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Arene exchange in the cationic (benzene)rhodacarboranes $[(\eta\text{-}7,8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_9)Rh(\eta\text{-}C_6H_6)]^+$ (R = H, Me)

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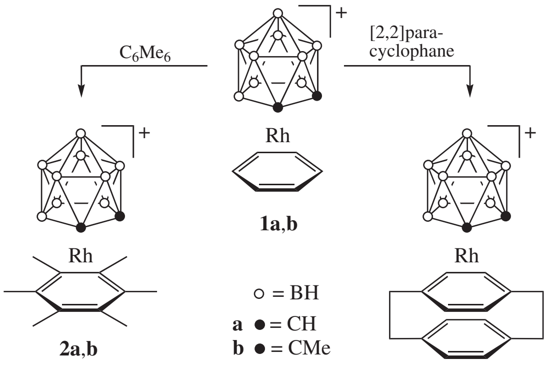
The benzene ligand in cations $[(\eta\text{-}7,8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_9)Rh(\eta\text{-}C_6H_6)]^+$ (R = H, Me) is replaced by hexamethylbenzene and [2.2]paracyclophane in refluxing nitromethane.

The benzene ligand in complexes $[LM(\eta\text{-}C_6H_6)]^n$ (n = 0, +1, +2) is often substitutionally labile making them useful synthons of $[ML]^n$ fragments. In particular, benzene exchange for other arenes is known for $[ML]^n$ = $M(CO)_3$ (M = Cr, Mo, W),[1] $[FeCp]^+$,[2] $[Fe(\eta\text{-cyclohexadienyl})]^+$,[3] $[Co(\eta\text{-}C_4Me_4)]^+$,[4] $[Co(\eta\text{-}C_4H_4BOH)]^+$,[5] $[M(cod)]^+$ (M = Rh, Ir),[6] and $[MCp]^{2+}$ (M = Co, Rh).[1(b),7] However, examples of arene exchange for metallacarborane complexes are still rare. Grimes *et al.*[8] have described the replacement of naphthalene by biphenyl in $(\eta\text{-}Et_2C_2B_4H_4)Fe(\eta\text{-}C_{10}H_8)$. Recently,[9] we have found that the benzene ligand in the cationic (tricarbollide)iron complex $[(\eta\text{-}1\text{-}Bu^tNH\text{-}1,7,9\text{-}C_3B_8H_{10})Fe(\eta\text{-}C_6H_6)]^+$ can be replaced by alkyl-substituted benzenes. Substitution of benzene by anisole was observed for the rhodium complex $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(\eta\text{-}C_6H_6)]^{2+}$ containing monoanionic charge-compensated dicarbollide.[10] Herein we report the first examples of arene exchange reactions for complexes $[(\eta\text{-}7,8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_9)Rh(\eta\text{-}C_6H_6)]^+$ [R = H (**1a**), Me (**1b**)] containing dianionic dicarbollide ligand.

The cationic benzene complexes **1a**,**b** were prepared by reaction of the cyclooctenyl derivatives $(\eta\text{-}7,8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_9)Rh(\eta^3\text{-}C_8H_{13})$ with C_6H_6 in boiling trifluoroacetic acid.[11] Noteworthy, the parent cyclooctenyl complex $(\eta\text{-}7,8\text{-}C_2B_9H_{11})Rh(\eta^3\text{-}C_8H_{13})$ is unstable at room temperature,[12] and therefore it was generated in solution by protonation of anion $[(\eta\text{-}7,8\text{-}C_2B_9H_{11})Rh(cod)]^-$ at –73 °C.[†]

Cations **1a**,**b** undergo slow hydrolysis by traces of water in acetone with elimination of free benzene, indicating substitutional lability of the benzene ligand. Such a lability was proved by reactions of **1a**,**b** with hexamethylbenzene and [2.2]paracyclophane (pcp) in refluxing nitromethane giving the corresponding arene complexes **2a**,**b** and **3a**,**b** (Scheme 1).[‡] Tetrafluoroborates of cations **1**–**3** are air-stable salts and were analyzed by ^1H and ^{11}B NMR spectroscopy. Similar to dicationic complexes $[(\eta\text{-}C_5R_5)Rh(arene)]^{2+}$ and $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(arene)]^{2+}$, the signals of arene ring protons are downfield shifted relative to the free arene.[10,13]



