Electrophilic mercuration of icosahedral monocobaltacarboranes

A. Ya. Usyatinsky,* O. B. Zhidkova, P. V. Petrovskii, and V. I. Bregadze

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

Electrophilic mercuration of cobaltacarboranes 1,2-R_2-3-Cp-3,1,2-$CoC_2B_9H_9$ (**1**) where R = H (**1a**), CH_2OH (**1b**) was studied. Dimercurated complexes containing Hg atoms bound with boron atoms in positions 9 and 12 of the dicarbollyl ligand are the main products of the reaction with strong electrophiles such as mercury acetate or trifluoroacetate in the corresponding acids. Mercuration of **1a** under milder conditions, *i.e.*, with $Hg(OCOCF_3)_2$ in CH_2Cl_2 or $Hg(OAc)_2$ in a CH_2Cl_2—AcOH mixture, affords 9-monomercurated complexes as the main products.

Key words: cobaltacarboranes, mercuration, mercury.

Previously we reported mercuration of bis(dicarbolyl)nickel and $CpCoC_2(CH_2OH)_2B_9H_9$[1] and some other cobaltacarboranes.[2,3] It was found that the main reaction products are 9,9′-mercurated nickelacarboranes and 9-mercurated cobaltacarboranes. 9-Chloromercuroferracarborane was shown to be the major product of mercuration of 3-Cp-3,1,2-$FeC_2B_9H_{11}$.[4] At the same time it is known that the B atoms optimal for electrophilic substitution are located in positions 9, 12, and 8 of metallacarboranes, which are most remote from the C atom of the carborane nucleus. In fact, bromination of $[(1,2\text{-}C_2B_9H_{11})_2Co]^-$ affords the corresponding hexabromo derivative in which the bromine atoms are attached to the B atoms in positions 9,9′, 12,12′, and 8,8′.[5] In the present work we continue investigations in the field of mercuration of icosahedral metallacarboranes.

Results and Discussion

We have found that the reaction of cobaltacarborane (**1a**) with mercuric trifluoroacetate in trifluoroacetic acid in the 1:1 ratio affords a mixture of products from which pure 9,12-$(ClHg)_2$-3-Cp-3,12-$CoC_2B_9H_9$ (**2a**) was isolated after treatment of the mixture with chloride ions (Scheme 1). The degree of conversion of the starting substrate was 35 %, the yield of **2a** was 60 % based on the reacted **1a**. Along with compound **2a**, a practically insoluble red precipitate (40 %) was formed, which contains, according to X-ray fluorescence analysis, 3.5 Hg atoms per each molecule of the substrate. The structure of compound **2a** was determined on the basis of ^{11}B NMR spectra (Table 1). The ^1H NMR spectrum of complex **2a** in DMSO-d_6 exhibits the following signals (δ): 5.76 (5 H, Cp), 4.76 (2 H, C—H carb., $J_{^1H-^{199}Hg}$ = 40 Hz). The equivalency of the protons of the C—H bonds and the presence of mercury satellites at the signals for these protons provide additional evidence for the fact that the Hg atoms are bonded with the B atoms in positions 9 and 12 of the carborane cage. In order to prevent polymercuration, we studied a similar reaction under less electrophilic conditions: the reaction of compounds **1** with mercury acetate in acetic acid. It turned out that in this case the complex dimercurated in positions 9 and 12 is also the prevailing product (Scheme 1). At a 1:1 ratio between the reactants the extent of conversion of substrate **1a** is 45 %, and the yield of **2a** is 65 % based on the reacted carborane. The reactions of compounds **1a,b** with $Hg(OAc)_2$ in AcOH at a 2:1 ratio afford products **2a,b** in 70 % and 75 % yield, respectively. These data indicate that $Hg(OAc)_2$ in AcOH is too powerful electrophile for the monomercurated cobaltacarborane to be obtained. Therefore, to carry out the desired reaction, we used still milder conditions (mercury trifluoroacetate in methylene chloride). It turned out that in this case the major reaction product is (3-Cp-3,1,2-$CoC_2B_9H_{10}$-9)$HgOCOCF_3$ (**3**), which was isolated in 40 % yield by column chromatography (Scheme 1). Along with compound **3**, a mixture of monomercurated products was obtained in 22 % yield. Based on the data of ^1H and ^{11}B NMR spectra it may be inferred that the mixture contains compound **3** and (3-Cp-3,1,2-$CoC_2B_9H_{10}$-8)$HgOCOCF_3$ (**4**) in a ratio of 3:2.5.*

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* Proportions of the products in the mixture were determined from the ratio of integral intensities of the signals for the Cp groups in the ^1H NMR spectrum and the singlets for the substituted boron atoms in the ^{11}B NMR spectrum.

