Cationic arenerhodacarboranes
[(η-arene)Rh(η-7,8-Me₂-7,8-C₂B₉H₉)]BF₄

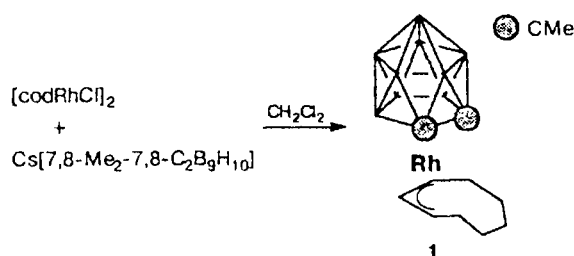*A. R. Kudinov,* R. T.Bogoudinov, P. V. Petrovskii, and M. I. Rybinskaya*

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A new procedure was developed for the synthesis of (η³-C₈H₁₃)Rh(η-7,8-Me₂-7,8-C₂B₉H₉) (1). This method involves the interaction of [codRhCl]₂ with Cs[7,8-Me₂-7,8-C₂B₉H₁₀] in CH₂Cl₂. The reactions of compound 1 with arenes in trifluoroacetic acid afforded the previously unknown cationic arenerhodacarboranes [(η-arene)Rh(η-7,8-Me₂-7,8-C₂B₉H₉)]BF₄ in high yields.

Key words: rhodacarboranes, arene ligands, rhodium complexes.

Presently, the chemistry of rhodacarboranes is well studied.[1–3] The rhodium atom in these compounds is generally coordinated with phosphines and CO as well as with allyl, diene, and dienyl ligands. In this work, we report the synthesis of the first representatives of cationic rhodacarboranes containing arene ligands.
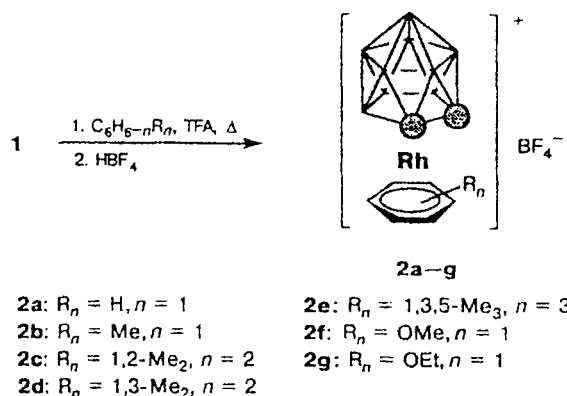
Previously, we have developed a general procedure for the synthesis of cationic arene complexes of transition metals by replacing various ligands with arenes in a medium of trifluoroacetic acid (TFA).[4] This procedure appeared to be applicable also for preparing cationic arenerhodacarboranes. We used the 16-electron cyclooctenyl complex (η³-C₈H₁₃)Rh(η-7,8-Me₂-7,8-C₂B₉H₉) (1), which we synthesized in CH₂Cl₂ (90% yield) by the direct reaction of [codRhCl]₂ with Cs[7,8-Me₂-7,8-C₂B₉H₁₀], as a starting compound:

Complex 1 has been reported previously.[5] However, it has been prepared according to a more complex procedure. Thus, the reaction of [codRhCl]₂ with [7,8-Me₂-7,8-C₂B₉H₉]²⁻ afforded the anionic complex [codRh(η-7,8-Me₂-7,8-C₂B₉H₉)]⁻, whose protonation with TFA yielded complex 1.

We found that the reaction of 1 with arenes in boiling TFA afforded the previously unknown cationic arenerhodacarboranes **2a—g** isolated as salts with the BF₄⁻ anion:

2a: Rₙ = H, n = 1
2b: Rₙ = Me, n = 1
2c: Rₙ = 1,2-Me₂, n = 2
2d: Rₙ = 1,3-Me₂, n = 2
2e: Rₙ = 1,3,5-Me₃, n = 3
2f: Rₙ = OMe, n = 1
2g: Rₙ = OEt, n = 1

We used benzene and its methyl and alkoxy derivatives as arenes. The introduction of donor methyl and alkoxy groups substantially accelerates the reaction. Apparently, the function of TFA is to protonate the cyclooctenyl ligand to form cyclooctene, followed by its replacement with arenes to form stable 18-electron cationic arene complexes. This exchange can occur through the intermediate formation of labile trifluoroacetate complexes.

Complexes **2a—g** are air-stable colorless or pale-yellow crystalline compounds. These compounds are readily soluble in acetone and undergo slow hydrolysis in the presence of water in acetone.

