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Organometallic Chemistry

Reaction of ruthenacarborane with trifluoroacetoxymercuroferracarborane

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The reaction of *exo-nido*-ruthenacarborane *exo-nido*-5,6,10-[Cl$(Ph_3P)_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-$C_2B_9H_8$ (**1**) with the 8-trifluoroacetoxymercury derivative of ferracarborane 3-(η^5-Cp)-4-SMe_2-8-CF_3COOHg-3,1,2-$FeC_2B_9H_9$ (**2**) was studied. It was demonstrated for the first time that metallacarborane **2** can be used as a mercurating agent. The reaction afforded 5´,6´,10´-*exo-nido*-[Cl$(Ph_3P)_2$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´-$C_2B_9H_8$ (**3**) existing as two isomers. The structure of *trans* isomer **3a** was established by X-ray diffraction analysis.

Key word: *exo-nido*-ruthenacarborane, ferracarborane, mercuration, X-ray diffraction analysis.

Several examples of mercuration of icosahedral metallacarboranes among which are cyclopentadienylferracarborane, cyclopentadienylcobaltacarborane,[1,2] bisdicarbollylcobalt,[2] and some other cobaltacarboranes[3] are known. Previously, we have studied electrophilic substitution in ferracarborane 3-(η^5-Cp)-4-SMe_2-3,1,2-$FeC_2B_9H_{10}$, which was derived from the charge-compensated monoanion $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$,[4] and mercuration of *exo-nido*-ruthenacarborane *exo-nido*-5,6,10-[Cl$(Ph_3P)_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-$C_2B_9H_8$ (**1**)[5] with various mercurating agents, including the 9-trifluoroacetoxymercury derivative of *o*-carborane.

In the present study, we examined mercuration of *exo-nido*-ruthenacarborane **1** using for the first time mercurated metallacarborane 3-(η^5-Cp)-4-SMe_2-8-CF_3COOHg-3,1,2-$FeC_2B_9H_9$ (**2**)[4] as mercurating agent.

Results and Discussion

The reaction of compound **1** with one equivalent of metallacarborane **2** in a THF—water—ethanol mixture in the presence of KOH at 20 °C afforded the only product, *viz.*, 5,6,10-*exo-nido*-[Cl$(Ph_3P)_2$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-$C_2B_9H_8$ (**3**). Like all *exo-nido*-ruthenacarboranes prepared earlier,[5,6] complex **3** was obtained as a mixture of geometric isomers, which differ by the mutual arrangement

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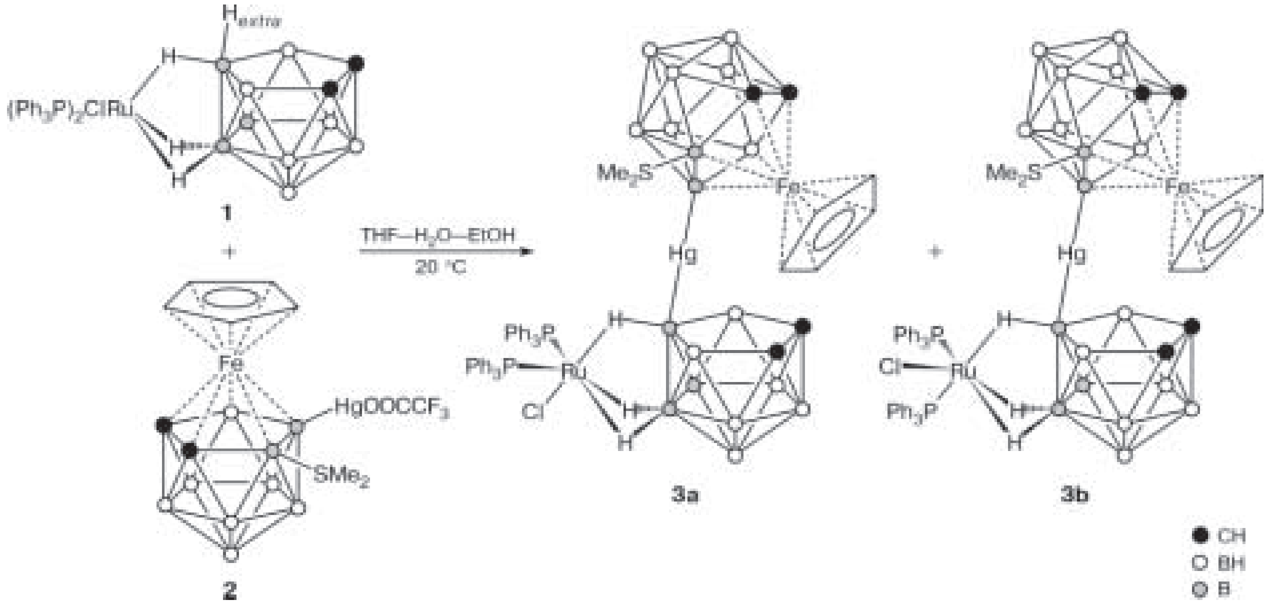
Scheme 1



of the ligands with respect to the six-coordinate ruthenium atom (Scheme 1). In isomer **3a**, the HB(10) atom of the open face of the *exo-nido*-carborane ligand and the chlorine atom are in *trans* positions, whereas these atoms in isomer **3b** are in *cis* positions.