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Table 1. Parameters of ^{11}B NMR spectra

Compound	ppm	$J_{^{11}B-H}$ / Hz	$J_{^{11}B-^{199}Hg}$ / Hz	Intensity	The assignment of signals for the B atoms
2a	6.43	144		1	8
	2.32	160		1	10
	−2.81	0	2536	2	9, 12
	−5.62	157		2	7, 4
	−10.34	176		2	5, 11
	−22.92	187		1	6
3	6.07	129		1	8
	2.62	149		1	10
	−1.81	0	2454	1	9
	−5.04	151		3	7, 4, 12
	−15.84	161		2	5, 11
	−22.21	175		1	6
6	5.67	176		1	8
	2.30	163		1	10
	−3.67	0	2569	1	9
	−5.30	168		3	7, 4, 12
	−16.12	160		2	5, 11
	−22.93	176		1	6
7	6.64	0	2728	1	8
	2.98	153		1	10
	−5.41	147		4	7, 4, 9, 12
	−16.45	158		2	5, 11
	−21.2	152		1	6
8	5.56	147		1	8
	2.12	150		1	10
	−2.92	0	2412	2	9, 12
	−5.39	144		2	7, 4
	−16.21	173		2	5, 11
	−24.45	202		1	6

Thus, mercuration of **1a** with $Hg(OCOCF_3)_2$ in CH_2Cl_2 affords 9-substituted complex **3** (54 %) and 8-substituted product **4** (11 %), along with unidentified products of polymercuration.

The use of a 'milder' system, such as $Hg(OAc)_2$ in CH_2Cl_2, for electrophilic mercuration does not result in mercuration of **1a**: after boiling for 12 h the starting cobaltacarborane was quantitatively recovered. However, the reaction of **1a** with $Hg(OAc)_2$ in a 7:1 CH_2Cl_2/AcOH mixture results in its mercuration to give 9- and 8-monosubstituted complexes (**6** and **7**) and 9,12-dimercurated product (**8**). The extent of conversion of **1a** is 73 %, and the yields of compounds **6**, **7**, and **8** are 62, 14, and 8 %, respectively, based on the reacted **1a**.

We also studied mercuration of the anionic complex $[commo\text{-}3,3\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-Cs$ (**9**). It turned out that the reaction of compound **9** with $Hg(OCOCF_3)_2$ in CF_3CO_2H affords a polymercurated product. Therefore, we used a «milder» system, $Hg(OAc)_2$ in AcOH, for mercuration. However, in this case we also did not manage to isolate the product of mercuration of compound **9**, probably, due to a partial ion exchange of Cs^+ for Hg^{2+}. Therefore, we synthesized the mercury salt of bis(dicarbollyl)cobalt (**10**), which was then mercurated with $Hg(OAc)_2$ in AcOH to give the 9,9′-substituted complex:

$$Cs[(C_2B_9H_{11})_2Co] \xrightarrow{H^+} H[(C_2B_9H_{11})_2Co] \xrightarrow{1/2\,Hg^{2+}} \underset{\mathbf{10}}{Hg[(C_2B_9H_{11})_2Co]_2}$$

$$\mathbf{10} \xrightarrow[AcOH]{Hg(OAc)_2} \underset{\mathbf{11}}{Hg[Co(C_2B_9H_{11}(HgOAc)\text{-}9)_2]_2}$$

Thus, from the foregoing data one may conclude that icosahedral cobaltacarboranes undergo electrophilic mercuration under milder conditions than icosahedral carboranes,[6] and that the substitution predominantly occurs at the B atoms most remote from C atoms.

Experimental

^{1}H NMR and ^{11}B NMR spectra were recorded on a Bruker WP 200 SY spectrometer operating at 200 MHz (^{1}H) and 64.2 MHz (^{11}B) using TMS and $BF_3 \cdot OEt_2$ as the external standards.

The starting compounds **1a** and **1b** were prepared by the previously reported[7,8] procedures.

