Electrochemical study of boron-mercurated derivatives of 3-cyclopentadienyl-3-cobalta-1,2-dicarba-*closo*-dodecaborane

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The cyclic voltammetry and rotating disc electrode methods were used to study the electrochemical reduction and oxidation of boron-mercurated mono- and dimercury derivatives of 3-cyclopentadienyl-3-cobalta-1,2-dicarba-*closo*-dodecaborane and boron-mercurated dicobaltacarborane on platinum and glassy carbon electrodes in MeCN and DMF solutions. The first reduction step was the reversible electron transfer to the cobalt atom. This process is complicated by adsorption of the reaction product on the electrode, which is especially pronounced when the electrode is coated by metallic mercury evolved at later steps of reduction. The presumptive mechanisms of electroreduction are discussed in detail.

Key words: 3-cyclopentadienyl-3-cobalta-1,2-dicarba-*closo*-dodecaborane, boron-mercurated derivatives, electroreduction, cyclic voltammetry, reduction mechanism.

The mercuration of carboranes (dicarba-*closo*-dodecaboranes) by treatment of *ortho*-, *meta*-, and *para*-carboranes with a strong mercurating reagent, mercury trifluoroacetate in trifluoroacetic acid, discovered in 1976 made it possible to prepare a new class of compounds with a stable boron—mercury σ-bond.[1] In recent years, the structure and the chemical properties of these compounds have been studied in detail,[2] in particular, studies of electrochemical properties of boron-mercurated carboranes were reported.[3—6] Then it has been shown that replacement of the boron atom in the carborane cage by a metal atom results in milder mercuration conditions for this metallacarborane cluster compared to those for the starting carborane.[7] In addition, mercuration of cobalta- and dicobaltacarboranes (like that of carboranes) involves both the boron atoms located on the dodecahedron edge opposite to the edge formed by the carbon atoms and the boron atoms adjacent to cobalt.[7,8] To study the properties of the boron—mercury σ-bond in cobaltacarborane, it is pertinent to estimate the electrochemical behavior of these compounds as compared to that of mercury derivatives of parent carboranes.

Results and Discussion

This study deals with the electrochemical behavior of 3-cyclopentadienyl-3-cobalta-1,2-dicarba-*closo*-dodecaborane (**1**); six its mono- and dimercury derivatives (**2—7**) containing B—Hg bonds in cobaltacarborane positions 9 or 9, 12; boron-mercurated dicobaltacarborane **8**; and 3,3′-*commo*-bis(1,2-dicarba-3-cobalta-*closo*-dodecaborane) (**9**).

Electrochemical measurements were carried out by cyclic voltammetery (CV) on stationary glassy carbon (GC) and Pt electrodes and with a Pt rotating disc electrode (RDE) using 0.05 *M* solutions of Bu_4NBF_4 in MeCN and 0.1 *M* solutions of Bu_4NClO_4 in DMF as inert electrolytes. The number of transferred electrons was determined from the wave limiting current in RDE experiments. The potentials were measured *versus* a saturated silver chloride electrode. The obtained results are summarized in Tables 1 and 2.

Compounds 1 and 9 have already been studied by electrochemical measurements (see a review[9] and references cited therein). Compound **1** is reduced giving a reversible wave at a potential of about −1.2 V and an irreversible peak, which is detected only at the GC electrode at high cathodic potentials (−2.37 V). Oxidation occurs as a single irreversible step ($E_{1/2}$ = 2.27 V for the Pt electrode and E_p = 2.41 V for the GC electrode). According to a previous publication,[9] these three redox processes can be interpreted as consecutive transitions where the oxidation state of cobalt changes from Co^{IV} to Co^{I} (Scheme 1).

Compound **9** behaves in a similar way, in particular, it exhibits two redox transitions in the cathodic region, only the first one being reversible, and one quasi-reversible

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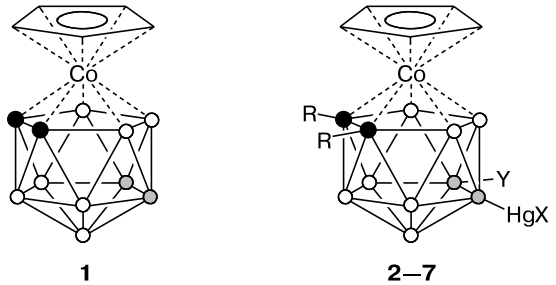
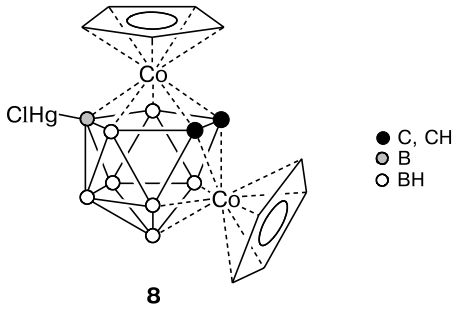
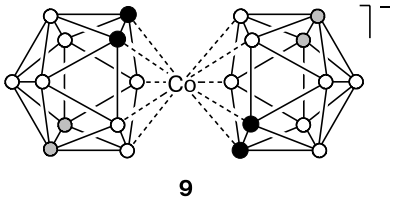






