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Reaction of *exo-nido*-ruthenacarborane $[Cl(Ph_3P)_2Ru]$-5,6,10-$(\mu\text{-}H)_3$-10-H-7,8-$C_2B_9H_8$ with bromine

S. V. Timofeev, I. A. Lobanova, P. V. Petrovskii, Z. A. Starikova, and V. I. Bregadze★

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E mail: bre@ineos.ac.ru

The reaction of bromine with *exo-nido*-ruthenacarborane $[Cl(Ph_3P)_2Ru]$-5,6,10-$(\mu\text{-}H)_3$-10-H-7,8-$C_2B_9H_8$ (**1**) led to the replacement of the chlorine atom by the bromine atom in the octahedral environment of the ruthenium atom rather than to the substitution in the carborane cage. The structure of $[Br(Ph_3P)_2Ru]$-5,6,10-$(\mu\text{-}H)_3$-10-H-7,8-$C_2B_9H_8$ was established by NMR and IR spectroscopy and X-ray diffraction analysis.

Key words: *exo-nido*-ruthenacarborane, bromination, X-ray diffraction analysis.

Previously, we have studied mercuration of *exo-nido*-ruthenacarborane $[Cl(Ph_3P)_2Ru]$-5,6,10-$(\mu\text{-}H)_3$-10-H-7,8-$C_2B_9H_8$ (**1**)[1] using various mercurating agents.[2] These reactions led to substitutions at the B(10) atom of the carborane cage.[2] In the present study, we examined the reactions of complex **1** with bromine and *N*-bromosuccinimide.

Results and Discussion

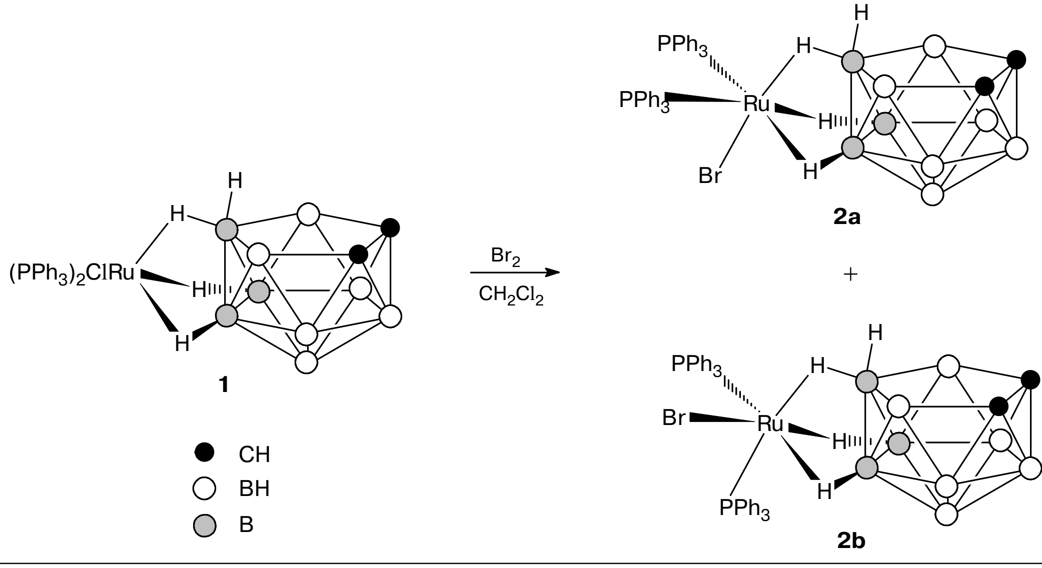
We found that the reaction of complex **1** with bromine in dichloromethane resulted in the replacement of the chlorine atom by the bromine atom in the octahedral environment of the ruthenium atom rather than in the substitution in the carborane cage (Scheme 1).

The use of a solution of *N*-bromosuccinimide in dichloromethane as a brominating agent gave the same result; however, the reaction proceeded much more slowly to produce complex **2** in substantially lower yield. The use of an excess of bromine led to decomposition of compound **1**.