Scheme 1

[†] A mixture of $[(cod)RhCl]_2$ (100 mg, 0.203 mmol), $Tl[Tl(\eta\text{-}7,8\text{-}C_2B_9H_{11})]$ (220 mg, 0.406 mmol), and THF (3 ml) was stirred for 2 h. The precipitate of TlCl was centrifuged off and the centrifugate was evaporated *in vacuo*. Benzene (1 ml) was added to the residue containing $Tl[(\eta\text{-}7,8\text{-}C_2B_9H_{11})Rh(cod)]$. After cooling to –73 °C, CF_3COOH (1.5 ml) and $(CF_3CO)_2O$ (0.5 ml) were added, and the reaction mixture was refluxed with vigorous stirring for 1.5 h. After cooling to room temperature, $HBF_4\cdot Et_2O$ (0.2 ml) was added and the solvent was removed *in vacuo*. The residue was washed with diethyl ether and dissolved in nitromethane (1 ml). Then an excess of HCl/Et_2O was added to precipitate TlCl, which was centrifuged off. Diethyl ether (5 ml) was added to the centrifugate to precipitate complex [**1a**][BF_4] as a white solid. Yield 59 mg (36%). ^1H NMR (acetone-d_6) δ: 8.00 (s, 6H, C_6H_6), 5.88 (s, 2H, CH). $^{11}B\{^1H\}$ NMR (acetone-d_6) δ: 15.15 (1B), 14.54 (1B), 2.68 (2B), –1.01 (s, 1B, BF_4), –2.27 (2B), –11.13 (2B), –19.25 (1B). Found (%): C, 23.81; H, 4.36; B, 26.77. Calc. for $C_8H_{17}B_{10}F_4Rh$ (%): C, 24.01; H, 4.28; B, 27.01.

[‡] Nitromethane (2 ml) was added to a mixture of [**1a**,**b**][BF_4] (30 mg, 0.070–0.075 mmol) and arene (0.4–0.7 mmol). The reaction mixture was refluxed with vigorous stirring for 2 h. The solvent was removed *in vacuo* and the residue was washed with diethyl ether and repricipitated from acetone by diethyl ether. Complexes $[(\eta\text{-}7,8\text{-}R_2\text{-}7,8\text{-}C_2B_9H_9)Rh(arene)]BF_4$ were obtained as white ([**2a**,**b**][BF_4]) or yellow ([**3a**,**b**][BF_4]) solids.

[**2a**][BF_4]: 64% yield. ^1H NMR (acetone-d_6) δ: 5.18 (s, 2H, CH), 2.67 (s, 18H, C_6Me_6). $^{11}B\{^1H\}$ NMR (acetone-d_6) δ: 18.20 (1B), 10.50 (1B), 4.87 (2B), –1.06 (s, 1B, BF_4), –2.88 (2B), –11.98 (2B), –18.89 (1B). Found (%): C, 34.58; H, 5.84; B, 22.37. Calc. for $C_{14}H_{29}B_{10}F_4Rh$ (%): C, 34.71; H, 6.03; B, 22.32.

[**2b**][BF_4]: 86% yield. ^1H NMR (acetone-d_6) δ: 2.57 (s, 18H, C_6Me_6), 2.35 (s, 6H, CMe). $^{11}B\{^1H\}$ NMR (acetone-d_6) δ: 17.62 (1B), 12.66 (1B), 8.27 (2B), –1.09 (s, 1B, BF_4), –4.46 (2B), –8.89 (3B). Found (%): C, 37.41; H, 6.48; B, 20.91. Calc. for $C_{16}H_{33}B_{10}F_4Rh$ (%): C, 37.50; H, 6.49; B, 21.10.

[**3a**][BF_4]: 68% yield. ^1H NMR (acetone-d_6) δ: 7.17 (s, 4H, C_6H_4), 7.12 (s, 4H, C_6H_4), 5.52 (s, 2H, CH), 3.51 (m, 8H, CH_2). $^{11}B\{^1H\}$ NMR (acetone-d_6) δ: 13.56 (2B), 1.79 (2B), –0.96 (s, 1B, BF_4), –3.13 (2B), –11.90 (2B), –20.09 (1B). Found (%): C, 39.95; H, 5.08; B, 19.97. Calc. for $C_{18}H_{27}B_{10}F_4Rh$ (%): C, 40.76; H, 5.13; B, 20.38.

[**3b**][BF_4]: 72% yield. ^1H NMR (acetone-d_6) δ: 7.22 (s, 4H, C_6H_4), 7.11 (s, 4H, C_6H_4), 3.52 (m, 8H, CH_2), 2.53 (s, 6H, CMe). $^{11}B\{^1H\}$ NMR (acetone-d_6) δ: 14.55 (1B), 12.73 (1B), 5.69 (2B), –0.77 (s, 1B, BF_4), –4.07 (2B), –8.08 (2B), –11.15 (1B). Found (%): C, 43.04; H, 5.39; B, 19.31. Calc. for $C_{20}H_{31}B_{10}F_4Rh$ (%): C, 43.01; H, 5.60; B, 19.36.

