2Cl_2—hexane mixture as the eluent). Dibromide **7** was isolated in a yield of 0.58 g (72%). Found (%): C, 21.34; H, 3.42. $C_7H_{13}B_8Br_2Co$. Calculated (%): C, 20.89; H, 3.26. ^{1}H NMR ($CDCl_3$), δ: 8.79 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 168 Hz); 5.50 (s, 1 H, C(2)H); 5.37 (s, 5 H, Cp); 4.13 (s, 1 H, C(4)H); 3.32 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 159 Hz); 2.00 (m, 2 H, BH); −1.50 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 163 Hz).

Bromination of 4. A solution of Br_2 (0.04 mL, 0.128 g, 0.8 mmol) in CCl_4 (2 mL) was added to a solution of compound **4** (0.2 g, 0.775 mmol) in CCl_4 (6 mL) at ~20 °C and the reaction mixture was stirred for 3 h. The solvent was removed *in vacuo* and the residue was chromatographed on a column with SiO_2 (a 1 : 2 benzene—hexane mixture as the eluent). Bromide **6** was isolated in a yield of 0.21 g (80.3%). MS, *m/z* (I_{rel} (%)): 336 $[M]^+$ (79), 256 $[M - Br]^+$ (100), 212 $[M - Br - CpCo]^+$ (8.5). ^{1}H NMR ($CDCl_3$) δ: 8.80 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 162 Hz); 5.57 (s, 1 H, CH); 5.33 (s, 5 H, Cp); 3.93 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 152 Hz); 3.10 (m, 2 H, BH); 1.83 (s, 3 H, Me); 1.3 (m, 2 H, BH); −1.9 (q (1 : 1 : 1 : 1), 1 H, BH, *J* = 150 Hz).

Mercuration of 1. $Hg(OCOCF_3)_2$ (1 g, 2.34 mmol) was added with stirring to a solution of compound **1** (0.5 g, 2 mmol) in CH_2Cl_2 (10 mL) at ~20 °C. The reaction mixture was stirred for 4 h and the solvent was removed *in vacuo*. The residue was dissolved in acetone and then a saturated aqueous solution of NaCl was slowly added with stirring at 20 °C. The precipitate that formed was filtered off, washed with water, chromatographed on a column with SiO_2 (a 1 : 1 CH_2Cl_2—hexane mixture as the eluent), and recrystallized from a CH_2Cl_2—heptane mixture. 6-Chloromercurio-1-cyclopentadienyl-1-cobalta-2,4-dicarba-*closo*-octaborane(9) (**8**) was isolated in a yield of 0.58 g (60.4%). Found (%): C, 17.82; H, 3.29; B, 17.90. $C_7H_{14}B_8ClCoHg$. Calculated (%): C, 17.53; H, 2.94; B, 18.03. MS, *m/z* (I_{rel} (%)): 278 $[M - Hg]^+$ (100), 242 $[M - HgCl]^+$ (41). ^{1}H NMR ($CDCl_3$), δ: 5.50 (s, 1 H, CH); 5.34 (s, 5 H, Cp); 5.24 (s, 1 H, CH); 4.01 (m, 2 H, BH).

The reaction of compound 8 with bromine. A solution of Br_2 (0.076 mL, 0.24 g, 1.5 mmol) in CH_2Cl_2 (5 mL) was added with stirring to a solution of compound **8** (0.67 g, 1.4 mmol) in CH_2Cl_2 (10 mL) at ~20 °C. The reaction mixture was stirred for 2 h and concentrated. The residue was recrystallized from a CH_2Cl_2—heptane mixture. Compound **3** was isolated in a yield of 0.4 g (88.4%).