	2	3	4	5	6	7
R	H	H	CH_2OH	H	H	H
X	Cl	Cl	Cl	Br	Br	$OCOCF_3$
Y	H	HgCl	HgCl	H	HgBr	H

transition in the anodic region with currents of the reverse and forward peaks being related as 1 : 1. Since compound **9** has a negative charge, the anodic wave potential is 0.65 V less positive than that for compound **1**. Correspondingly, in the reduction, the first reversible wave of compound **9** is shifted to more cathodic potentials, whereas the second, irreversible wave occurs at less negative potentials than those for compound **1** (by 0.12 V). Hence, the second step of reduction is influenced more appreciably by the change in the ligand nature than by the change in the charge on passing from **1** to **9**.

Monomercurated compounds 2, 5, and 7. The electrochemistry of mercurated carboranes has been extensively studied.[3—6,10—14] These compounds can be separated into

Scheme 1

$$[Co^{IV}]^{+} \xrightarrow[\text{Irreversible step}]{2.41\ V} [Co^{III}] \xrightarrow[\text{Reversible step}]{-1.25\ V} [Co^{II}]^{-} \xrightarrow[\text{Irreversible step}]{-2.37\ V} [Co^{I}]^{2-}$$

Table 1. Electrochemical reduction potentials (E^{Red}) of compounds **1—9** on a clean surface of glassy carbon (GC) and Pt electrodes in MeCN and DMF (a 0.05 *M* solution of Bu_4NClO_4, *vs.* Ag/AgCl/KCl(sat.), 20 °C)

Compound	$-E^{Red}$/V			
	MeCN[a]		DMF[a]	
	CG	Pt	CG	Pt
1	1.25/1.19, 2.37	1.25/1.19 (1.21, 2.11)[b] [1.22 (1 e)]	—	—
2	1.11/1.04, 1.95, 2.30	1.08/1.01, 1.99 [1.08, 1.98]	0.97/0.91, 1.86, 2.12/1.86 (2.03)[b]	0.95/0.88
3	0.90/0.84, 1.15/1.08, 1.64, 2.30, 2.48	0.88/0.72, 1.18/1.08, 1.64, 2.27 [0.80, 1.13]	0.63/0.69, 0.90/0.84, 1.79	0.70/0.64, 0.87/0.80, 1.54, 1.72 [0.68, 0.84, 1.80]
4[c]	0.95/0.89, 1.05/0.99, 1.53	0.93/0.87, 1.05/0.99, 1.48 [0.78, 1.03]	0.90/0.84, 0.99/0.94, 1.50	0.87/0.81, 0.97/0.93 [0.80][d]
5[c]	0.90/0.84, 1.08/1.00, 1.83, 2.03, 2.30	0.90/0.84, 1.10/1.04, 1.86, 2.07 [1.05, 1.86, 2.05]	1.02/0.95, 1.85, 2.22	0.97/0.90, 1.92, 2.27 [1.00, 1.92, 2.30]
6[c]	0.90/0.78, 1.08/1.00, 1.94, 2.03, 2.20, 2.41	0.90/0.84, 1.08/1.00, 1.88, 2.23 [0.68, 1.10, 1.94]	0.83/0.77, 0.97/0.91, 1.85, 2.31	0.88/0.82, 1.01/0.95, 1.83 [0.83, 0.98, 1.93]
7	1.23/1.16, 1.32/1.26, 2.08, 2.24	1.23/1.16, 1.32/1.26, 2.08, 2.26 [1.28, 2.25]	0.96/0.92, 1.10/1.04, 1.91, 2.36	0.96/0.92, 1.12/1.06, 1.96 [1.04, 1.87]
8[c]	0.90/0.78, 1.67, 1.92, 2.25	0.86/0.75, 1.50, 2.20 [0.73, 1.45, 2.16]	0.80/0.71, 1.44[e], 1.99, 2.21	0.73/0.66, 1.44[e] [0.70, 1.42, 1.57]
9	1.38/1.32, 1.96	1.36/1.27 (1.36, 2.34)[b] [1.25]	—	—

[a] For reversible processes, potentials of reverse peaks are given after the slash (if no slash is present, the process is electrochemically and chemically irreversible); the $E_{1/2}$ values are given in brackets and published data are in parentheses. The potential sweep velocity on stationary electrodes was 200 mV s^{-1}, that on the RDE was 20 mV s^{-1} for a rotation velocity of 1350 rpm.
[b] See Ref. 9 and references cited therein.
[c] The substance is poorly soluble in MeCN.
[d] With a pre-wave. [e] Peak splitting is observed.