Compound **2**, like all known *exo-nido*-ruthena-[1] and osmacarboranes,[3] exists in solutions as a mixture of geometric isomers (*trans* (**2a**) and *cis* (**2b**)) with respect to the six-coordinated ruthenium atom. The ratio of the *cis* and *trans* isomers remained unchanged in the course of the reaction.

Bright-orange crystalline compound **2** is air-stable in the solid state, soluble in most of organic solvents, and insoluble in saturated hydrocarbons and water. In solutions, complex **2** slowly decomposes.

Scheme 1



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The IR spectrum of complex **1** has a band at 320 cm^{-1} corresponding to the Ru—Cl bond, whereas the IR spectrum of complex **2** has a band at 194 cm^{-1} characteristic of the Ru—Br bond.

The ^{11}B, ^{31}P, and ^{1}H NMR spectra of the initial ruthenacarborane **1** are virtually identical with those of compound **2**. Thus, the hydride region of the ^{1}H NMR spectrum (in $CDCl_3$) of complex **2** has signals at δ −1.34 (*extra*-$\underline{H}_{\mathbf{a},\mathbf{b}}B^{10}$), −4.40 (μ-$H_{\mathbf{a}}B^{5(6)}$), −5.35 ($H_{\mathbf{a}}B^{5,6}$), −7.35 ($H_{\mathbf{b}}B^{10}$), −14.87 ($H_{\mathbf{b}}B^{6(5)}$), and −16.18 ($H_{\mathbf{a}}B^{10}$). The signals of the protons of the phenyl rings and of $\underline{H}C_{carb}$ are observed in the usual region (at δ 7—7.6 and 2, respectively). The ^{31}P NMR spectrum (in $CDCl_3$) also has a double set of signals, *viz.*, a singlet at δ 49.52 for *trans*-isomer **2a** and two doublets at δ 53.15 (J_{P-H} = 29.8 Hz) and δ 45.47 (J_{P-H} = 29 Hz) for **2b**. According the ^{31}P NMR spectroscopic data, the ratio **2a** : **2b** was 1.0 : 0.8.

The structure of isomer **2a** was established by X-ray diffraction analysis. It should be noted that all *exo-nido*-metallacarboranes whose structures have been studied previously by X-ray diffraction analysis were also *trans* isomers.[1—4] Single crystals of **2a** were prepared by recrystallization from a benzene—heptane mixture.

Crystal structure of isomer 2a. The structure contains molecules of complex **2a** (Fig. 1) and also involves the benzene and heptane molecules of solvation. The heptane molecules are disordered over two positions, which are related by the center of symmetry (0,0,0). The benzene molecules are centrosymmetrical.

As can be seen from Fig. 1, the H(10A) and Br(1) atoms are arranged in such a way that the *trans*-pseudotorsion H(10A)—B(10)—Ru(1)—Br(1) angle is 170.5°. The coordination octahedron of the Ru(1) atom is formed by three hydrogen atoms bound to the B(5), B(6), and B(10) atoms of one triangular face of the carborane cage, two phosphorus atoms, and one bromine atom. The P(1), P(2), H(5B), and H(6B) atoms are located in the equatorial plane of the octahedron, the H(10B) and Br(1) atoms occupy the axial positions, and the H(10B)—Ru(1)—Br(1) angle is 175(1)°. Complex **1**[1] and *exo-nido*-$[Cl(Ph_3P)_2Os]$-5,6,10-$(\mu\text{-}H)_3$-10-H-7,8-$Me_2C_2B_9H_6$ (**3**)[3] have similar molecular structures in which the metal atoms also form two-electron three-center M—H—B bonds. It should be noted that some bond lengths in molecule **2a** (Ru(1)...P(1), 2.3100(7) Å; Ru(1)...P(2), 2.3060(7) Å; Ru(1)...H(5B), 1.96(3) Å; Ru(1)...H(6B), 1.94(3) Å; Ru(1)...H(10B), 1.73(3) Å) are closer to the corresponding bond lengths in the *exo-nido*-osmacarborane complex[3] (Os...P(1), 2.312(1) Å; Os...P(2) 2.309(1), Å; Os...H(5B), 1.90(6) Å; Os...H(6B), 1.97(6) Å; Os...H(10B), 1.79(5) Å) than to those in the initial molecule **1** (Ru...P(1), 2.304(2) Å; Ru...P(2), 2.301(2) Å; Ru...H(5B), 1.82(5) Å; Ru...H(6B), 1.85(4) Å; Ru...H(10B), 1.57(5) Å).[1]

