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Synthesis and structure of rhodium complexes with monoanionic carborane ligand $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$

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Abstract

(Rhodacarborane)halide complexes $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})RhX_2]_2$ (**4a**: X = Cl; **4b**: X = Br; **4c**: X = I), which are analogous to $[Cp^*RhX_2]_2$, were synthesized by reaction of $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(cod)$ (cod = 1,5-cyclooctadiene) with HX. Compounds **4** were used to prepare several sandwich and half-sandwich complexes containing $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh$ fragment. 2e-Ligands destroy the dimeric structure of **4** to give the adducts $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})RhLX_2$, exemplified by preparation of $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(CO)I_2$ and $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(PPh_3)Cl_2$. The reaction of **4a** with dppe in the presence of $TlBF_4$ affords the cationic complex $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(dppe)Cl]BF_4$ (**7**BF_4). Sandwich complexes $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(\eta\text{-}C_5R_5)]CF_3SO_3$ (**11a**CF_3SO_3: R = H; **11b**CF_3SO_3: R = Me) were obtained by abstracting chloride from **4a** by CF_3SO_3Ag with subsequent treatment with C_5R_5H. Complex **11b**PF_6 was prepared by reaction of $[Cp^*RhCl_2]_2$ with $Na[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]$. Complex $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(\eta\text{-}7,8\text{-}C_2B_9H_{11})$, containing two carborane ligands, was obtained by reaction of **4a** with $Tl[Tl(\eta\text{-}7,8\text{-}C_2B_9H_{11})]$. Structures of **7**$BF_4$ and **11b**PF_6 were confirmed by X-ray diffraction study. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium; Metallacarboranes; X-ray structure

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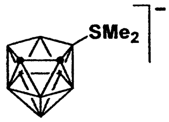
1. Introduction

Many works dedicated to synthesis of metal complexes of monoanionic (charge-compensated) carborane ligand $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (**1**) have been published [1–12]. Such compounds are of interest due to the isolobal analogy between $\mathbf{1}^-$ and Cp^-, exemplified by complex $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})_2Fe$ [6], an analogue of Cp_2Fe. In particular, several complexes of rhodium have been synthesized by Welch, e.g. $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})Rh(CO)_2$ [10] and $(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})\text{-}Rh(cod)$ (**2**) [5].



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(Pentamethylcyclopentadienyl)halide complexes of rhodium $[Cp^*RhX_2]_2$ (X = Cl, Br, I) (**3**) are widely used as precursors for organometallic compounds containing Cp*Rh fragment [14,15]. They also proved to be effective catalysts for homogeneous hydrogenation [16,17]. Herein we report an efficient synthesis of complexes $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})RhX_2]_2$ (X = Cl, Br, I) (**4a**–**c**), which are analogous to **3**, and their further reactions.

2. Results and discussion

2.1. Synthesis of $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})RhX_2]_2$ (X = Cl, Br, I)

The (rhodacarborane)halide complexes **4a**–**c** were prepared by reaction of (cyclooctadiene)rhodacarborane **2** with HX (X = Cl, Br, I) acids (Scheme 1) [13].

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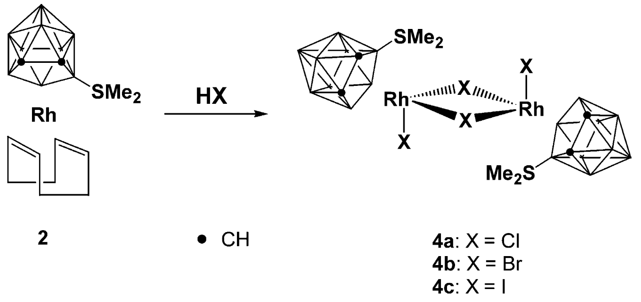
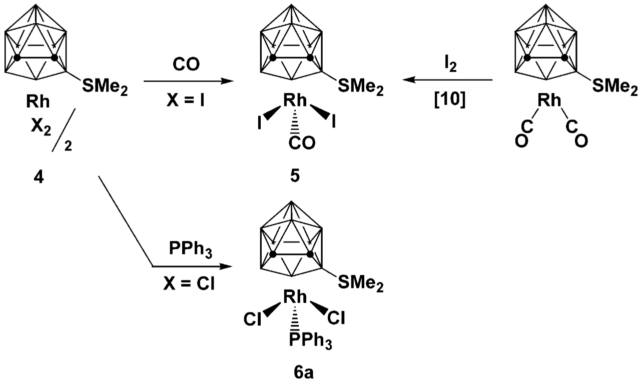


Scheme 1.



