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Brief Communications

Reaction of chloromercuriocobaltacarborane with derivatives of the undecaborate anion

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The reactions of the undecaborate anion $Cs^+C_2B_9H_{12}^-$ (**1**) and *exo-nido*-ruthenacarborane *exo-nido*-5,6,10-[Cl(Ph$_3$P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-$C_2B_9H_8$ (**2**) with the 9-chloromercurated cobaltacarborane, *viz.*, 3-(η^5-Cp)-9-ClHg-3,1,2-$CoC_2B_9H_{10}$ (**3**), afforded Cs[10-{3′-(η^5-Cp)-3′,1′,2′-$CoC_2B_9H_{10}$-9′-Hg}-7,8-$C_2B_9H_{11}$] (**4**) and 5,6,10-*exo-nido*-[Cl(Ph$_3$P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-{3′-(η^5-Cp)-3′,1′,2′-$CoC_2B_9H_{10}$-9′-Hg}-7,8-$C_2B_9H_8$ (**5**), respectively. The latter compound exists as two isomers. Compound **5** was prepared also by the reaction of compound **4** with Ru(PPh$_3$)$_3$Cl$_2$.

Key words: *exo-nido*-ruthenacarborane, cobaltacarborane, mercuration.

Earlier, we have studied the electrophilic substitution in ferracarborane[1,2] 3-(η^5-Cp)-4-SMe$_2$-3,1,2-$FeC_2B_9H_{10}$ derived from the charge-compensated monoanion [9-SMe$_2$-7,8-$C_2B_9H_{10}$]$^-$ as well as mercuration of *exo-nido*-ruthenacarborane *exo-nido*-5,6,10-[Cl(Ph$_3$P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-$C_2B_9H_8$ in detail.[3] We used various mercurating agents.[4,5] It was demonstrated for the first time that mercury salts of metallacarboranes or, more precisely, mercurated ferracarborane 3-(η^5-Cp)-4-SMe$_2$-8-CF$_3$COOHg-3,1,2-$FeC_2B_9H_9$, can be used for mercuration. This reaction afforded 5′,6′,10′-*exo-nido*-[Cl(Ph$_3$P)$_2$Ru]-5′,6′,10′-(μ-H)$_3$-10′-{3-(η^5-Cp)-4-SMe$_2$-3,1,2-$FeC_2B_9H_9$-8-Hg}-7′,8′-$C_2B_9H_8$.

The aim of the present study was to examine the possibility of using other mercurated metallacarboranes as mercurating agents. For this purpose, we carried out mercuration of the undecaborate anion $Cs^+C_2B_9H_{12}^-$ (**1**) and *exo-nido*-ruthenacarborane *exo-nido*-5,6,10-[Cl(Ph$_3$P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-$C_2B_9H_8$ (**2**) with 3-(η^5-Cp)-9-ClHg-3,1,2-$CoC_2B_9H_{10}$ (**3**).[6]

Results and Discussion

Mercuration of anion **1** and compound **2** with 9-chloromercurated cobaltacarborane **3** was carried out in a THF—water—EtOH mixture in the presence of alkali at room temperature. It was found that mercuration of undecaborate anion **1** gave rise to the only product, *viz.*, the anion of unsymmetrical mercuro derivative **4** (Scheme 1).

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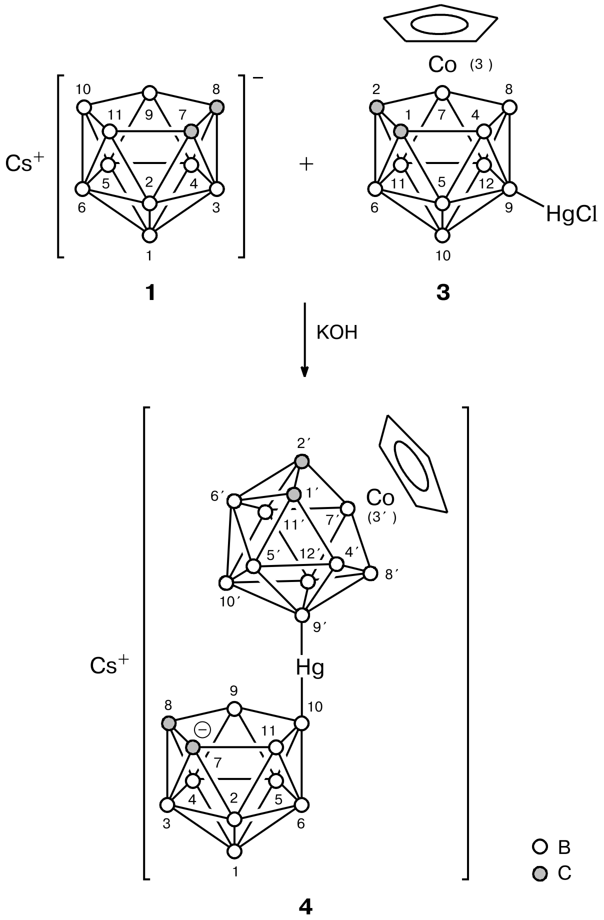
Scheme 1



Yellow-orange crystalline compound **4** is insoluble in nonpolar solvents and readily soluble in acetone and THF.