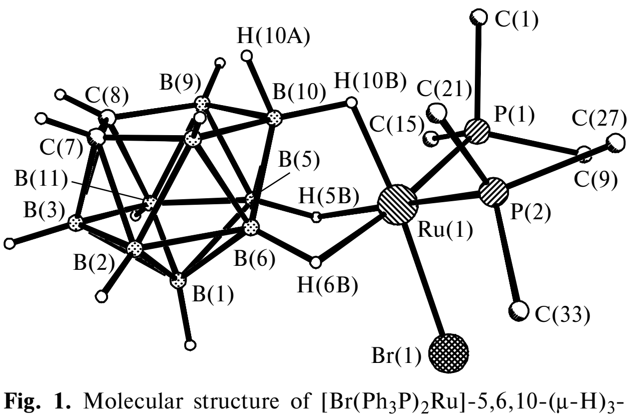

Fig. 1. Molecular structure of $[Br(Ph_3P)_2Ru]$-5,6,10-$(\mu\text{-}H)_3$-10-H-7,8-$C_2B_9H_8$ (the Ph rings are represented by one carbon atom each).

In all three complexes **1**, **2a**, and **3**, the B(10) atom is located at the shortest distance from the metal atom (2.284(6) (**1**), 2.287(3) (**2a**), and 2.275(5) Å (**3**)), whereas the M...B(6) distances are longest (2.399(6) (**1**), 2.377(3) (**2a**), and 2.379(5) Å (**3**)). It should be emphasized that the coordinated H(10B) atom is involved in the shortest Ru—H bond, while its bond with the B(10) atom is weakened (1.21(3) Å) compared to the analogous B(5)—H(5B) and B(6)—H(6B) bonds (1.14(3) and 1.12(3) Å, respectively). The involvement of the hydrogen atoms in coordination to the ruthenium atom leads to elongation of the corresponding B—H bonds, whereas the B—H bonds for the noncoordinated hydrogen atoms are somewhat shorter and are equal, on the average, to 1.05(3) Å.

The H(10A) *extra*-atom is oriented almost perpendicular to the $\{B_3C_2\}$ plane of the carborane cage; the angle between the B(10)—H(10A) bond and the mean plane of the B_3C_2 face is 158.7°. The H(10A)—B(10)—B(9) and H(10A)—B(10)—B(11) angles are 72(2) and 81(2)°, respectively, whereas the angles with the participation of the other hydrogen atoms are substantially larger (125—130°). The H(10A)—B(10)—H(10B) angle is 102(3)°.

Experimental

All reactions were carried out under an inert atmosphere using anhydrous solvents, which were prepared according to standard procedures. The products were isolated in air. The starting complex **1** was synthesized according to a known procedure.[1]

The ^{1}H, ^{11}B, and ^{31}P NMR spectra were recorded on a Bruker AMX-400 spectrometer operating at 400 MHz (^{1}H), 128.3 MHz (^{11}B), and 161.98 MHz (^{31}P). The IR spectra were measured on a Nicolet 700 Magna IR Fourier spectrometer.