X-ray diffraction study of compound 8. Dark-violet platelet-like crystals of $CpCoC_2B_8H_9HgCl$ (**8**) ($C_7H_{14}B_8ClCoHg$, M = 479.63) are monoclinic, at 110 K *a* = 7.2938(14) Å, *b* = 13.339(3) Å, *c* = 14.331(3) Å, β = 104.023(5)°, *V* = 1352.8(5) Å^3, space group $P2_1/c$, *Z* = 4, $d_{calc} = 2.355$ g cm^{-3}. A total of 16361 reflections were measured on a Bruker SMART CCD Area Detector diffractometer at 110 K (λ(Mo-K$_\alpha$) radiation, $2\theta_{max} = 63.84°$) from a single crystal of dimensions 0.1×0.2×0.2 mm. The equivalent reflections were merged into 4335 independent reflections ($R_{int} = 0.1022$), which were used for the structure solution and refinement. The absorption correction (μ = 12.723 mm^{-1}) was applied using the SADABS program**[14]** (T_{max} and T_{min} were 0.862 and 0.123, respectively). The structure was solved by the direct method. The positions of all non-hydrogen atoms were revealed from difference electron density syntheses and refined anisotropically. All hydrogen atoms (except for three hydrogen atoms in the Cp ring) were also located and refined isotropically. Three H atoms were placed in geometrically calculated positions and refined using the riding model with *U*(H) = 1.2*U*(C), where *U*(C) is the equivalent thermal parameter of the C atom to which the corresponding H atom is attached. The final values of the *R* factors were as follows: $R_1 = 0.0600$ (calculated based on F_{hkl} for 2660 reflections with $I > 2\sigma(I)$), $wR_2 = 0.1803$ (calculated based on F^2_{hkl} for all 4295 reflections), GOOF = 0.943, 203 parameters were refined.

All calculations were carried out using the SHELXTL PLUS 5 program package.**[15]**

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References

1. A. Ya. Usyatinskii, O. B. Zhidkova, P. V. Petrovskii, and V. I. Bregadze, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 719 [*Russ. Chem. Bull.*, 1994, **43**, 671 (Engl. Transl.)].
2. S. V. Timofeev, I. A. Lobanova, A. R. Kudinov, V. I. Meshcheryakov, O. L. Tok, P. V. Petrovskii, F. M.

Dolgushin, Z. A. Starikova, and V. I. Bregadze, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1609 [*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1598].

3. B. M. Graybill and M. F. Hawthorne, *Inorg. Chem.*, 1969, **8**, 1799.
4. L. I. Zakharkin, L. N. Kanakhina, A. I. Yanovsky, V. A. Antonovich, and Yu. T. Struchkov, *Koord. Khim.,* 1981, **7**, 1692 [*Sov. J. Coord. Chem.,* 1981, **7** (Engl. Transl.)].
5. S. Hermanek, *Chem Rev.*, 1992, **92**, 325.
6. C. J. Jones, J. N. Francis, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1972, **94**, 8391.
7. W. J. Ewans and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1971, **93**, 3063.
8. R. R. Rietz, R. S. Schaeffer, and E. Walter, *J. Organomet. Chem.*, 1973, **63**, 1.
9. M. Bown, B. Gruner, B. Stibr, X. L. R. Fortaine, M. Thornton-Pett, and J. D. Kennedy, *J. Organomet. Chem.*, 2000, **614—615**, 269.
10. K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, J. Plesek, B. Stibr, and M. Thornton-Pett, *Inorg. Chem.*, 1989, **28**, 2219.
11. M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *Organometallics*, 1987, **6**, 2254.
12. G. K. Barker, N. R. Godfrey, M. Green, H. E. Parge, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc.*, *Chem. Commun.*, 1983, 277.
13. M. R. Churchill and K. Gold, *Inorg. Chem.*, 1973, **12**, 1157.
14. G. M. Sheldrick, *SADABS*, 1997, Bruker AXS Inc., Madison, WI-53719, USA.
15. G. M. Sheldrick, *SHELXTL Ver. 5.0, Software Reference Manual*, Siemens Industrial Automation, Inc., Madison, 1995.

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