Table 2. Electrochemical oxidation potentials (E^{Ox}) of compounds **1—9** on a clean surface of glassy carbon (GC) and Pt electrodes in MeCN and DMF (a 0.05 *M* solution of Bu_4NClO_4, *vs.* Ag/AgCl/KCl(sat.), 20 °C)

Compound	E^{Ox}/V	
	GC	Pt
1	2.41	2.27 (2.07)[a] [2.27]
2	—[b]	1.61—1.90[c] [1.61 (0.45 e)][d]
3	—[b]	—[b]
4	—[b]	1.52—1.67[c] [1.60]
5	1.92	1.42—1.88[c] [1.50][d]
6	1.92	1.42—1.88[c]
7	—[b]	—[b]
8	—[b]	1.71 [1.71]
9	1.76/1.66 (1 : 1)	1.74/1.64 (1 : 1) [1.70 (2 e)]

Note. For the experimental conditions, see note *a* to Table 1.
[a] See Ref. 9 and references cited therein.
[b] No clearly pronounced waves.
[c] On repeated scanning, the potential shifts to the anodic region within the range indicated.
[d] The wave is characterized by the decay of current; therefore, the observed number of transferred electrons is underestimated.

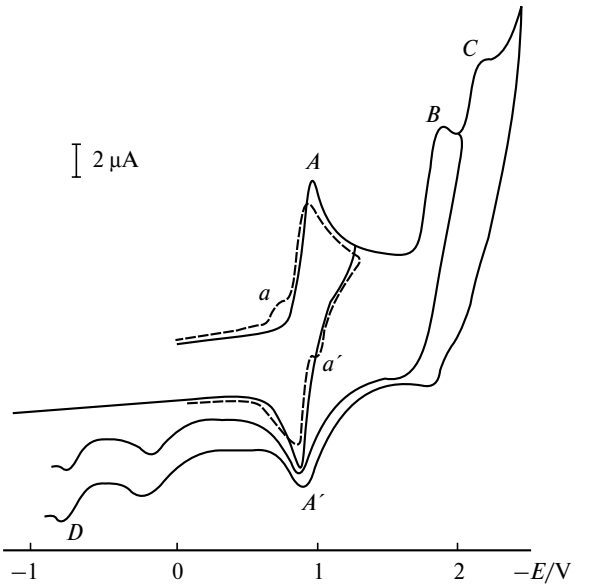
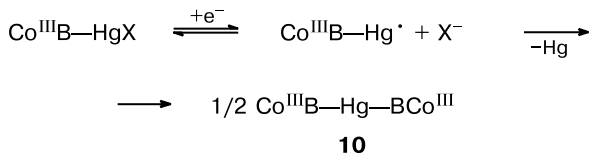


Fig. 1. Polarization curves for compound **2** ($1 \cdot 10^{-3}$ mol L^{-1}) during the first (continuous lines) and second (dashed line) scans on a clean surface of a glassy carbon electrode in DMF containing a 0.1 *M* solution of Bu_4NClO_4; the potential is reversed after passing peaks *A*, *B*, or *C* (the potential sweep velocity was 200 mV s^{-1}; the potentials were measured *vs.* Ag/AgCl/KCl(sat.)). *D* is the peak of the oxidative desorption of mercury.

two main types, namely, *C*-mercurated and *B*-mercurated derivatives. It was shown that the C—Hg bond is reduced more easily than the B—Hg bond.

