Brief Communications

Synthesis and structure of (boratabenzene)rhodacarborane (η-7,8-$C_2B_9H_{11}$)Rh(η-C_5H_5BMe)

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The bromide complex [(η-C_5H_5BMe)$RhBr_2$]$_2$ (**1**) was synthesized by the reaction of the cyclooctadiene derivative (η-C_5H_5BMe)Rh(1,5-C_8H_{12}) with Br_2. The reaction of compound **1** with Tl[Tl(η-7,8-$C_2B_9H_{11}$)] gave (boratabenzene)rhodacarborane (η-7,8-$C_2B_9H_{11}$)Rh-(η-C_5H_5BMe) (**2**). The structure of compound **2** was determined by X-ray diffraction.

Key words: metallacarboranes, sandwich compounds, rhodium.

The boratabenzene anion $[C_5H_5BR]^-$ is isolobal to Cp^- and has the same charge, which pre-determines resemblance of their organometallic compounds. For instance, the reaction of cobaltocene with $RBCl_2$ afforded boratabenzene complexes $[CpCo(\eta\text{-}C_5H_5BR)]^+$ (R = Ph, Me)[1,2] similar to the cobaltocenium cation. (Boratabenzene)cobaltacarborane (η-7,8-$C_2B_9H_{11}$)Co(η-C_5H_5BPh), an analog of (η-7,8-$C_2B_9H_{11}$)CoCp, was synthesized[3] by the reduction of the latter with sodium followed by the treatment with $PhBCl_2$. In the present work, we synthesized and determined the structure of the related rhodium complex (η-7,8-$C_2B_9H_{11}$)Rh(η-C_5H_5BMe).

Results and Discussion

The general method for the synthesis of rhodacarboranes (η-7,8-$C_2B_9H_{11}$)Rh(ring) is the reaction of halide complexes [(ring)RhX_2]$_2$ (X = Cl, Br, I) with $[C_2B_9H_{11}]^{2-}$ (see Refs 4—7). In particular, we have recently found[8] that the reaction of [(η^5-$C_9H_2Me_5$)RhI_2]$_2$ with thallium dicarbollide Tl[Tl(η-7,8-$C_2B_9H_{11}$)] gives the pentamethylindenyl derivative (η-7,8-$C_2B_9H_{11}$)Rh(η^5-$C_9H_2Me_5$). An analogous reaction of [(η-C_5H_5BMe)$RhBr_2$]$_2$ (**1**) with Tl[Tl(η-7,8-$C_2B_9H_{11}$)] allowed us to obtain the boratabenzene complex (η-7,8-$C_2B_9H_{11}$)Rh(η-C_5H_5BMe) (**2**) (Scheme 1). The initial bromide **1** was synthesized by the reaction of the cyclooctadiene derivative (η-C_5H_5BMe)-Rh(1,5-C_8H_{12}) with bromine.

Due to the enhanced capability of the boron-containing heterocycles to bificial bonding simultaneously with two metal atoms, rhodacarborane **2** can be considered as a promising starting compound for the synthesis of triple-decked complexes.[9—14]

The structure of rhodacarborane **2** was studied by X-ray diffraction (Fig. 1). The main bond lengths and bond angles are listed in Table 1. The complex has a sandwich

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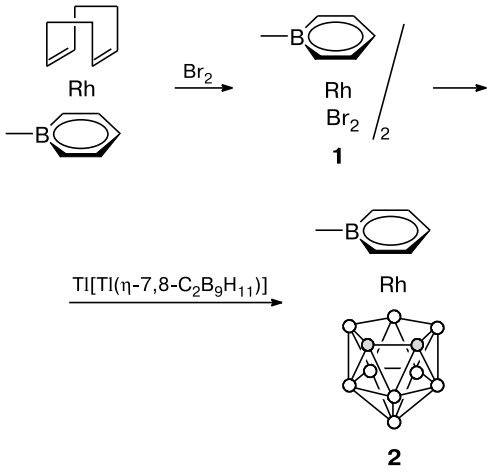
Scheme 1



structure; the angle between the planes of the C_5B and C_2B_3 rings is 2.9°. The mutual conformation of the C_5B and C_2B_3 rings (at which the B(1) atom is located under the B(8) atom) is caused, most likely, by the *trans*-effect of the C(1)—C(2) bond in the carborane ligand. The boron atom in the boratabenzene ligand deviates from the plane of the carbon atoms to the opposite side from the metal (the angle between the C(3)B(1)C(7) and C(3)C(4)C(5)C(6)C(7) planes is 8.0°). The Rh(1)—B(1) bond (2.398(2) Å) is substantially longer than the Rh—C(C_5B) bonds (2.230(2)—2.255(2) Å, average 2.245 Å). Similar pattern is observed for the bonds of the rhodium atom with the boron and carbon atoms of the carborane ligand.