9,12-Di(chloromercuro)-3-cyclopentadienyl-3-cobalta-1,2-dicarba-closo-dodecaborane (2a). 2.6 g (0.01 mol) of **1a** was added to a solution of 2.16 g (0.01 mol) of HgO in 70 mL of CF_3CO_2H and the mixture was stirred for 3 h at ~20 °C and for 2 h at 40 °C. Then the solution was cooled, concentrated to half its volume, and poured into 150 mL of an aqueous solution of NaCl (5 g). The precipitate was filtered off, washed with water (3×25 mL), and once again filtered off. From the combined filtrates, 1.6 g of the starting **1a** was isolated. The remaining precipitate was treated with hot THF (2×50 mL) and the solution was concentrated and diluted with 70 mL of water. The precipitate was separated, washed with water, and dried over P_2O_5 to give 1.65 g of compound **2a** (Table 1). The precipitate, which did not dissolve in THF (1.5 g), contained 3.5 Hg atoms per one molecule of **1a**, according to X-ray fluorescence analysis.

The reaction of 1a with $Hg(OAc)_2$ in AcOH. The reaction of 2.56 g of **1a** with a solution of 2.16 g of HgO in 100 mL of AcOH for 8 h at 50 °C followed by a similar workup afforded 2.1 g of compound **2a**.

1,2-Bis(hydroxymethyl)-9,12-di(chloromercuro)-3-cyclopentadienyl-3-cobalta-1,2- dicarba-closo-dodecaborane (2b). 3.2 g (0.01 mol) of **1b** was added to a solution of 2.16 g (0.01 mol) of HgO in 70 mL of CH_3COOH. Compound **1b** dissolved on stirring (30 min, 25 °C). The reaction mixture was stirred for 4 h and poured into 200 mL of an aqueous solution of NaCl (5 g). The precipitate was separated, dried, and reprecipitated by water from THF to give 5.9 g (75 %) of compound **2b** (Table 2).

3-Cyclopentadienyl-9-(trifluoroacetatomercuro)-3-cobalta-1,2-dicarba-closo-dodecaborane (3). 1.6 g (0.05 mol) of $Hg(OCOCF_3)_2$ was added to a solution of 1.3 g (0.05 mol) of compound **1a** in 70 mL of CH_2Cl_2. The mixture was stirred for 3 h at ~20 °C and for 2 h with boiling, cooled, and the solvent was removed *in vacuo*. The solid precipitate was washed with water (2×25 mL), dried *in vacuo* over P_2O_5, dissolved in CH_2Cl_2, and separated on a 25 cm column (1 cm in diameter) with silica gel; a CH_2Cl_2/hexane mixture was used as the