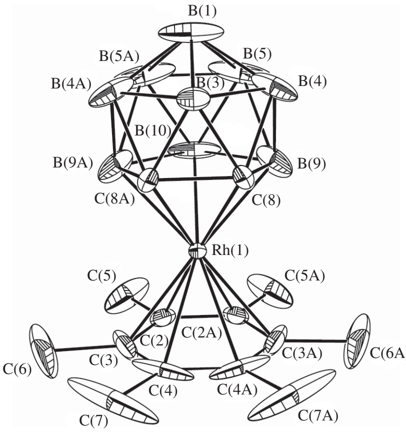


Figure 1 Structure of cation **2a**. Ellipsoids are shown at the 30% level. Selected bond lengths (Å): Rh(1)–C(8) 2.179(7), Rh(1)–B(9) 2.152(10), Rh(1)–B(10) 2.159(12), Rh(1)–C(2) 2.192(8), Rh(1)–C(3) 2.253(8), Rh(1)–C(4) 2.286(8), C(8)–B(9) 1.707(12), B(9)–B(10) 1.818(16), C(2)–C(3) 1.415(15), C(3)–C(4) 1.379(18).

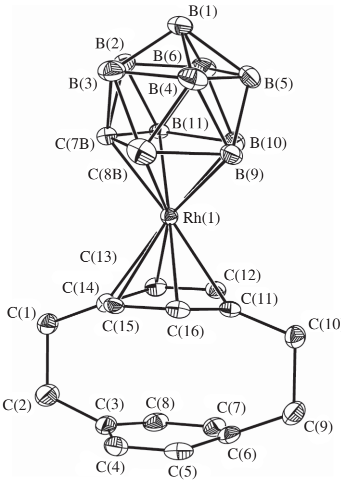


Figure 2 Structure of cation **3a**. Ellipsoids are shown at the 50% level. Selected bond lengths (Å): Rh(1)–C(7B) 2.143(3), Rh(1)–C(8B) 2.176(3), Rh(1)–B(9) 2.190(3), Rh(1)–B(10) 2.182(3), Rh(1)–B(11) 2.158(3), Rh(1)–C(11) 2.341(3), Rh(1)–C(12) 2.235(3), Rh(1)–C(13) 2.301(3), Rh(1)–C(14) 2.466(3), Rh(1)–C(15) 2.259(3), Rh(1)–C(16) 2.198(3), C(7B)–C(8B) 1.738(5), C(8B)–B(9) 1.838(5), B(9)–B(10) 1.834(5), B(10)–B(11) 1.732(5), C(7B)–B(11) 1.638(4), C(11)–C(12) 1.425(4), C(12)–C(13) 1.410(4), C(13)–C(14) 1.406(4), C(14)–C(15) 1.410(4), C(15)–C(16) 1.411(4), C(11)–C(16) 1.415(4).

The structures of [**2a**][$\mathrm{BF_4}$] and [**3a**][$\mathrm{BF_4}$] were confirmed by X-ray diffraction (Figures 1 and 2).[§] The metal-to-ring $\mathrm{Rh\cdots C_2B_3}$ distances [1.580(6) Å in **2a**, 1.574(8) Å in **3a**] are close to those in the related rhodium complexes with dicarbollide ligand, *e.g.*, $(\eta\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})\mathrm{RhCp}$ (1.578 Å),[14] $(\eta\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})\mathrm{Rh}(\eta^5\text{-}\mathrm{C_9H_2Me_5})$ (1.585 Å),[15] and $(\eta\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})\mathrm{Rh}(\eta\text{-}\mathrm{C_5H_5BMe})$ (1.585 Å).[14] However, the $\mathrm{Rh\cdots C_6Me_6}$ distance in cation **2a** (1.756 Å) is considerably longer than the corresponding distance in the cyclopentadienyl analogue $[\mathrm{CpRh}(\eta\text{-}\mathrm{C_6Me_6})]^{2+}$ (1.689 Å),[13(*b*)] suggesting weaker bonding of hexamethylbenzene with the $[\mathrm{Rh}(\eta\text{-}7,8\text{-}\mathrm{C_2B_9H_{11}})]^+$ fragment compared with $[\mathrm{RhCp}]^{2+}$.

