(Arene)ruthenium complexes with the monoanionic carborane ligand $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ *

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The ruthenium arene complexes $[(\eta\text{-arene})Ru(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})]^+$ (arene = C_6H_6 (**3a**); arene = 1,3,5-$C_6H_3Me_3$ (**3b**)) with the monoanionic carborane ligand were synthesized by the reactions of the $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anion with $[(\eta\text{-arene})RuCl_2]_2$. The structure of the compound [**3a**]BPh_4 was established by single-crystal X-ray diffraction analysis.

Key words: metallacarboranes, ruthenium, sandwich compounds, structure.

Transition metal complexes (Mn,[1] Pd,[2] Fe,[3,4] Mo,[5] Ru,[6] and Rh [2,7]) with the monoanionic carborane ligand $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (**1**) have attracted considerable attention of researchers. This interest stems from the fact that ligand **1**, unlike the dicarbollide dianion $[7,8\text{-}C_2B_9H_{11}]^{2-}$ (**2**) studied in detail,[8] is not only isolobal but also equally charged with the cyclopentadienide anion due to the presence of the charge-compensating SMe_2 group. Previously, we have prepared complexes of anion **1** with different transition metals (Fe,[9] Co,[9] Ni,[10] Ru,[10] Rh,[11] and Ir [12]).

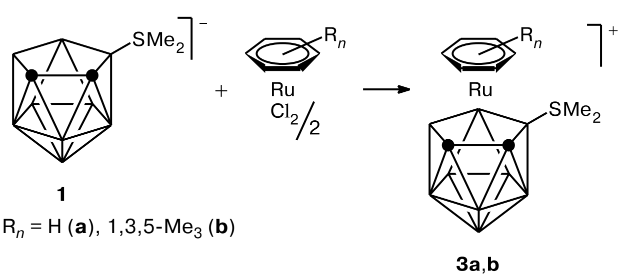
A large number of structurally characterized (arene)ruthenium complexes with dianion **2** were described.[13—17] However, analogous compounds with monoanionic carborane ligands remained unknown. In the present study, we report the synthesis of the $[(\eta\text{-arene})Ru(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})]^+$ complexes (arene = C_6H_6 (**3a**) or 1,3,5-$C_6H_3Me_3$ (**3b**)) containing ligand **1**.

Results and Discussion

The main method for the synthesis of the cyclopentadienyl(arene)ruthenium complexes $[CpRu(\eta\text{-arene})]^+$ is based on the reaction of the chloride complexes $[(\eta\text{-arene})RuCl_2]_2$ with CpTl.[18] We used an analogous approach for the preparation of (arene)ruthenium complexes containing carborane ligand **1**. We found that the reactions of the $[(\eta\text{-arene})RuCl_2]_2$ complexes with a sodium salt of anion **1** in MeCN afforded cationic complexes **3a**,**b** in *ca.* 50% yield (Scheme 1).

By contrast, the reactions of anion **1** (as the sodium or thallium salt) with the osmium complexes $[(\eta\text{-}C_6H_6)OsX_2]_2$ (X = Cl or I) or $[(\eta\text{-}C_6H_6)Os(MeCN)_3]PF_6$ did not give the complex $[(\eta\text{-}C_6H_6)Os(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})]^+$ due, apparently, to the lower reactivities of the starting osmium compounds compared to those of the ruthenium analogs.

Scheme 1



Cations **3a**,**b** were isolated as salts with the PF_6^- anion and characterized by elemental analysis and ^1H and ^{11}B NMR spectroscopy. The ^1H NMR spectra of cations **3a**,**b** have signals for the protons of the aromatic ligand, two broad singlets for the protons of the CH groups of the carborane ligand, and two narrow singlets for the protons of the nonequivalent Me groups of the SMe_2 substituent (Table 1). The ^{11}B NMR spectra show eight doublets (average spin-spin coupling constants $J(^1H\text{-}^{11}B)$ = 170 Hz) and one singlet corresponding to the B(9) atom bound to the SMe_2 group.

With the aim of establishing the structure of the resulting compound, we carried out X-ray diffraction analysis of the tetraphenylborate [**3a**]BPh_4. The structure of cation **3a** is shown in Fig. 1. The selected bond lengths are given in Table 2.

Cation **3a** has a sandwich structure. The distance from the ruthenium atom to the C_2B_3 plane of the carborane ligand (1.630 Å) differs only slightly from the analogous distance in the complex

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* Dedicated to the blessed memory of M. I. Rybinskaya.

