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Synthesis of rhodacarborane halide complexes $[(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})RhX_2]_2$ (X = Cl, Br, or I)

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The reactions of the complex $(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})Rh(\eta\text{-cod})$ (cod is 1,5-cyclooctadiene) with HX acids (X = Cl, Br, or I) in acetone afforded rhodacarborane halide complexes $[(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})RhX_2]_2$, which are carborane analogs of cyclopentadienyl halide rhodium complexes $[(\eta\text{-}C_5R_5)RhX_2]_2$.

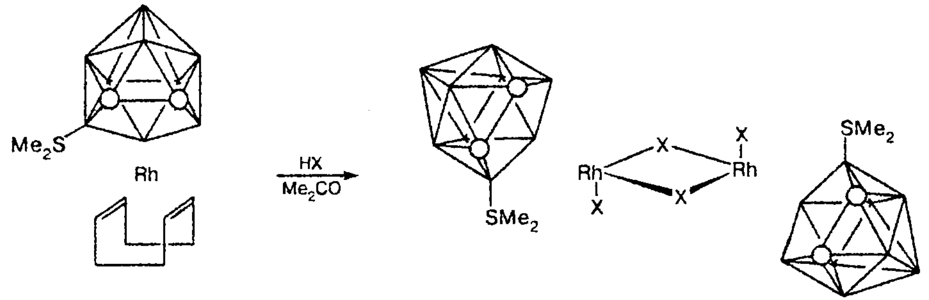
Key words: metallacarboranes, rhodium.

As part of continuing studies[1,2] devoted to the synthesis of transition metal π-complexes with the charge-compensated anion $[9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]^-$ isolobal to the cyclopentadienyl anion, we studied the reaction of (cyclooctadiene)rhodacarborane **1**[3] with HX acids (X = Cl, Br, or I). We found that this reaction proceeds readily in acetone at room temperature to form rhodacarborane halide complexes **2a—c** in ~80% yields (Scheme 1).

The rate of the reaction decreases in the order Br > Cl > I. This reaction is analogous to the reactions of HCl with $(\eta\text{-}C_5Me_5)Rh(\eta\text{-chd})$ (chd is 1,3-cyclohexadiene) and $(\eta\text{-arene})Ru(\eta\text{-cod})$ to form rhodium and ruthenium compounds, *viz.*, $[(\eta\text{-}C_5Me_5)RhCl_2]_2$ [4] and $[(\eta\text{-arene})RuCl_2]_2$,[5] respectively.

Compounds **2a—c** were characterized by the data of elemental analysis and ^1H and ^{11}B NMR spectroscopy (Table 1). The NMR spectra of these compounds are

Scheme 1



1

2a—c

○ CH

X = Cl (**a**), Br (**b**), I (**c**)

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Table 1. Parameters of the ^1H and $^{11}B\{^1H\}$ NMR spectra of compounds **2a—c** (in DMF-d_7)

Compound	δ ^1H		δ $^{11}B\{^1H\}$
	CH of carborane (br.s, 1 H)	SMe_2 (s, 3 H)	
2a	6.08, 5.43	3.12, 2.95	8.41 (1 B); 7.49 (1 B); −0.71 (2 B); −7.14 (1 B); −9.56 (1 B); −14.25 (1 B); −16.51 (1 B); −25.70 (1 B)
2b	6.13, 5.45	3.12, 2.94	8.89 (1 B); 5.88 (1 B); −0.78 (2 B); −6.80 (1 B); −9.56 (1 B); −14.13 (1 B); −16.18 (1 B); −25.56 (1 B)
2c	6.02, 5.50	3.12, 2.94	8.80 (1 B); 2.19 (1 B); −0.42 (1 B); −3.95 (1 B); −6.73 (1 B); −9.68 (1 B); −14.31 (1 B); −16.91 (1 B); −25.35 (1 B)

similar to those of other π-complexes of the $[\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10}]^-$ anion with transition metals and, in particular, of the $(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})M(\eta\text{-}C_5R_5)$ (R = H or Me; M = Fe [1] or Ru [2]) and $(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})Co(\eta\text{-}C_4Me_4)$ [1] compounds, synthesized by us previously. Dimeric structures were suggested for compounds **2a—c** based on the requirements of the 18-electron environment at the rhodium atoms as well as on their similarity to $[(\eta\text{-}C_5Me_5)RhX_2]_2$ complexes (X = Cl, Br, or I), whose structures were confirmed by X-ray diffraction analysis.[6—8]

Complexes **2a—c** are bright-colored air-stable crystalline compounds, which are readily soluble in highly polar coordinating solvents, such as DMF and DMSO, and less soluble in MeCN. The solubility in MeCN increases in the order Cl < Br < I. Apparently, the dissolving ability of these solvents is associated with splitting of the dimers to form the solvate complexes $(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})RhX_2(Solv)$.

Rhodacarborane halide complexes **2a—c** can be considered as carborane analogs of cyclopentadienyl halide rhodium complexes $[(\eta\text{-}C_5R_5)RhX_2]_2$ (R = H or Alk; X = Cl, Br, or I), which are the key compounds in the synthesis of various derivatives containing the $(\eta\text{-}C_5R_5)Rh$ fragment.[9—12] Hence, it would be expected that analogous derivatives with the rhodacarborane fragment $(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})Rh$ will be synthesized based on complexes **2a—c**.

Experimental

All operations associated with the synthesis and isolation of compounds **2a—c** were carried out in air. The ^1H and ^{11}B NMR spectra were measured on a Bruker AMX-400 instrument. The ^{11}B NMR spectra were obtained with $BF_3 \cdot Et_2O$ as the external standard.

Bis[(η-9-dimethylsulfonio-7,8-dicarbollide)rhodiumdibromide], $[(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})RhBr_2]_2$ (2b). Concentrated HBr (0.6 mL) and Me_2CO (5 mL) were added to $(\eta\text{-}9\text{-}Me_2S\text{-}7,8\text{-}C_2B_9H_{10})Rh(\eta\text{-}cod)$ (1)[3] (40 mg, 0.1 mmol). The reaction mixture was stirred for 12 h and the solvent was distilled off *in vacuo*. The residue was washed several times with small portions of propan-2-ol and ether and dried *in vacuo*. A dark-red finely crystalline compound was obtained in a yield of 36 mg (79%). Found (%): C, 10.92; H, 3.26; Br, 34.72. $C_8H_{32}B_{18}Br_4Rh_2S_2$. Calculated (%): C, 10.53, H, 3.53, Br, 35.03.

Analogously, compounds **2a** (76%) and **2c** (80%) were obtained with the use of concentrated HCl and HI, respectively. In the case of the synthesis of complex **2c**, the reaction time was 48 h.

For **2a**, found (%): C, 14.73; H, 4.65; B, 25.11. $C_{9.5}H_{35}B_{18}Cl_4O_{0.5}Rh_2S_2$ (**2a** · $0.5Me_2CO$). Calculated (%): C, 14.94; H, 4.62; B, 25.48. For **2c**, found (%): C, 10.06; H, 3.05; B, 17.49. $C_{9.5}H_{35}B_{18}I_4O_{0.5}Rh_2S_2$ (**2c** · $0.5Me_2CO$). Calculated (%): C, 10.10; H, 3.12; B, 17.23.

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