Both benzene rings of the paracyclophane ligand in cation **3a** are deviated from planarity toward a boat conformation similar to the free ligand[16] and its known complexes.[17] Noteworthy, the C–C bonds of the coordinated six-membered ring (av. 1.413 Å) are longer than those of the uncoordinated one (av. 1.390 Å) owing to the loosening of π bonds upon coordination. Only one example of metallacarborane complex with paracyclophane, $(\eta\text{-}7\text{-}\mathrm{Bu^tNH}\text{-}7\text{-}\mathrm{CB_{10}H_{10}})\mathrm{Rh(pcp)}$, has been previously structurally characterized.[18] The $\mathrm{Rh\cdots C(12)C(13)C(15)C(16)}$ distance in **3a** (1.758 Å) is shorter than the corresponding distance in $(\eta\text{-}7\text{-}\mathrm{Bu^tNH}\text{-}7\text{-}\mathrm{CB_{10}H_{10}})\mathrm{Rh(pcp)}$ (1.810 Å) as a result of stronger bonding of the rhodium atom with the trianionic ligand $[7\text{-}\mathrm{Bu^tNH}\text{-}7\text{-}\mathrm{CB_{10}H_{10}}]^{3-}$.

We may conclude that the (benzene)rhodacarboranes $[(\eta\text{-}7,8\text{-}\mathrm{R_2}\text{-}7,8\text{-}\mathrm{C_2B_9H_9})\mathrm{Rh}(\eta\text{-}\mathrm{C_6H_6})]^+$ are capable of easy arene exchange making them useful synthons of the cationic rhodacarborane species $[\mathrm{Rh}(\eta\text{-}7,8\text{-}\mathrm{R_2}\text{-}7,8\text{-}\mathrm{C_2B_9H_9})]^+$.

[§] Crystals were grown up by slow diffusion in two-layer system, diethyl ether and a solution of the complex in $\mathrm{CH_2Cl_2}$ (for [**2a**][$\mathrm{BF_4}$]) or $\mathrm{Me_2CO}$ (for [**3a**][$\mathrm{BF_4}$]).

Crystal data for [**2a**][$\mathrm{BF_4}$]: $\mathrm{C_{14}H_{29}B_{10}F_4Rh}$, orthorhombic, space group $Pmc2_1$, $a = 11.342(3)$, $b = 11.684(3)$ and $c = 15.785(4)$ Å, $V = 2091.8(10)$ Å^3, $Z = 4$, $d_\mathrm{calc} = 1.538$ g cm^{-3}, $\mu = 0.849$ mm^{-1}, crystal size 0.60×0.45×0.30 mm, $F(000) = 976$, $T_\mathrm{min}/T_\mathrm{max}$ 0.6015/0.7460, $R_1 = 0.0429$ [from 2925 unique reflections with $I > 2\sigma(I)$] and $wR_2 = 0.1093$ (from all 3006 unique reflections).

Crystal data for [**3a**][$\mathrm{BF_4}$]: $\mathrm{C_{18}H_{27}B_{10}F_4Rh}$, monoclinic, space group $P2_1/c$, $a = 10.7249(6)$, $b = 21.4507(13)$ and $c = 10.0952(6)$ Å, $\beta = 100.7650(10)°$, $V = 2281.6(2)$ Å^3, $Z = 4$, $d_\mathrm{calc} = 1.544$ g cm^{-3}, $\mu = 0.786$ mm^{-1}, crystal size 0.35×0.25×0.20 mm, $F(000) = 1064$, $T_\mathrm{min}/T_\mathrm{max}$ 0.790/0.855, $R_1 = 0.0377$ [from 3987 unique reflections with $I > 2\sigma(I)$] and $wR_2 = 0.0865$ (from all 4427 unique reflections).

X-ray diffraction experiments were carried out with a Bruker SMART APEX2 CCD area detector at 100 K (for [**2a**][$\mathrm{BF_4}$]) or a Bruker SMART 1000 CCD area detector at 120 K (for [**3a**][$\mathrm{BF_4}$]), using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The absorption correction was applied semi-empirically using SADABS program. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms of the BH groups were found in the difference Fourier synthesis, and the positions of other hydrogen atoms were calculated. All hydrogen atoms were refined in isotropic approximation in riding model with the $U_\mathrm{iso}(\mathrm{H})$ parameters equal to $1.5U_\mathrm{eq}(\mathrm{C_i})$ for methyl groups and to $1.2U_\mathrm{eq}(\mathrm{C_{ii}})$ and $1.2U_\mathrm{eq}(\mathrm{B_i})$ for other atoms, where $U_\mathrm{eq}(\mathrm{B})$ and $U_\mathrm{eq}(\mathrm{C})$ are the equivalent thermal parameters of the atoms to which the corresponding H atoms are bound.

CCDC 780578 and 780579 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2011.

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