New compounds **2a—g** were caracterized by elemental analysis data and by ¹H and ¹¹B NMR spectra (Table 1). The ¹H NMR spectra have signals from the protons of the arene ligands along with signals from the

Table 1. Data of ^{1}H and ^{11}B NMR spectroscopy for the compounds [(η-arene)Rh(η-7,8-Me₂-7,8-C₂B₉H₉)]BF₄ (2a—g) in acetone-d_6

Compound, arene ligand	^{1}H NMR (δ, J/Hz) Me₂C₂B₉H₉	^{1}H NMR (δ, J/Hz) arene	^{11}B NMR (δ, J_{BH}/Hz)
2a, C₆H₆	2.81 (s, 6 H)	8.11 (s, 6 H, C₆H₆)	16.94 (1 B, J = 146), 14.27 (1 B, J = 155), 7.40 (2 B, J = 165), −0.12 (1 B, BF₄), −2.50 (2 B, J = 149), −6.26 (2 B, J = 163), −9.31 (1 B, J = 176)
2b, C₆H₅Me	2.75 (s, 6 H)	7.95 (m, 3 H, o,p-C₆H₃), 7.89 (m, 2 H, m-C₆H₂), 2.82 (s, 3 H, CH₃)	16.21 (1 B, J = 150), 15.01 (1 B, J = 156), 8.05 (2 B, J = 164), −0.16 (1 B, BF₄), −2.65 (2 B, J = 149), −6.52 (2 B, J = 163), −9.03 (1 B, J = 176)
2c, o-C₆H₄Me₂	2.71 (s, 6 H)	7.81 (s, 4 H, C₆H₄), 2.71 (s, 6 H, CH₃)	16.71 (1 B, J = 152), 15.58 (1 B, J = 147), 8.62 (2 B, J = 164), −0.16 (1 B, BF₄), −2.75 (2 B, J = 148), −6.68 (2 B, J = 163), −8.86 (1 B, J = 174)
2d, m-C₆H₄Me₂	2.70 (s, 6 H)	7.76 (m, 3 H, 4,5,6-C₆H₃), 7.70 (s, 1 H, 2 C₆H), 2.76 (s, 6 H, CH₃)	15.48 (2 B, J = 152), 8.79 (2 B, J = 163), −0.16 (1 B, BF₄), −2.77 (2 B, J = 149), −6.70 (2 B, J = 165), −8.73 (1 B, J = 174)
2e, 1,3,5-C₆H₃Me₃	2.62 (s, 6 H)	7.59 (s, 3 H, C₆H₃), 2.69 (s, 9 H, CH₃)	15.27 (2 B, J = 153), 8.47 (2 B, J = 161), 0.18 (1 B, BF₄), −3.06 (2 B, J = 151), −6.87 (2 B, J = 174), −8.74 (1 B, J = 174)
2f, C₆H₅OMe	2.69 (s, 6 H)	7.88 (m, 2 H, m-C₆H₂), 7.77 (m, 2 H, o-C₆H₂), 7.72 (m, 1 H, p-C₆H), 4.38 (s, 3 H, CH₃)	15.52 (1 B, J = 163), 14.15 (1 B, J = 167), 6.79 (2 B, J = 165), −0.13 (1 B, BF₄), −3.03 (2 B, J = 151), −7.05 (2 B, J = 165), −9.60 (1 B, J = 175)
2g, C₆H₅OEt	2.69 (s, 6 H)	7.86 (m, 2 H, m-C₆H₂), 7.73 (m, 2 H, o-C₆H₂), 7.71 (m, 1 H, p-C₆H), 4.69 (q, 2 H, CH₂, J = 7), 1.55 (t, 3 H, CH₃, J = 7)	15.42 (1 B, J = 154), 14.18 (1 B, J = 160), 6.78 (2 B, J = 165), −0.13 (1 B, BF₄), −3.06 (2 B, J = 151), −7.09 (2 B, J = 165), −9.63 (1 B, J = 173)

protons of the methyl groups in the carborane cage at δ 2.7—2.8. The ^{11}B NMR spectra have five or six doublets from the boron atoms of the carborane cage (J_{BH} = 148—176 Hz) along with a singlet of the BF₄⁻ anion.

It is well known[6] that the dianion [C₂B₉H₁₁]²⁻ is analogous to the C₅H₅⁻ anion and particularly to the C₅Me₅⁻ anion. Therefore, the resulting compounds 2a—g can be considered as analogs of the dicationic arene complexes [(η-C₅Me₅)Rh(η-arene)]²⁺ reported previously.[4,7-10] Actually, both types of compounds are formed under analogous conditions (in a TFA medium), exhibit similar chemical properties (in particular, they eliminate the arene ligand under the action of strongly coordinating solvents), and are characterized by a downfield shift of signals from the protons of the benzene ring compared to those observed in the free ligand.