Scheme 1

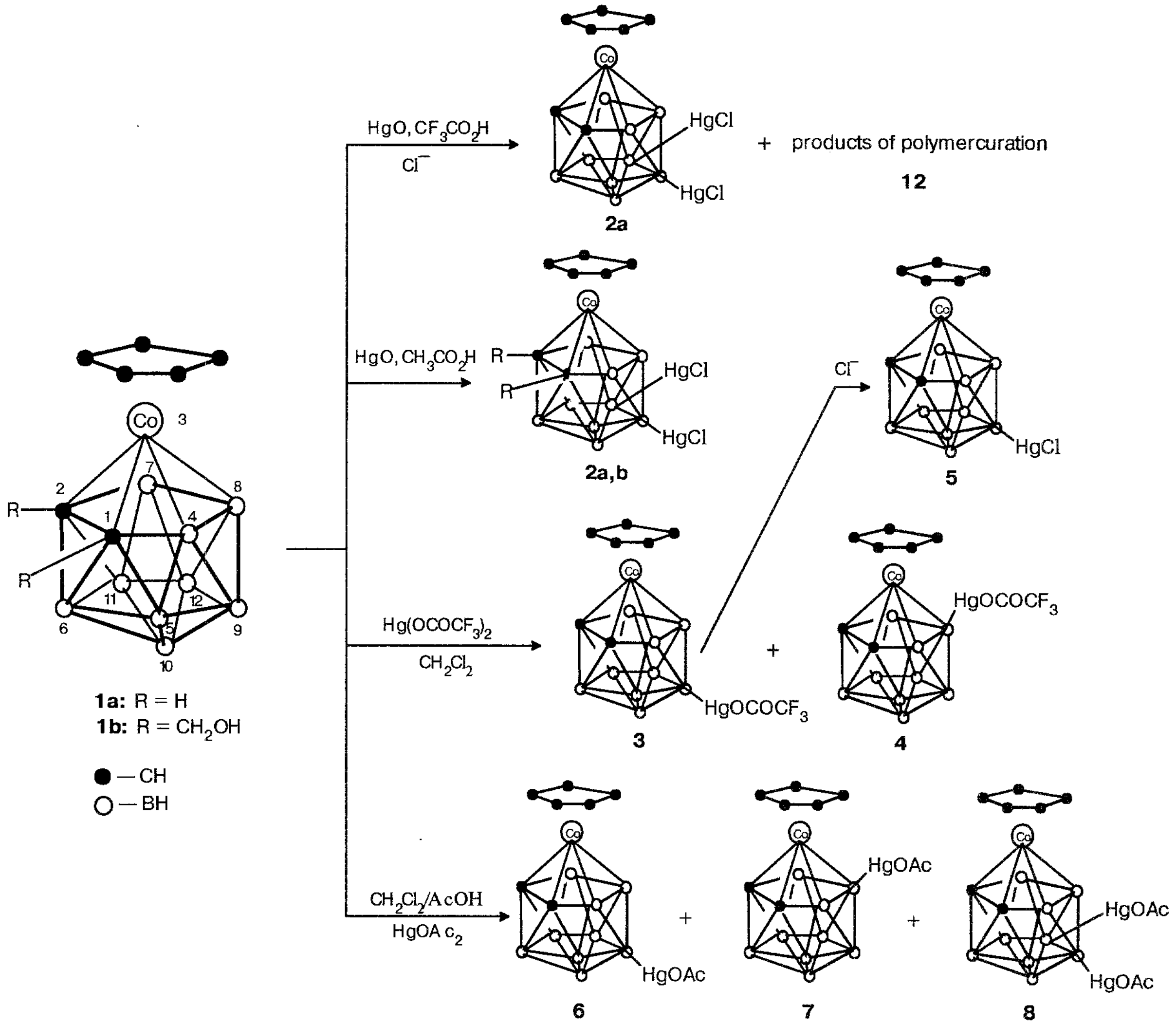

Table 2. Characteristics of compounds synthesized

Compound	Molecular formula	M.p./ °C	Found / Calculated (%) C	H	B	Hg	Co
2a	$C_7H_{14}B_9CoCl_2Hg_2$	325—328	11.7	1.9	13.0	53.2	—
			11.5	1.9	13.3	55.1	
2b	$C_9H_{18}B_9CoCl_2Hg_2O_2$	205—208	12.3	2.3	11.4	49.3	—
			13.7	2.2	12.3	50.8	
3	$C_9H_{15}B_9CoHgF_3O_2$	170	18.4	2.7	16.8	36.0	10.2
			19.0	2.6	17.1	36.1	10.4
5	$C_7H_{15}B_9CoClHg$	283—285	17.2	2.9	19.3	38.5	11.4
			17.1	3.0	19.7	40.7	12.0
6	$C_9H_{18}B_9CoHgO_2$	165	20.7	3.6	18.7	39.1	10.9
			21.0	3.5	18.9	38.8	11.4
7	$C_9H_{18}B_9CoHgO_2$	195—198	21.2	3.4	19.1	38.6	11.6
			21.0	3.5	18.9	38.8	11.4
8	$C_{11}H_{20}B_9CoO_4Hg_2$	209—211	17.9	3.1	12.2	53.4	—
			17.8	2.7	13.1	54.0	
11	$C_{16}B_{36}H_{52}O_8Co_2Hg_5$	185	10.5	2.4	18.3	55.1	10.9
		(dec.)	10.2	2.3	20.6	53.3	11.4

eluent; the CH_2Cl_2:hexane ratio was gradually increased from 3:1 to 7:1. Three yellow fractions were successively obtained: the starting **1a** (0.31 g); compound **3** (0.870 g), and the third fraction (0.415 g), which consisted, according to ^1H and ^{11}B NMR, of compound **3** and 3-cyclopentadienyl-8-(trifluoroacetatomercuro)-3-cobalta-1,2-dicarba-closo-dodecaborane (**4**). ^1H NMR spectrum of the mixture, δ: 6.14 (Cp **4**), 5.95 (Cp **3**), 4.76 (2 H, C—H_{carb}, **4**), 4.73 (1 H, C—H_{carb}, **3**), 4.63 (1 H, C—H_{carb}, **3**). The ^{11}B NMR spectrum in $(CD_3)_2CO$ was badly resolved, however, two singlets at δ 6.05 and −4.23 can be distinguished in it, corresponding to the B(8) atom in compound **4** and B(9) in compound **3**, $J_{^{11}B\_^{119}Hg}$ = 2460 and 2667 Hz for **3** and **4**, respectively. The **3**:**4** ratio was 3:2.5.