5,6,10-*exo-nido*-([Bis(triphenylphosphine]bromoruthena)-5,6,10-*tris*-hydrido-7,8-dicarba-*nido*-undecaborane(8) (2). A solution of bromine (0.038 mL, 0.12 g, 0.75 mmol) in CH_2Cl_2 (20 mL) was slowly added dropwise with stirring to a solution of complex **1** (0.5 g, 0.63 mmol) in CH_2Cl_2 (130 mL) at 0 °C. Then the reaction mixture was stirred at ~20 °C for 15 h and filtered through a silica gel layer. The solution was concentrated and the residue was chromatographed on a column with SiO_2 using benzene as the eluent. Product **2** and the starting compound **1** were isolated in yields of 0.2 g (37.8%)

and 0.04 g (8%), respectively. ^{11}B NMR (CDCl$_3$), δ: 3.54 (br.d, $B_{\mathbf{a,b}}$(2(3,4))); 1.44 (br.d, $B_{\mathbf{a,b}}$(3(2,4))); −14.92 (br.d, $B_{\mathbf{a,b}}$(4(2,3))); −21.25 (d, $B_{\mathbf{b}}$(5(6)), *J* = 81 Hz); −24.67 (d, $B_{\mathbf{a,b}}$(9,11)+$B_{\mathbf{a}}$(5,6), *J* = 98 Hz); −26.63 (d, $B_{\mathbf{b}}$(6(5)), *J* = 106 Hz); −33.53 (d, $B_{\mathbf{a,b}}$(1), *J* = 100 Hz); −41.77 (br.t, $B_{\mathbf{a}}$(10), *J* = 64 Hz); −44.45 (t, $B_{\mathbf{b}}$(10), *J* = 88 Hz). The specimen for analysis was prepared by recrystallization from a mixture of benzene and heptane. Found (%): C, 58.05; H, 5.65. $C_{38}H_{41}B_9BrP_2Ru \cdot 0.5(C_6H_6) \cdot 0.5(C_7H_{14})$. Calculated (%): C, 57.59; H, 5.76.

X-ray diffraction study of complex 2a. Red-orange platelet-like crystals of **2a** · $0.5(C_6H_6) \cdot 0.5(C_7H_{16})$ ($C_{44.5}H_{53}B_9BrP_2Ru$, M = 928.08) are monoclinic, at 110 K *a* = 12.592(1), *b* = 20.687(2) Å, *c* = 16.628(2) Å, β = 94.372(3)°, *V* = 4318.9(8) Å^3, d_{calc} = 1.427 g cm^{-3}, space group $P2_1/n$, *Z* = 4. A total of 50303 reflections were collected from a single crystal of dimensions 0.40×0.20×0.06 mm on a Bruker SMART 1000 CCD diffractometer equipped with a low-temperature Oxford Cryosystems Cryostream Cooler attachment at 110 K (MoKα radiation, graphite monochromator, the distance from the crystal to the detector was 3.932 cm, the ω scan step was 0.3°, frames were exposed for 10 s, $\theta_{\max}$ = 30.09°). The parameters were refined with the use of 1007 reflections in the range 5.1 < θ < 56.3°. The corrections for the detector area and absorption (μ = 13.95 mm) were applied using the SADABS program[6] (the maximum and minimum transmission coefficients were 0.802 and 0.537, respectively). The X-ray data were processed using the SAINT program[7] to obtain 12517 independent reflections (R_{int} = 0.0624). The structure was solved by the direct method. The positions of the nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method based on F^2_{hkl}. The positions of the hydrogen atoms (except for the H atoms of the disordered heptane molecule) were revealed from difference Fourier syntheses and refined isotropically. The C atoms of the C_7H_{16} molecule were refined with the restrictions (DFIX) imposed on the C—C bond lengths (1.54 Å). The coordinates of the H atoms were calculated geometrically and refined with fixed B_{iso}(H) = 1.5B_{equiv}(C), where B_{equiv}(C) is the equivalent thermal parameter of the C atom to which the corresponding H atom is attached. The final *R* factors were as follows: R_1 = 0.0434 (calculated based on F_{hkl} using 8367 reflections with $I > \sigma(I)$), wR_2 = 0.1003 (calculated based on F^2_{hkl} using all reflections); 730 independent parameters were refined.

All calculations were carried out using the SHELXTL PLUS 5 program package.[8] The atomic coordinates, anisotropic thermal parameters, and the complete geometric characteristics were deposited with the Cambridge Structural Database.

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