In the cathodic region, mono-*B*-mercurated compounds **2**, **5**, and **7** are responsible for three to five peaks (in the CV curves) and two or three waves at a platinum RDE (see Table 1). The polarization pattern depends appreciably on the state of the working electrode surface. When the surface is thoroughly cleaned (by electrolysis in a saturated aqueous solution of KCl at a potential of +1 V with subsequent washing with acetone, drying, and mechanical polishing), an initial reversible redox transition followed by two irreversible peaks are observed for compound **2** on a GC electrode in both MeCN and DMF. Figure 1 shows the polarization curves of compound **2** recorded during the first and second scans on a clean surface of a GC electrode in DMF. When the potential is reversed after peak *A* has been passed, no peaks occur on the anodic branch in the potential range from 0 to +1 V; however, when the potential is reversed after peaks *B* and *C*, the peaks for oxidation (anodic dissolution) of the metallic mercury—Cl^- system appear in the range from +0.2 to +0.8 V (region *D*). Thus, mercury is evolved at later steps of reduction of compound **2** (peak *B*), while peak *A* should be attributed to reduction involving cobalt. The peaks (or waves) are diffusional on both the Pt and GC electrodes, which is confirmed by the linear dependence of i_p on $v^{1/2}$ (i_p is the current at the peak potential, v is the potential sweep velocity). However, the reverse anodic peak is somewhat higher than the forward cathodic peak (see Fig. 1), which is a diagnostic criterion for weak adsorption of the electroreduction product.[15] If the potential is swept from 0 to far cathodic region, the electrode surface becomes partially coated by metallic mercury. Mercury is evolved at rather cathodic potentials as the final product of reduction of mercury compounds. During repeated recording of the CV curve, a pre-peak appears ahead of the cathodic peak for the reversible redox pair and an additional peak appears in the reverse scan ahead of the principal anodic peak. The newly formed pre-peak is of the adsorption nature, as indicated by the fact that i_p follows a linear dependence on v in the range from 20 to 1000 mV s^{-1}. The formation of the adsorption pre-peak before the usual peak characterizes strong adsorption of the product formed in the first step of electroreduction.[15] This pre-peak grows during the subsequent potential scans from 0 to −2 V and back, *i.e.*, as the electrode becomes more coated with mercury. If the electrode is precoated by a mercury film deposited through an electrolysis of a solution of $Hg(NO_3)_2$, the adsorption pre-peaks are found even during the first recording of the

Scheme 2



B is the carborane bridge between Co and Hg atoms

X = Cl, Br, $OCOCF_3$

polarization curve, *i.e.*, the product of the first reduction step of compound **2** (peak *A*) is adsorbed much more efficiently on Hg than on GC or Pt.

Trifluoroacetate **7** differs from compound **2** by the fact that its CV curves exhibit two reversible reduction peaks in the cathodic region. They are located at very close potentials and can be detected only by CV measurements, whereas RDE shows a single unified wave at −1.28 V (see Table 1). The morphology of the polarization curve does not depend on the electrode material (Pt or GC) or on the solvent (MeCN or DMF). It should be noted, however, that the peak potentials in DMF differ somewhat from those in MeCN and, in addition, evolution of metallic mercury upon reduction is clearly seen in DMF. Indeed, the appearance of a gray deposit on the electrode can be observed by sight, and when the potential is reversed after the preliminary cathodic scan to −2.3 V, an anodic peak appears at about +0.5 V, evidently due to mercury dissolution. The deposition of mercury during the reduction of trifluoroacetate **7** in MeCN can hardly be seen visually. However, as in the case of compound **2**, potential scanning between 0 and −2 V repeated many times results in the adsorption pre-peak appearing in the CV curves of compound **7** ahead of the reversible cathodic peaks. If the electrode is precoated by a mercury film, this pre-peak appears already during the first recording of the polarization curve. Repeated potential scan between 0 and −1.2 V does not result in clear-cut adsorption pre-peaks.

Compound **5** in MeCN behaves similarly to compound **7** (see Table 1), exhibiting two reversible peaks, a cathodic adsorption pre-peak upon repeated potential scan between 0 and −2 V, and an anodic peak for mercury desorption. However in DMF, the first two peaks are not resolved and only one reversible peak is observed (see Table 1).

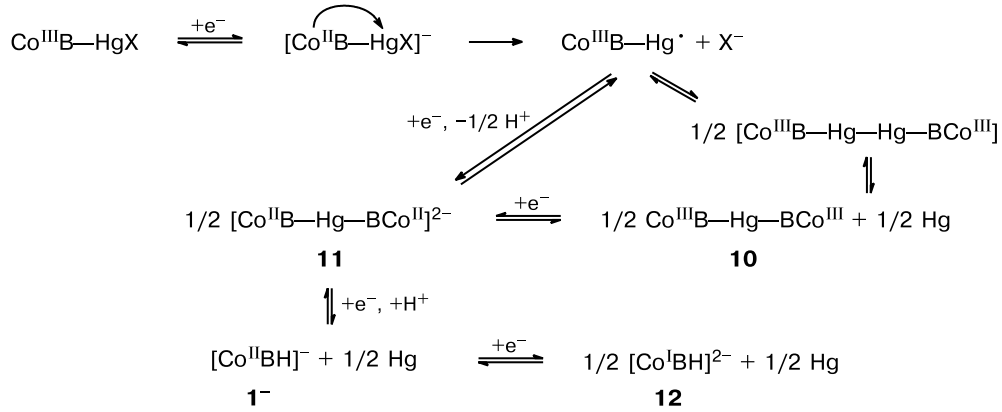
The mechanism of electroreduction of organomercury salts RHgX at a mercury drop electrode was established[16] back in 1951. The first step is single-electron cleavage of the Hg—X bond with elimination of the X^- anion to give a symmetrical organomercury compound. As applied to objects studied here, this mechanism can be described by Scheme 2.