3-Cyclopentadienyl-9-(chloromercuro)-3-cobalta-1,2-dicarba-closo-dodecaborane (5). A solution of 0.3 g of complex **3** in 50 mL of acetone was mixed with 100 mL of an aqueous solution of NaCl (2 g). The precipitate was filtered off, dried over P_2O_5, and reprecipitated from THF with hexane to give 0.194 g (70 %) of compound **5**, m.p. and the results of elemental analysis are listed in Table 2.

3-Cyclopentadienyl-9-(acetomercuro)-3-cobalta-1,2-dicarba-closo-dodecaborane (6). 1.3 g of compound **1a** was added to a solution of 1.3 g of $Hg(OAc)_2$ in a CH_2Cl_2/AcOH mixture (80 mL, 7:1). The reaction mixture was stirred for 12 h at 40 °C and cooled, the solvent was evaporated *in vacuo*, and the solid precipitate was dried over P_2O_5, dissolved in CH_2Cl_2, and chromatographed on a column with silica gel (a 2:1 CH_2Cl_2/hexane mixture was used as the eluent, the content of CH_2Cl_2 was gradually increased to 100 %) to isolate four yellow fractions: the starting **1a** (0.34 g); complex **6** (1.20 g); 3-cyclopentadienyl-8-(acetomercuro)-3-cobalta-1,2-dicarba-closo-dodecaborane (**7**, 0.27 g), and 3-cyclopentadienyl-9,12-bis(acetomercuro)-3-cobalta-1,2-dicarba-closo-dodecaborane (**8**, 0.18 g). ^1H NMR of complex **6**, δ: 5.98 (5 H, Cp), 4.67 (1 H, C—H_{carb}), 4.52 (1 H, C—H_{carb}), 2.06 (3 H, CH_3CO).

$Hg[commo\text{-}3,3\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]_2$ (10). 4.6 g (0.01 mol) of $Cs[Co(1,2\text{-}C_2B_9H_{11})_2]$ was added to 100 mL of 10 % H_2SO_4. The reaction mixture was stirred for 2 h and extracted with ether (3×50 mL). The ethereal extracts were separated and washed with water. The ether was evaporated and the residue was dissolved in 70 mL of H_2O and filtered into 50 mL of an aqueous solution of $Hg(OAc)_2$ (2.2 g, 0.07 mol). The yellow precipitate was filtered off, washed with water, and dried *in vacuo* over P_2O_5 to give 3.6 g (35 %) of compound **10**, m.p. 320 °C (dec.). Found (%): B, 45.4; Hg, 24.2. $C_8H_{44}B_{36}Co_2Hg$. Calculated (%): B, 45.9; Hg, 23.6.

$Hg[commo\text{-}3,3\text{-}Co\{(C_2B_9H_{10}\text{-}9)HgOCOCH_3\}_2]_2$ (11). 3.0 g (3.5 mmol) of compound **10** was added to a solution of 1.5 g (7 mmol) of HgO in 90 mL of AcOH. The reaction mixture was stirred for 1 h at ~20 °C and for 3 h with boiling. Cooling the reaction mixture gave a yellow precipitate, which was filtered off. The mother liquor was concentrated to about 10 mL and the precipitate was filtered off. The precipitates were combined, washed with 50 mL of water containing 2 mL of AcOH, dried, and recrystallized from AcOH (twice) to afford 4.3 g (65 %) of complex **11**. ^{11}B NMR* $\{^1H\}$ (DMSO-d_6) δ: 12.8 (B-8); 10.4 (B-1); 0.59 (B-9, 12, $J_{^{11}B\_^{119}Hg}$ = 2747 Hz); −1.01 (B-7, 4, 5, 11); −2.33(B-6). ^1H NMR (DMSO-d_6) δ: 4.54 (1 H, C—$H_{carb.}$), 4.41 (1 H, C—$H_{carb.}$); 2.04(CH_3).

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* The spectrum was badly resolved, therefore, determination of chemical shifts and the assignment of signals are only approximate.