Red-orange crystalline compound **3** is readily soluble in acetone, THF, dichloromethane, and chloroform and insoluble in hexane. In the solid state, complex **3** is stable in air, but it slowly decomposes in solutions.

The composition and the structure of complex **3** were established based on the data from elemental analysis and ^{1}H, ^{11}B, and ^{31}P NMR spectroscopy. Thus the hydride region of the ^{1}H NMR spectrum (in $(CD_3)_2CO$) of complexes **3a,b** has multiplets from the bridging B—$\underline{H}$—Ru protons at δ −4.25, −5.35, −6.30, and −16.50, whereas the signal from the *extra*-hydrogen atom is absent. In addition, the ^{1}H NMR spectra have a singlet from the protons of the Cp ring at δ 4.73, singlets from the protons at the carbon atoms of the carborane cage at δ 5.81, 4.29, and 3.68, a singlet from the methyl groups at the sulfur atom at δ 2.56, and multiplets from the protons of the phenyl rings at δ 7.10—7.75. The ^{11}B NMR spectrum has a double set of signals assigned to two isomers containing two carborane ligands, two singlets from the B(8) atoms of the *closo*-ferracarborane cage of two isomers **3a,b** at δ 10.17 and 9.68 (with the equal B—Hg coupling constants J = 1970 Hz) being prominent. Two doublets with equal intensities assigned to isomer **3a** and a singlet from the phosphorus atoms of isomer **3b** are observed in the ^{31}P NMR spectrum (acetone-d$_6$). The **3a** : **3b** ratio is 1 : 5, *i.e.*, *cis*-isomer **3b** prevails in solution.

However, crystallization from a dichloromethane—hexane mixture afforded *trans* isomer **3a** whose structure was confirmed by X-ray diffraction analysis.

Crystal structure of 3a. There are two independent structurally identical molecules (**A** and **B**) and 1.5 hexane molecules per asymmetric unit. The overall view of one independent molecule is shown in Fig. 1. The Ru atom is involved in three two-electron three-center bridging Ru—H—B bonds with the *nido*-carborane ligand. In the coordination octahedron of the ruthenium atom, the Cl and H(10) atoms are in *trans* positions (the Cl—Ru—B(10) angles are 172.2 and 156.4° in two independent molecules). The geometric parameters of molecules **A** and **B** have close values. The Ru—P bond lengths range from 2.288(4) to 2.305(4) Å (the average is 2.298 Å), the Ru—Cl bond lengths are 2.384(4) and 2.389(4) Å, the Ru—H bond lengths and the Ru...B distances are in the ranges of 1.87—2.11 and 2.33(2)—2.38(1) Å, respectively. The Cl—Ru—P bond angles are in the ranges of 89.8°—97.9(1)° (**A**) and 96.4°—96.7(2)° (**B**), the P—Ru—P angles are 99.2(1)° (**A**) and 100.1(2)° (**B**), the Cl—Ru...B(5´), Cl—Ru...B(6´), Cl—Ru...B(10´), and Hg—B(10´)—Ru angles are 103.0(4)°, 107.9(4)°, 145.6(4)°, and 135.4(7)° (**A**) and 103.8(5)°, 104.8(4)°, 142.3(4)°, and 138.7(8)° (**B**), respectively.

No systematic differences in the Ru...B distances are observed. The shortest distances in two molecules are Ru...B(10´) (2.33 Å) and Ru...B(6´) (2.35 Å). Apparently, this is associated with a rather low accuracy of the structure refinement. In the analogous molecule of 5´,6´,10´-*exo-nido*-5´,6´,10-[Cl(Ph$_3$P)$_2$Ru]-5´,6´,10´-