With some corrections, this mechanism still remains generally accepted.[17,18] However, study of the electrochemical reduction of alkyl- and arylmercury salts[19–21] has shown that this mechanism is valid only for mercury cathodes, whereas reduction at Pt, Au, or GC electrodes proceeds to show a pattern similar to that described here, in particular, during recording of the first polarization curve, one wave is detected and metallic mercury is evolved. If recording is repeated without cleaning the electrode, the situation sharply changes: the single wave is split into two, the first one being observed at less cathodic potentials and growing in the subsequent measurements as the electrode becomes coated with mercury.

The present experimental results, together with the data reported previously[19,20] are interpreted most rationally in terms of the following sequence of reactions proceeding at Pt or GC electrodes in solutions of compounds **2**, **5**, and **7** (Scheme 3).

Scheme 3 should be considered as one possible sequence of electrochemical and chemical steps involved in a complex process. First, at relatively low cathodic potentials, reduction at cobalt takes place to give a radical

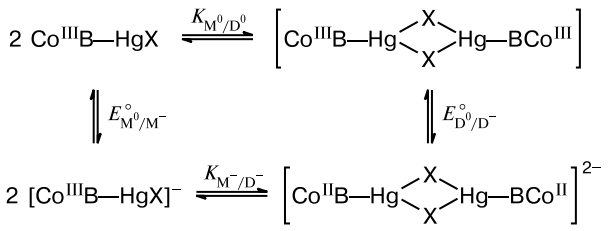
Scheme 3



anion containing a Co atom formally in the oxidation state +2. In our opinion, in this radical anion, intramolecular charge transfer to the Hg—X σ*-bond with elimination of X^- takes place to give a neutral B—Hg radical containing Co^{III}. Repeated reduction at cobalt is accompanied by dimerization of neutral radicals and by reductive elimination of the Hg atom to give dianion **11**. In the medium cathodic region (approximately from −1.5 to −2.1 V), two-electron reduction of this dianion with participation of two protons takes place, and ultimately no mercury remains in the molecule. Finally, in the far cathodic region (the potential is more negative than −2.2 V), the 3-cyclopentadienyl-3-cobalta-1,2-dicarba-*closo*-dodecaborane anion (**1**$^-$) is reduced (*cf.* Scheme 1).

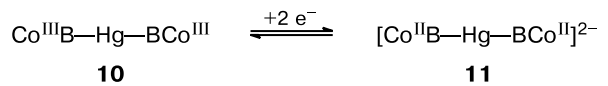
The reason for splitting of the first reversible wave in the case of compounds **5** and **7** was not specially studied. Probably, this is due to different rates of intramolecular charge transfer depending on the substituent X or to the fact that for X = Cl, the reduction potentials of the initial compound **5** and product **10** are very similar, and, therefore, in the case of compound **2**, the peaks are not split. The splitting may also be due to the formation of dimers (Scheme 4). The standard redox potentials E° can be different for the monomers (E°_M) and dimers (E°_D). When X = Br, the tendency to form dimers is more pronounced than for X = Cl, because the Br atom has a higher affinity to Hg than Cl, and trifluoroacetate is coordinated by two O atoms to give six-membered rings, which are more stable than four-membered rings.[22]

Scheme 4



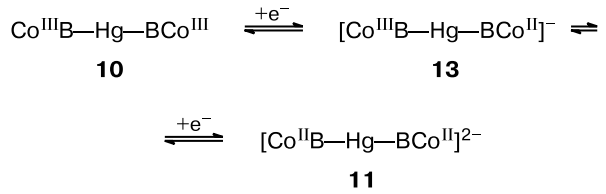
If the redox transitions that take place for compound **10** are identified with those shown in Scheme 1, two sequences of electrochemical transformations can, in principle, be conceived for this compound. First, two cobalt centers can be reduced independently of each other; this would give rise to two-electron transitions (Scheme 5).

Scheme 5



Second, single-electron transitions can take place with intermediate formation of a mixed-valence compound **13** in which the oxidation numbers of the two Co atoms differ by unity; this would increase the number of observed transitions (Scheme 6).