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Table 1. ^{1}H and ^{11}B{^{1}H} spectroscopic data for complexes **3a** and **3b** (in acetone-d_6)

Compound	δ	
	^{1}H	^{11}B{^{1}H}
3a	2.70 (s, 3 H, SMe_2); 2.80 (s, 3 H, SMe_2); 4.62 (br.s, 1 H, cage CH); 5.36 (br.s, 1 H, cage CH); 6.74 (s, 6 H, C_6H_6)	−23.47 (1 B); −20.30 (1 B); −18.70 (1 B); −11.59 (1 B); −7.35 (1 B); −6.49 (1 B); −0.73 (1 B); 0.89 (2 B)
3b	2.44 (s, 9 H, 1,3,5-$C_6H_3Me_3$); 2.73 (s, 3 H, SMe_2); 2.80 (s, 3 H, SMe_2); 4.08 (br.s, 1 H, cage CH); 4.91 (br.s, 1 H, cage CH); 6.44 (s, 3 H, 1,3,5-$C_6H_3Me_3$)	−23.56 (1 B); −19.94 (1 B); −18.87 (1 B); −11.68 (1 B); −7.89 (1 B); −6.50 (1 B); −1.15 (1 B); −0.16 (1 B); 3.12 (1 B)

Table 2. Selected bond lengths (*d*) in cation **3a**

Bond	*d*/Å
Ru(1)—C(7)	2.175(2)
Ru(1)—C(8)	2.186(2)
Ru(1)—B(9)	2.206(3)
Ru(1)—C(13)	2.210(3)
Ru(1)—C(14)	2.217(3)
Ru(1)—B(11)	2.220(3)
Ru(1)—C(18)	2.237(3)
Ru(1)—C(15)	2.240(3)
Ru(1)—B(10)	2.249(3)
Ru(1)—C(17)	2.250(3)
Ru(1)—C(16)	2.257(3)
B(9)—C(8)	1.723(3)
B(9)—B(10)	1.811(4)
B(9)—S(1)	1.914(3)
B(10)—B(11)	1.822(4)
B(11)—C(7)	1.745(4)
S(1)—C(19)	1.810(3)
S(1)—C(20)	1.814(3)
C(7)—C(8)	1.650(3)
C(13)—C(18)	1.415(5)
C(13)—C(14)	1.438(6)
C(14)—C(15)	1.411(5)
C(15)—C(16)	1.406(4)
C(16)—C(17)	1.402(4)
C(17)—C(18)	1.405(5)

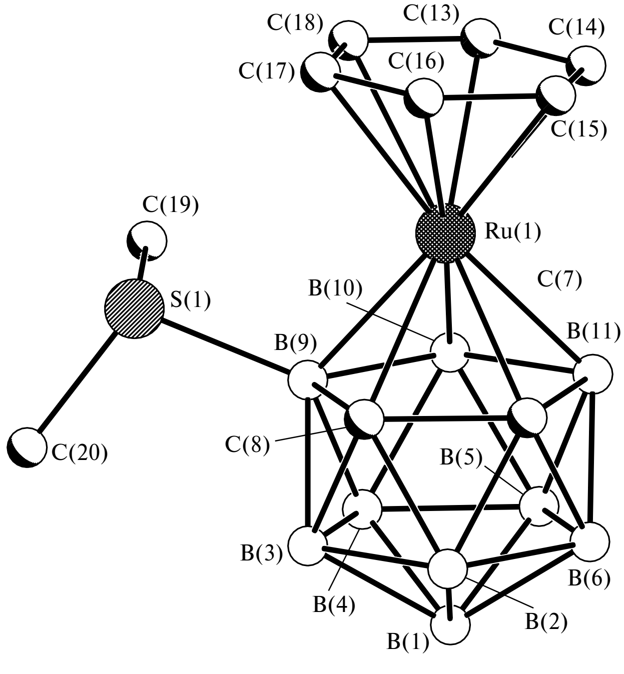

Fig. 1. Crystal structure of cation **3a**.

[(η-C_6H_6)Ru(η-7,8-$C_2B_9H_{11}$)] (**4**) (1.622 Å) containing dianion **2**.[13] The Ru—(C_6 plane) distance in complex **3a** (1.732 Å) is also close to that in **4** (1.715 Å). The angle between the planes of the benzene and carborane ligands in complex **3a** is 4.4° due, apparently, to the steric effect of the SMe_2 group. The C(17)—S(1) (3.624 Å) and C(18)—S(1) (3.534 Å) distances are much shorter than the sum of the van der Waals radii of the S and C atoms (3.94 Å). The close structural similarity of the RuC_2B_9 fragments in complexes **3a** and **4** indicates that the charge-compensating SMe_2 substituent has no substantial effect on the bonding between the carborane ligand and the ruthenium atom.