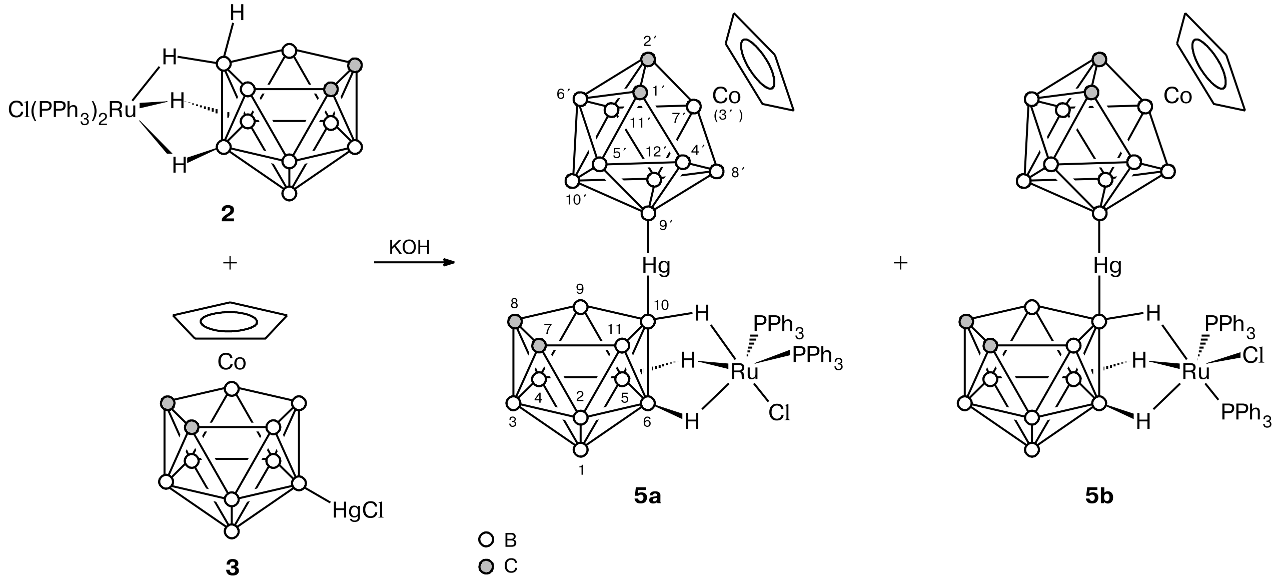
The ^{11}B NMR spectrum of **4** has signals of two carborane fragments at δ 13—35, among which is a singlet of the B(9) atom of the (η^5-Cp)-3′,1′,2′-$CoC_2B_9H_{10}$ fragment at δ 13.85.

Mercuration of *exo-nido*-ruthenacarborane **2** with compound **3** afforded 5,6,10-*exo-nido*-[$Cl(Ph_3P)_2Ru$]-5,6,10-(μ-H)$_3$-10-{3′-(η^5-Cp)-3′,1′,2′-$CoC_2B_9H_{10}$-9′-Hg}-7,8-$C_2B_9H_8$ (**5**). Like all *exo-nido*-ruthenacarboranes synthesized earlier, complex **5** was prepared as a mixture of geometric isomers due to isomerism of the ligands with respect to the six-coordinate ruthenium atom.[3,4,7] In isomer **5a**, the HB(10) hydrogen atom of the open plane of the *exo-nido*-carborane ligand and the chlorine atom are in *trans* positions, whereas these atoms in another isomer (**5b**) are in *cis* positions (Scheme 2). The ^{31}P NMR spectrum (acetone-d_6) has two doublets with equal integral intensities of isomer **5b** and a singlet of the phosphorus atoms of isomer **5a**. The **5a** : **5b** ratio is 2.2 : 1, *i.e.*, *trans* isomer **5a** prevails in solution.

The independent synthesis of compound **5** by the reaction of complex **4** with $Ru(PPh_3)_3Cl_2$ in THF at room temperature also gave rise to the *trans* isomer as the major product (the *trans*/*cis* ratio was 1.37).

Red-orange crystalline compound **5** is readily soluble in acetone, THF, CH_2Cl_2, and $CHCl_3$ and insoluble in hexane. This compound is air-stable in the solid state and slowly decomposes in solutions. The composition and structure of complex **5** were determined by elemental analysis and ^{1}H and ^{11}B NMR spectroscopy. The ^{1}H NMR spectrum (in $(CD_3)_2CO$) of **5a,b** has no signals of the

Scheme 2



extra hydrogen atom in the hydride region and shows multiplets of the bridging protons B—H—Ru at δ –4—17. In addition, the ^{1}H NMR spectra have singlets of the protons of the Cp ring at δ 5.96 and 6.01, singlets of the protons at the carbon atoms of the carborane cages at δ 4.77 and 4.48, and multiplets of the protons of the phenyl rings at δ 7.10—7.75. The ^{11}B NMR spectrum of compound **5a** has a double set of signals of two carborane ligands, among which a singlet of the B(9) atom of the *closo*-cobaltacarborane core at δ 11.20 is pronounced.