Scheme 6



The mechanism of redox reactions depends, first of all, on the extent of interaction of the two Co atoms with each other through the B—Hg—B bridge; if such interaction is lacking, the reaction proceeds *via* two two-electron steps, whereas efficient interaction may be responsible for a reaction consisting of four single-electron steps.

In organometallic chemistry, mixed-valence compounds have been studied most extensively for ferrocene derivatives, because the ferrocenyl group is usually stable when the formal oxidation number of iron is +2 or +3. The possibility of formation of mixed-valence compounds has been studied as a function of the distance, the nature of the bridge between two or more interacting ferrocenyl groups, and on the relative orientation of the groups.[23]

For diferrocenyl compounds with different bridges between the Cp groups, it has been shown, for example, that the Fc—Hg—Fc molecule, which resembles most closely product **10**, is oxidized in MeCN as one two-electron step[24] without the formation of a mixed-valence compound, *i.e.*, no interaction between the two Fe atoms through the Cp—Hg—Cp bridge is involved; $FcCMe_2CMe_2Fc$ is also responsible for one two-electron wave with a slope corresponding to single-electron transfer.[24] However, whereas in MeCN, $FcCH_2CH_2Fc$ exhibits one two-electron wave with $E_{1/2}$ = 0.37 V,[24] in the 0.2 *M* $LiClO_4$—(MeCN (75%)+CCl_4 (15%) +H_2O (10%)) system, it displays two single-electron waves with $E_{1/2}$ = 0.284 and 0.494 V.[25] Thus, the conditions of the electrochemical experiment have a crucial influence on the feasibility of identification of mixed-valence compounds.

In Scheme 6, mixed-valence compound **13** is considered as an intermediate in the reduction of $Co^{III}B—Hg—BCo^{III}$ to $[Co^{II}B—Hg—BCo^{II}]^{2-}$.

Dimercury compounds 3, 4, and 6. 9,12-Di(chloromercurio)-3-cyclopentadienyl-3-cobalta-1,2-dicarba-*closo*-dodecaborane (**3**) is reduced in several steps. On a clean surface of a GC or Pt electrode in MeCN, it first exhibits two reversible closely located transitions, *a*/*a*′ and *A*/*A*′ (Fig. 2), which are followed by three (GC electrode) or two (Pt electrode) irreversible peaks at negative potentials down to −2.5 V. Unlike monomercurated com-

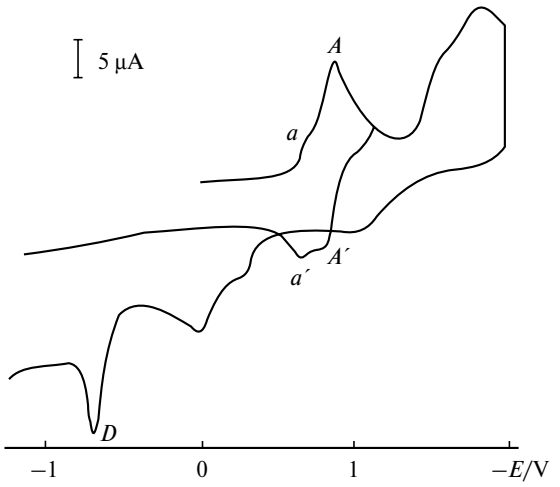
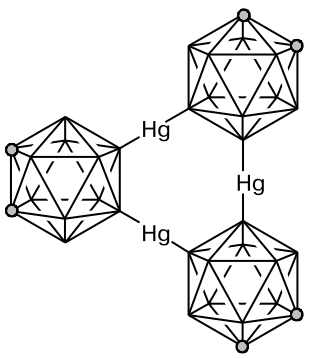


Fig. 2. Polarization curves for compound **3** ($1.3 \cdot 10^{-3}$ mol L^{-1}) on a glassy carbon electrode in DMF containing a 0.1 *M* solution of Bu_4NClO_4 (both curves were recorded on a clean surface in the first scan with a potential sweep velocity of 200 mV s^{-1}; as a potential of −2.0 V was attained, a 8-s delay was done prior to the reverse scanning; the potentials were measured *vs.* Ag/AgCl/KCl(sat.)). *D* is the peak of the oxidative desorption of mercury.

pounds, in the case of dimercurated salts, peaks *a* and *A´*, which have an adsorption character, appear already during the first scan on a thoroughly cleaned electrode and somewhat increase during repeated potential cycling. When the direction of potential sweep is reversed after peak *C*, peaks for chloride ion oxidation and oxidative desorption of mercury appear on the anode branch (see Fig. 2, region *D*). The sharp peak *D* resembling a spike or a steeple has no diffusion tail and becomes especially large after preliminary recording of the polarization curve using the RDE with slow potential sweep (Fig. 3, *a* and *b*).