The distance from the rhodium atom to the plane of the C_2B_3 ring of the carborane ligand (1.585 Å) is very similar to the corresponding distances in the related complexes (η-7,8-$C_2B_9H_{11}$)RhCp (1.578 Å)* and (η-7,8-$C_2B_9H_{11}$)Rh(η^5-$C_9H_2Me_5$) (1.585 Å),[8] which indicates

* D. A. Loginov and A. R. Kudinov: unpublished results.

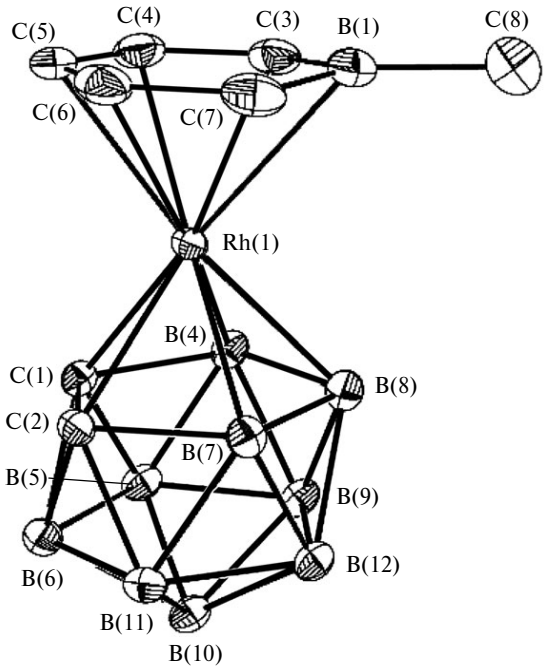


Fig. 1. Structure of complex **2** (thermal ellipsoids of 50% probability).

that the boratobenzene, cyclopentadienyl, and indenyl ligands are close.

Experimental

The reactions were carried out under argon using anhydrous solvents prepared by standard procedures. The procedures on product isolation were carried out in air. The starting compounds (η-C_5H_5BMe)Rh(1,5-C_8H_{12})[15] and Tl[Tl(η-7,8-$C_2B_9H_{11}$)][16] were synthesized according to known procedures. ^{1}H NMR spectra were recorded on a Bruker Avance-400 instrument (400.13 MHz (^{1}H), 128.38 MHz (^{11}B)).

Bis[dibromo(η-boratabenzene)rhodium], [(η-C_5H_5BMe)-$RhBr_2]_2$ (1). A solution of Br_2 (0.02 mL, 0.388 mmol) in ether (3 mL) was added to a solution of the (η-C_5H_5BMe)Rh-

Table 1. Selected bond lengths (*d*) and angles (ω) in complex **2**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Rh(1)—B(4)	2.170(2)	C(1)—C(2)	1.619(3)	C(1)—C(2)—B(7)	111.5(1)
Rh(1)—B(7)	2.178(2)	C(1)—B(4)	1.749(3)	C(2)—B(7)—B(8)	105.1(7)
Rh(1)—B(8)	2.219(2)	C(2)—B(7)	1.755(3)	C(2)—C(1)—B(4)	111.7(1)
Rh(1)—C(1)	2.156(2)	B(4)—B(8)	1.823(3)	C(1)—B(4)—B(8)	105.4(1)
Rh(1)—C(2)	2.158(2)	B(7)—B(8)	1.819(3)	B(4)—B(8)—B(7)	106.0(1)
Rh(1)—B(1)	2.398(2)	C(3)—C(4)	1.400(3)	C(3)—C(4)—C(5)	120.8(2)
Rh(1)—C(3)	2.251(2)	C(4)—C(5)	1.405(3)	C(4)—C(5)—C(6)	121.9(2)
Rh(1)—C(4)	2.234(2)	C(5)—C(6)	1.404(3)	C(5)—C(6)—C(7)	120.9(2)
Rh(1)—C(5)	2.230(2)	C(6)—C(7)	1.397(3)	C(6)—C(7)—B(1)	121.8(2)
Rh(1)—C(6)	2.253(2)	C(3)—B(1)	1.534(3)	B(1)—C(3)—C(4)	121.8(2)
Rh(1)—C(7)	2.255(2)	C(7)—B(1)	1.531(3)	C(3)—B(1)—C(7)	112.1(2)

(1,5-C_8H_{12}) complex (115 mg, 0.381 mmol) in the same solvent (3 mL). The reaction mixture was stirred for 2 h (no inert atmosphere is needed). The precipitate that formed was filtered off and washed with acetone. The brown solid was obtained in a yield of 80 mg (59%). Found (%): C, 20.57; H, 2.28. $C_6H_8BBr_2Rh$. Calculated (%): C, 20.38; H, 2.28. $^{11}B\{^1H\}$ NMR (DMSO-d_6), δ: 31.7.