Experimental

All reactions were performed under an atmosphere of argon with the use of anhydrous solvents. The reaction products were isolated in air. The initial compounds [codRhCl]₂[11] and Cs[7,8-Me₂-7,8-C₂B₉H₁₀][12] were prepared according to known procedures. The ^{1}H and ^{11}B NMR spectra were recorded on a Bruker AMX-400 instrument. The chemical shifts in the ^{11}B NMR spectra are given relative to the external standard BF₃·Et₂O.

Complex (η³-C₈H₁₃)Rh(η-7,8-Me₂-7,8-C₂B₉H₉) (1). A mixture of [codRhCl]₂ (246 mg, 0.5 mmol), Cs[7,8-Me₂-7,8-C₂B₉H₁₀] (294 mg, 1 mmol), and CH₂Cl₂ (10 mL) was stirred for 12 h. In the course of the reaction, the color of the mixture changed from yellow to red. The reaction mixture was filtered, the precipitate was washed with CH₂Cl₂, and an equal volume of heptane was added to the filtrate. The resulting solution was concentrated *in vacuo* to approximately one-half of the initial volume. Orange crystals that precipitated were filtered off. The yield was 335 mg (90%). Found (%): C, 38.74; H, 7.84; B, 26.46. C₁₂H₂₈B₉Rh. Calculated (%): C, 38.69; H, 7.58; B, 26.12. ^{1}H NMR (CD₂Cl₂), δ: 5.85 (q, 2 H, allylic CH, J = 8 Hz), 4.69 (t, 1 H, allylic CH, J = 8 Hz), 2.56 (m, 2 H, CH₂), 2.20 (s, 6 H, CH₃), 1.80 (m, 4 H, CH₂), 1.44 (m, 2 H, CH₂), 1.07 (m, 2 H, CH₂) (virtually completely coincides with the ^{1}H NMR spectral data reported in Ref. 5). ^{11}B NMR (CD₂Cl₂), δ: 4.41 (1 B, J = 144 Hz), −1.70 (1 B, J = 152 Hz), −4.06 (2 B, J = 156 Hz), −10.87 (2 B, J = 144 Hz), −15.77 (3 B, J = 160 Hz).

Complexes [(η-arene)Rh(η-7,8-Me₂-7,8-C₂B₉H₉)]BF₄ (2a—g). Arene (excess, 0.5 mL) and CF₃CO₂H (3 mL) were added to compound 1 (74.5 mg, 0.2 mmol). The reaction mixture was boiled until the orange tint disappeared (for 1—4 h depending on the arene used). After cooling to ~20 °C, HBF₄·Et₂O (0.2 mL) was added and the reaction mixture was concentrated *in vacuo*. The residue was washed with ether and reprecipitated with ether from acetone. The resulting complexes were obtained as colorless or pale-yellow solid compounds in 65—90% yields.

Complex 2a, arene $= C_6H_6$. Found (%): C, 27.68; H, 4.87. $C_{10}H_{21}B_{10}F_4Rh$. Calculated (%): C, 28.04; H, 4.94.

Complex 2b, arene $= C_6H_5Me$. Found (%): C, 29.85; H, 5.27. $C_{11}H_{23}B_{10}F_4Rh$. Calculated (%): C, 29.87; H, 5.24.

Complex 2c, arene $= o\text{-}C_6H_4Me_2$. Found (%): C, 31.69; H, 5.58. $C_{12}H_{25}B_{10}F_4Rh$. Calculated (%): C, 31.58; H, 5.52.

Complex 2d, arene $= m\text{-}C_6H_4Me_2$. Found (%): C, 31.87; H, 5.42. $C_{12}H_{25}B_{10}F_4Rh$. Calculated (%): C, 31.58; H, 5.52.

Complex 2e, arene $= 1,3,5\text{-}C_6H_3Me_3$. Found (%): C, 33.26; H, 5.89. $C_{13}H_{27}B_{10}F_4Rh$. Calculated (%): C, 33.19; H, 5.78.

Complex 2f, arene $= C_6H_5OMe$. Found (%): C, 29.31; H, 4.85. $C_{11}H_{23}B_{10}F_4ORh$. Calculated (%): C, 28.83; H, 5.06.

Complex 2g, arene $= C_6H_5OEt$. Found (%): C, 30.56; H, 5.27. $C_{12}H_{25}B_{10}F_4ORh$. Calculated (%): C, 30.51; H, 5.34.

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