A similar situation is found for dibromide **6**. However, in the case of bis(hydroxymethyl) dichloride **4**, the number of clearly identifiable peaks decreases. It can be said that at initial stages of reduction, compounds **3** and **6** behave similarly to monomercurated compounds **5** and **7**. With the RDE, the two initial reversible transitions show



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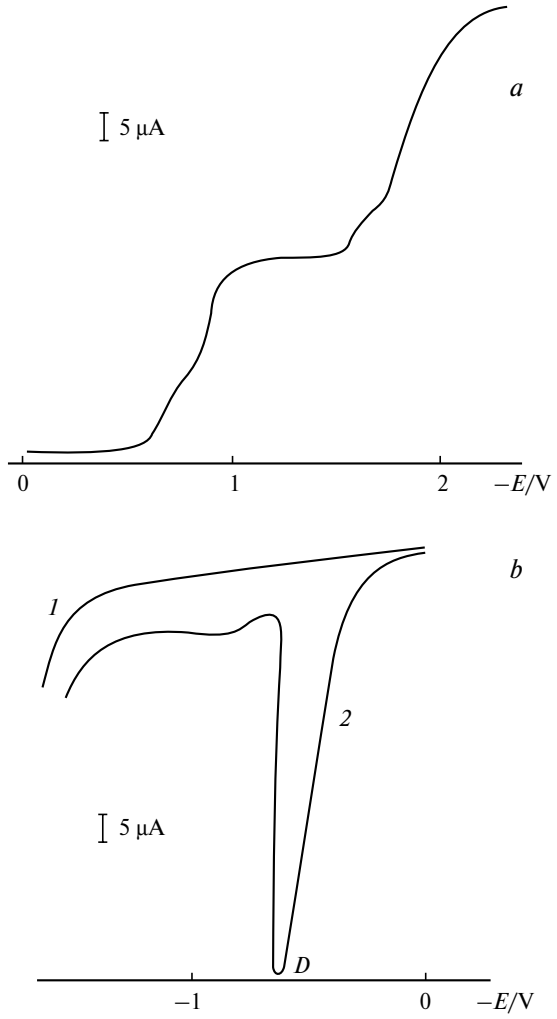


Fig. 3. Polarization curves for compound **3** ($1.3 \cdot 10^{-3}$ mol L^{-1}) on a rotating disc Pt electrode in DMF containing a 0.1 *M* solution of Bu_4NClO_4 at a potential sweep velocity of 20 mV s^{-1} (*a*) and anodic polarization curves (*b*): (*1*) background, (*2*) the curve recorded immediately after the curve shown in Fig. *a* (*D* is the peak of oxidative desorption of mercury). The potentials were measured *vs.* Ag/AgCl/KCl(sat.).

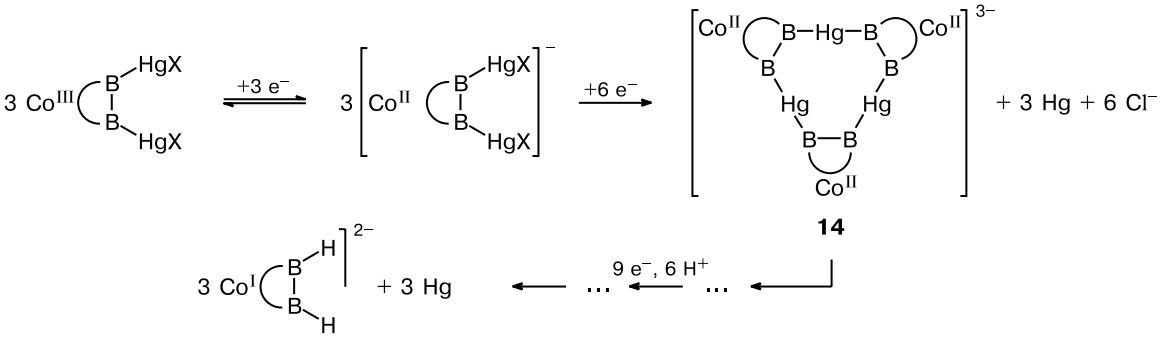
themselves as a single unseparated wave with a pre-wave (see Fig. 3, *a*), as in the case of monomercurated compounds (see Table 1).

It is known from the literature[26] that the chemical reduction on treatment with $NaBH_4$ of *B*,*B´*-dichloromercurio-*ortho*-carborane *C*-silylated with $SiMe_2Bu^t$ groups gives rise to substituted [9]mercuracarborand-3 (**14**).

Tricobalta derivatives of this type might also be formed upon elecrochemical reduction of compounds **3**, **4**, and **6** at medium potentials. However, the initial reduction involves cobalt.