(η-7,8-Dicarbollyl)(η-boratabenzene)rhodium, (η-7,8-$C_2B_9H_{11}$)Rh(η-C_5H_5BMe) (2). Acetonitrile (2 mL) was added to a mixture of complex **1** (41 mg, 0.058 mmol) and Tl[Tl(η-7,8-$C_2B_9H_{11}$)] (69 mg, 0.127 mmol), and the mixture was stirred for 24 h. The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2, and the solution was eluted through a column with Al_2O_3 (15 cm). The solvent was evaporated to a volume of 0.5—1 mL, and petroleum ether excess was added. A colorless precipitate that formed was filtered off. After the storage of the filtrate in an open flask in air for 1 day, a minor amount of complex **2** as colorless crystals was obtained. The total yield was 22 mg (58%). Found (%): C, 29.51; H, 6.04. $C_8H_{19}B_{10}Rh$. Calculated (%): C, 29.45; H, 5.87. ^1H NMR ($CDCl_3$), δ: 0.77 (s, 3 H, Me); 4.21 (s, 2 H, CH); 5.81 (d, 2 H, *o*-C_5H_5B, J = 8.8 Hz); 6.39 (t, 1 H, *p*-C_5H_5B, J = 6.4 Hz); 6.51 (m, 2 H, *m*-C_5H_5B). $^{11}B\{^1H\}$ NMR ($CDCl_3$), δ: −22.4 (s, 1 B); −15.7 (s, 2 B); −5.4 (s, 2 B); −2.7 (s, 2 B); 8.0 (s, 1 B); 9.9 (s, 1 B); 28.8 (br.s, 1 B, C_5H_5B).

X-ray diffraction study of complex 2. The colorless needle-like crystals of $C_8H_{19}B_{10}Rh$ are tetragonal and were grown by slow diffusion in a two-layer system petroleum ether—a solution of the complex in CH_2Cl_2. The unit cell parameters are as follows: $a = b = 20.2283(17)$ Å, $c = 6.6913(6)$ Å, $V = 2738.0(4)$ Å^3, space group $P4_2/n$, $Z = 8$, $d_{calc} = 1.583$ g cm^{-3}. An experimental array of 29 113 reflections was obtained on a Bruker APEX II CCD diffractometer at 100 K (Mo-Kα radiation, $2\theta_{max} = 55.98°$) from a single crystal 0.60×0.25×0.20 mm in size. After equivalent reflections were averaged, 3299 independent reflections were obtained (R_{int} = 0.0316) and used for structure solution and refinement. An absorption correction (μ = 1.215 mm^{-1}) was applied using the SADABS program (T_{max} and T_{min} are 0.793 and 0.529, respectively). The structure was solved by a direct method, all non-hydrogen atoms were localized in electron density difference syntheses and refined on F^2_{hkl} in the anisotropic approximation. The hydrogen atoms in the carborane fragment were localized in electron density difference syntheses, and other hydrogen atoms were placed in the geometrically calculated positions. All hydrogen atoms were refined in the isotropic approximation in the riding model with $U(H) = nU(C)$, where $U(C)$ is the equivalent temperature factor of the carbon atom to which the H atoms is bound, n = 1.2 for the CH groups, and n = 1.5 for the Me groups. The final values of the R factors are $R_1 = 0.0216$ (calculated on F_{hkl} for 2842 reflections with $I > 2\sigma(I)$), $wR_2 = 0.0533$ (calculated on F^2_{hkl} for all 3299 reflections), 217 refined parameters, GOOF = 1.019. All calculations were performed using the SHELXTL program package.[17] The coordinates of atoms, bond lengths and bond angles, and the temperature parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC 753443) and are available free of charge on request at www.ccdc.cam.uk/conts/retrieving.html (or CCDC, 12 Union Road, Cambridge CB2 1EZ; fax: +44 1223 335 033; deposit@ccdc.cam.ac.uk).

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