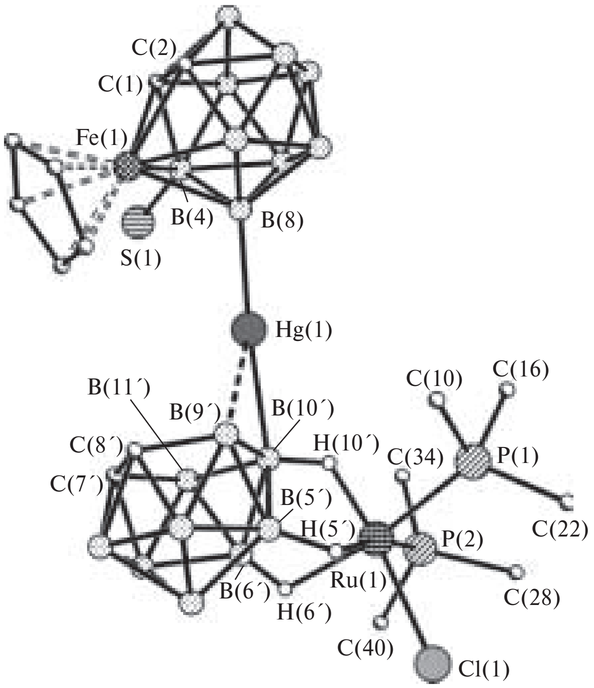


Fig. 1. Molecular structure of **3a** (the Ph rings are represented by one *ipso*-carbon atom each; the Me groups at the sulfur atom and the hydrogen atoms in the carborane fragments are omitted).

(μ-H)$_3$-10´-(1,2-$C_2B_{10}H_{11}$Hg-9)-7´,8´-$C_2B_9H_8$ (**4**),[5] which differs from molecule **3a** in that it does not contain the SMe_2 and Fe(Cp) substituents, the Ru...B(5), Ru...B(6), and Ru...B(10) distances are 2.33, 2.45, and 2.33 Å, respectively. In the starting complex **1** and the osmium analog of **1**, *viz.*, *exo-nido*-[Cl(Ph_3P)$_2$Os]-5,6,10-(μ-H)$_3$-10-H-7,8-$Me_2C_2B_9H_6$,[7] the M...B distances are equal to within the experimental error (2.384—2.399(6) Å in **1**). Since the B(10´) atom in complexes **3a** and **4** is additionally coordinated to the mercury atom, one would expect elongation of the Ru...B(10´) distance. However, no pronounced increase in this distance is observed in mercurated molecules **3b** and **4**.

The Hg atom is linearly coordinated by the boron atoms. In both molecules, the B(10)—Hg—B(8) angle is close to 180° (175.0(6)° and 178.9(6)°) and the corresponding bond lengths are 2.16(2) Å (Hg—B(8)), 2.30, and 2.38(2) Å (Hg—B(10´)). In addition, there is one weaker Hg—B bond in molecule **A** (Hg—B(9´), 2.50(2) Å) and two weaker Hg—B bonds in molecule **B** (Hg—B(9´), 2.78(2) Å; Hg—B(11´), 2.65(2) Å). This distinction between molecules **A** and **B** is also manifested in the Cl—Ru—B(10´)—Hg pseudotorsion angle (150.7° in **A** and 177.4° in **B**) and is consistent with the difference in inclination of the linear B(8)—Hg—B(10´) fragment to the open face of the *nido*-carborane cage (the angle of inclination ψ is 15° (**A**) and 11° (**B**)). Four independent molecules, which, in actuality, are present in the structure, differ by the mutual orientation of the carborane cages, which is reflected in the ψ angle. It can be assumed that only the packing effects in the crystal structure are responsible for these differences with consideration also for the difference in the twist angles of the Ph rings in the Ph_3P ligands in all molecules.

To summarize, we demonstrated for the first time that the mercury derivative of metallacarborane can be used as the mercurating agent and prepared the asymmetrical metallacarborane cluster in which the *closo*-ferra- and *exo-nido*-ruthenacarborane 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 complexes **1** and **2** were synthesized according to known procedures.[6,4]

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

5,6,10-*exo-nido*-(*Bis*-triphenylphosphinechlororuthena)-5,6,10-*tris*-hydrido-10-(8´-mercuro-3´-cyclopentadienyl-4´-dimethylsulfido-3´-ferra-1´,2´-dicarba-*closo*-dodecaborane)-7,8-dicarba-*nido*-undecaborane(8) (3). Compound **1** (0.16 g, 0.12 mmol) and a solution of compound **2** (0.10 g, 0.16 mmol) in THF (10 mL) were added to a solution of KOH (0.01 g, 0.26 mmol) in water (2 mL) and alcohol (1 mL). The reaction mixture was stirred at 20 °C for 4 h, concentrated, chromatographed on SiO_2 using CH_2Cl_2 as the eluent, and recrytsallized from a dichloromethane—hexane mixture. Compound **3** was isolated in a yield of 0.06 g (23%). Found (%): C, 44.86; H, 4.83. $C_{47}H_{61}B_{18}ClFeHgP_2RuS$. Calculated (%): C, 44.38; H, 4.83. ^{31}P NMR (acetone-d_6), δ: 54.58 (s, 2 P); 50.16 (d, 1 P, ^1J = 26 Hz); 48.06 (d, 1 P, J = 27 Hz). ^{11}B NMR (acetone-d_6), δ: 10.17 (s); 9.68 (s); −2.55 (br.d); −3.30 (br.d); −7.80 (br.d, J = 150 Hz); −11.13 (d, J = 155 Hz); −14.18 (d, J = 144 Hz); −20.28 (d, J = 79 Hz); −20.67 (d, J = 80 Hz); −22.22 (d, J = 100 Hz); −23.32 (d, B, J = 80 Hz); −25.50 (br.m); −33.04 (br.d).