To summarize, we demonstrated that 3-(η^{5}-Cp)-9-ClHg-3,1,2-$CoC_2B_9H_{10}$ can be used as a mercurating agent and prepared unsymmetrical metallacarborane clusters in which the *exo-nido*-ruthenacarborane and *closo*-cobalta- or dicarbo-*nido*-undecaborate fragments are linked through the mercury atom.

Experimental

All reactions were carried out under an inert atmosphere. The products were isolated in air. The starting compounds **1**,[3] **2**,[8] **3**,[6] and $Ru(PPh_3)_3Cl_2$ [9] were prepared according to known procedures.

The ^{1}H, ^{31}P, and ^{11}B NMR spectra were measured on a Bruker AMX-400 spectrometer operating at 400.13 (^{1}H), 161.98 (^{31}P), and 128.38 MHz (^{11}B), respectively.

Cesium 10-(3´-cyclopentadienyl-9´-mercurio-3´-cobalta-1´,2´-dicarba-*closo*-dodecaborane)-7,8-dicarba-*nido*-undecaborate(8) (4). Compound **1** (0.06 g, 0.37 mmol) and a solution of **3** (0.18 g, 0.37 mmol) in THF (15 mL) were added to a solution of KOH (0.05 g, 0.85 mmol) in water (2 mL) and 95% EtOH (0.5 mL) at 5—7 °C. The reaction mixture was stirred at 20 °C for 6 h and then concentrated. The residue was dissolved in acetone and a transparent solution of CsCl in water was added. The precipitate that formed was filtered off, washed with water, and dried to prepare compound **4** in a yield of 0.18 g (69%). Found (%): C, 15.72; H, 3.61; B, 27.00. $C_9H_{26}B_{18}CoCsHg$. Calculated (%): C, 15.00; H, 3.63; B, 26.98. ^{1}H NMR (acetone-d_6), δ: 5.88 (s, 5 H, Cp ring); 4.66 (s, 1 H, C—H of carborane); 4.32 (s, 1 H, C—H of carborane). ^{11}B NMR (acetone-d_6), δ: 13.85 (s, 1 B, B(9)); 8.74 (d, 1 B, J = 143 Hz); 4.86 (d, 1 B, J = 148 Hz); –3.40 (d, 3 B, J = 142 Hz); –13.21 (d, 2 B, J = 167 Hz); –14.69 (d, 4 B, J = 160 Hz); –16.20 (d, 1 B, J = 182 Hz); –17.58 (d, 1 B, J = 186 Hz); –21.36 (d, 3 B, J = 147 Hz); –34.43 (d, 1 B, J = 135 Hz).

5,6,10-*exo-nido*-(Bis-triphenylphosphinochlororuthena)-5,6,10-tris-hydrido-10-(3´-cyclopentadienyl-9´-mercurio-3´-cobalta-1´,2´-dicarba-*closo*-dodecaborane)-7,8-dicarba-*nido*-undecaborane(8) (5). ***A.*** Compound **2** (0.30 g, 0.38 mmol) and a solution of **3** (0.29 g, 0.59 mmol) in THF (25 mL) were added to a solution of KOH (0.04 g, 0.70 mmol) in water (4 mL) and 95% EtOH (2 mL). The reaction mixture was stirred at 20 °C for 2 h, concentrated, and chromatographed on SiO_2 (CH_2Cl_2 as the eluent). After recrystallization from a CH_2Cl_2—hexane mixture, compound **5** was obtained in a yield of 0.41 g (89%). Found (%): C, 43.42; H, 4.65; B, 15.53. $C_{45}H_{56}B_{18}CoHgP_2Ru$. Calculated (%): C, 43.25; H, 4.52; B, 15.57. Compound **5b** (0.11 g) and compound **5a** (0.27 g) were successively eluted by repeated chromatography on SiO_2 (CH_2Cl_2).

Compound 5a. ^{31}P NMR (acetone-d_6), δ: 47.72 (s, 2 P). ^{11}B NMR (acetone-d_6), δ: 11.20 (s, 1 B); 7.77 (d, 1 B, J = 140 Hz); 4.08 (d, 1 B, J = 140 Hz); –3.77 (d, 5 B, J = 124 Hz); –4.63 (d, 1 B); –14.91 (br.m, 3 B); –20.77 (d, 3 B, J = 96 Hz); –22.41 (d, 1 B, J = 89 Hz); –24.85 (d, 1 B, J = 76 Hz); –33.14 (br.m, 1 B).

Compound 5b. ^{31}P NMR (acetone-d_6), δ: 54.29 and 47.62 (both d, 1 P each, J = 29 Hz).

B. A solution of compound **4** (0.04 g, 0.055 mmol) and $Ru(PPh_3)_3Cl_2$ (0.06 g, 0.063 mmol) in THF (10 mL) was stirred at 20 °C for 4 h, concentrated, and chromatographed on SiO_2 (CH_2Cl_2 as the eluent). Compound **5** was prepared in a yield of 0.04 g (57%).

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