Experimental

All reactions were carried out under argon with the use of anhydrous solvents. The NMR spectra were recorded on a Bruker AM-400 instrument (400 MHz for ^{1}H and 128 MHz for ^{11}B). The [(η-arene)$RuCl_2$]$_2$ complexes[19] and a solution of Na[9-SMe_2-7,8-$C_2B_9H_{10}$][3] in THF were prepared according to known procedures.

(Benzene)(9-dimethylsulfonio-7,8-dicarbollyl)ruthenium hexafluorophosphate, [(η-C_6H_6)Ru(η-9-SMe_2-7,8-$C_2B_9H_{10}$)]PF_6 ([3a]PF_6). A mixture of [(η-C_6H_6)$RuCl_2$]$_2$ (74 mg, 0.15 mmol) and MeCN (5 mL) was placed in a Schlenk tube equipped with a magnetic stirrer and then a solution of Na[9-SMe_2-7,8-$C_2B_9H_{10}$] in THF (1.3 mL of a 0.25 *M* solution, 0.33 mmol) was added. The reaction mixture was stirred for 72 h. The process was accompanied by a slow change in the color of the suspension from bright-red to pale-orange. After completion of the reaction, the solvent was evaporated *in vacuo*. The residue was dissolved in H_2O (3 mL) and filtered. An excess of an aqueous solution of NH_4PF_6 was added to the filtrate. The white precipitate that formed was filtered off, washed with water, and dried *in vacuo*. After reprecipitation with ether from a solution in CH_2Cl_2, the [**3a**]PF_6 complex was obtained in a yield of 68 mg (44%) as a white powder. The [**3a**]PF_6 complex is stable in air and is readily soluble in acetone, CH_2Cl_2, and THF. Found (%): C, 23.59; H, 4.22; B, 18.77. $C_{10}H_{22}B_9F_6PRuS$. Calculated (%): C, 23.20; H, 4.28; B, 18.80.

(Mesitylene)(9-dimethylsulfonio-7,8-dicarbollyl)ruthenium hexafluorophosphate, [(η-$C_6H_3Me_3$)Ru(η-9-SMe_2-7,8-$C_2B_9H_{10}$)]PF_6 ([3b]PF_6). The analogous reaction of [(η-1,3,5-$C_6H_3Me_3$)$RuCl_2$]$_2$ (88 mg, 0.15 mmol) with Na[9-SMe_2-7,8-$C_2B_9H_{10}$] (1.3 mL of a 0.25 *M* solution in THF, 0.33 mmol) in MeCN (5 mL) afforded the [**3b**]PF_6 complex in a yield of 77 mg (46%). Found (%): C, 27.93; H, 5.04; B, 17.14. $C_{13}H_{28}B_9F_6PRuS$. Calculated (%): C, 27.90; H, 5.04, B, 17.38.

Table 3. Crystallographic data and details of X-ray diffraction study of [**3a**]BPh_4

Parameter	Value
Formula	$C_{34}H_{42}B_{10}RuS$
Molecular weight	691.91
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	12.974(3)
b/Å	15.937(3)
c/Å	17.654(4)
β/deg	111.205(4)
V/Å^3	3403(1)
Z	4
d_{calc}/g cm^{-3}	1.350
μ/cm^{-1}	5.47
$2\theta_{max}$/deg	60.1
Number of measured reflections (R_{int})	9878
Number of reflections with $I \geq 2\sigma(I)$	7694
Number of refined parameters	559
R_1 ($I \geq 2\sigma(I)$)	0.0484
wR_2	0.1111

X-ray diffraction study of [3a]BPh_4. Crystals of [**3a**]BPh_4 were grown by slow diffusion of Et_2O into a solution of the complex in acetone. The X-ray diffraction data were collected on a three-circle SMART 1000 CCD diffractometer (λMo-Kα = 0.71072 Å, ω scan technique) at 120 K. The structure was solved by direct methods and refined by the full-matrix least-squares method in the anisotropic-isotropic approximation based on F^2. The hydrogen atoms were located from difference Fourier syntheses and refined isotropically. All calculations were carried out with the use of the SHELXTL PLUS 5.1 program package. The principal crystallographic characteristics and details of the refinement are given in Table 3.

The complete tables of atomic coordinates, thermal parameters, bond lengths, and bond angles were deposited with the Cambridge Structural Database.

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