X-ray diffraction study of 3a. Well-faceted red crystals of cubic habit appeared to be twins. Numerous attempts to split the crystals apart and to use maximum small fragments failed. All the crystals under examination were characterized by the same monoclinic unit cell. As a result, we chose a transparent crystal fragment with dimensions of 0.40×0.20×0.15 mm, which showed the smallest peak doubling in the analysis of peak profiles. This crystal was used for collecting the X-ray intensity data.

The crystals of $C_{47}H_{61}B_{18}ClFeHgP_2RuS \cdot 0.75(C_6H_{14})$ (M = 1372.13) are monoclinic, at 110 K a = 27.295(11) Å, b = 12.473(5) Å, c = 37.154(15) Å, β = 106.222(8)°, V = 12146(9) Å^3, space group $P2_1/c$, Z = 8, d_{calc} = 1.501 g cm^{-3}.

The X-ray data set consisting of 94153 reflections was collected on a three-circle Bruker SMART 1000 CCD diffractometer equipped with a low-temperature Oxford Cryosystems Cryostream Cooler attachment at 110 K (Mo-Kα radiation, graphite monochromator, the distance from the crystal to the detector was 3.900 cm, the detector angle θ = −28°, the ω scan step was 0.3° at φ = 0, 90, and 120°, frames were exposed for

10 s, θ_{max} = 25°). The corrections for the detector area and absorption (μ = 31.69 mm) were applied using the SADABS program[8] (the maximum and minimum transmission coefficients were 0.928 and 0.473, respectively). The X-ray data were processed using the SAINT program[9] to obtain 21313 independent reflections (R_{int} = 0.1364).

Initially, the structure was solved by the direct method within the non-centrosymmetric space group $P2_1$ (Z = 8). Four independent molecules of the complex differed by the mutual arrangement of the carborane fragments and the Ph rings in the Ph_3P ligands (the differences in the angles are up to 15°). Two ordered hexane molecules were revealed in the crystal structure. In addition, two groups of peaks were found, which were not unambiguously interpreted and are apparently attributable to substantially disordered solvent molecules. The structure was refined based on F^2_{hkl} by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. However, the number of refinable parameters (340 nonhydrogen atoms and 272 hydrogen atoms; more than 2500 parameters) was too large. This fact, in combination with disordering of the solvent molecules and the presence of the twin component in the X-ray data set, did not allow us to complete the structure refinement, which converged to R_1 = 0.0985, wR_2 = 0.2651. Some resulting geometric parameters have unreasonable values. An attempt to separate the experimental data, which were collected from the twin crystal, into individual components using the RLAT [10] and GEMINI programs[11] failed because twinning occurs along the ($x0z$) plane and is close to perfect twinning. Because of this, the structure was finally refined in the centrosymmetric space group ($P2_1$/c, Z = 8). The Ph and Cp rings in both independent molecules were refined as rigid groups (AFIX 66 and AFIX 59, respectively). The coordinates of the H atoms in the SMe_2 groups and in the hexane molecules were calculated geometrically and refined with fixed $B_{iso}(H)$ = $1.5B_{eq}(C)$ and $1.2B_{eq}(C)$ (for the CH_3 and CH_2 groups, respectively), where $B_{eq}(C)$ is the equivalent thermal parameter of the carbon atom to which the corresponding hydrogen atom is attached. The positions of the H atoms of the carborane fragments were revealed from difference electron density syntheses and included in the refinement with fixed $B_{iso}(H)$ = 0.05 Å^2 (AFIX 1). The final R factors were as follows: R_1 = 0.1124 (calculated based on F_{hkl} using 15037 reflections with $I > \sigma(I)$), wR_2 = 0.2268 (calculated based on F^2_{hkl} using a total of 21313 reflections), 1191 independent parameters were refined, GOF was 1.172.

All calculations were carried out using the SHELXTL PLUS 5 program package.[12] The atomic coordinates, anisotropic thermal parameters, and the complete geometric characteristics of the molecules were deposited with the Cambridge Structural Database.

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