Scheme 7 shows the possible sequence of reduction steps for molecule **3** on a GC electrode. The first step in the proposed mechanism is the reduction at cobalt. The reduction of the Hg—Cl bond takes place in the anion at

Scheme 7



X = Cl

a rather negative potential (−1.64 V). According to Scheme 7, the reduction of one molecule **3** requires six electrons and two protons.

Compound 8. The CV curves for binuclear compound **8** exhibit four cathodic reduction peaks, of which only the first one is reversible (Fig. 4). However, only three waves are observed on the RDE, the first one being much lower than the two subsequent waves. In the anodic region, one oxidation wave is present with a Pt electrode. As regards the morphology of the polarization curve, this compound resembles chloride **2**, which is reduced, presumably, by the mechanism shown in Scheme 3.

In conclusion, it can be stated that electrochemical reduction of the boron-mercurated cobaltacarborane derivatives studied here is characterized by the presence of an initial reversible step, which is followed by irreversible steps. The reversible steps are probably related to electron transfer to the Co atom, *i.e.*, the cobalt center exhibits the highest redox activity.

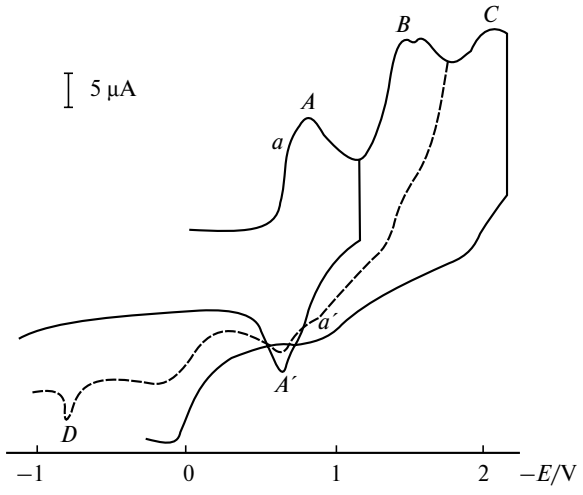


Fig. 4. Polarization curves for compound **8** ($2 \cdot 10^{-3}$ mol L^{-1}) on the clean surface of a stationary Pt electrode in DMF containing a 0.1 *M* solution of Bu_4NClO_4 recorded during the first scan at a potential sweep velocity of 200 mV s^{-1} (the potentials were measured *vs.* Ag/AgCl/KCl(sat.)). *D* is the peak of the oxidative desorption of mercury.

Experimental

Electrochemical measurements were carried out using a PI-50-1.1 potentiostat. A glassy carbon (1.8 mm in diameter) or platinum (3.5 mm) discs served as working electrodes; a 0.05 *M* solution of Bu_4NBF_4 or a 0.1 *M* solution of Bu_4NClO_4 in DMF served as the supporting electrolyte, and the reference electrode is represented by Ag/AgCl/KCl(sat.). All measurements were carried out under argon.

Compounds **1**,[27] **2**—**4**,[7] **7**,[7] **8**,[8] and **9**[28] were prepared by previously described procedures.

9-(Bromomercurio)-3-cyclopentadienyl-3-cobalta-1,2-dicarba-*closo*-dodecaborane (5). Compound **7** (0.9 g, 0.0016 mol) was dissolved in 50 mL of acetone and mixed with an aqueous solution of NaBr (5 g) and the precipitate was filtered off, washed with water and hexane, and dried over P_2O_5 to give 0.8 g (93%) of dodecaborane **5**. Found (%): C, 16.2; H, 2.9; B, 17.9; Co, 10.9. $C_7H_{15}B_9BrCoHg$. Calculated (%): C, 15.7; H, 2.8; B, 18.1; Co, 11.0.

9,12-Di(bromomercurio)-3-cyclopentadienyl-3-cobalta-1,2-dicarba-*closo*-dodecaborane (6). Compound **1** (1.3 g, 0.005 mol) was added to a solution of HgO (1.1 g, 0.005 mol) in 30 mL of CF_3COOH 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 a solution of NaBr (2.5 g) in 75 mL of water. The precipitated solid was washed with water (3×25 mL), dried over P_2O_5, and dissolved in 10 mL of CH_2Cl_2; the mixture was fractionated on a column (25×1 cm) with silica gel (using a 3 : 1 CH_2Cl_2—hexane mixture as the eluent) to give 1.2 g (30%) of dodecaborane **6**. Found (%): B, 10.7; Co, 7.9. $C_7H_{14}B_9Br_2CoHg_2$. Calculated (%): B, 11.5; Co, 7.2.

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