Scheme 2.

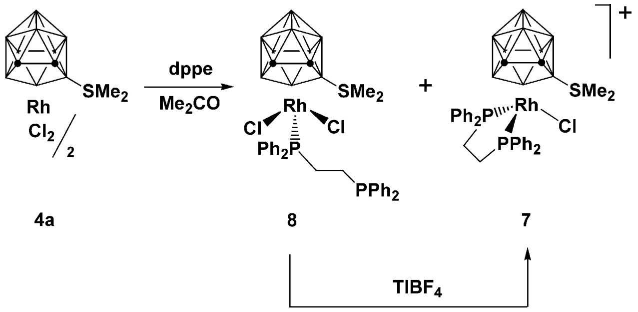
The ^{1}H-NMR data for **4a**–**c** as well as for other compounds described in this work are given in Table 1. Two broad singlets for CH-protons of carborane ligand and two sharp singlets for protons of methyl groups of SMe_2 substituent were observed for all compounds containing (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh fragment. Complexes **4a**–**c** are poorly soluble in non-coordinating solvents that inhibited growing-up crystals for X-ray study. Nevertheless, the dimeric structure can be suggested for these compounds based on the 18-electron rule as well as on their similarity to complexes **3**, the structure of which was unambiguously confirmed by X-ray diffraction [18–20].

2.2. *Adducts (η-9-SMe_2-7,8-$C_2B_9H_{10}$)$RhLX_2$*

Like in the case of compounds **3**, the dimeric structure of **4** is destroyed by 2e-ligands with the formation of adducts (η-9-SMe_2-7,8-$C_2B_9H_{10}$)$RhLX_2$. For instance, reaction of **4c** with CO in THF affords (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(CO)I_2 (**5**) in 89% yield; the same compound has been obtained earlier by Welch by reaction of (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh$(CO)_2$ with iodine [10] (Scheme 2). Analogous reaction of **4a** with PPh_3 in CH_2Cl_2 affords complex (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(PPh_3)Cl_2 (**6a**). Iodide analogue of **6a**, complex (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(PPh_3)I_2 (**6c**), has been obtained earlier by reaction of **5** with PPh_3 [10]. The NMR data for both compounds are very similar. In particular, in the $^{31}P\{^1H\}$-NMR spectra doublets are observed: for **6a** at 35.0 ppm, J(RhP) = 121.1 Hz; for **6c** at 34.8 ppm, J(RhP) = 124 Hz. Apparently, the dissolving ability of highly coordinating solvents (DMFA and DMSO) towards **4a**–**c** is associated with splitting of the dimers to form the solvate complexes (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(Solv)X_2.

2.3. *Synthesis and structure of [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(dppe)Cl]BF_4*

The reaction of **4a** with $Ph_2PCH_2CH_2PPh_2$ (dppe) in acetone gives a mixture of two products according to TLC and the ^{31}P-NMR spectrum (Scheme 3). The main product (ca. 90%) was shown to be the cationic complex [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(dppe)Cl]$^+$ (**7**). The by-product was proposed to be the neutral complex (η-9-



Scheme 3.

Table 1
^{1}H-NMR spectral data, δ (ppm)

Compound	SMe_2 (s, 3H)	CH-cage (bs, 1H)	Other
4a [a]	2.95, 3.12	5.43, 6.08	
4b [a]	2.94, 3.12	6.13, 5.45	
4c [a]	2.94, 3.12	6.02, 5.50	
6a [b]	2.74, 3.04	3.82, 5.42	7.3–7.5 (m, 9H, PPh_3), 7.8–7.9 (m, 6H, PPh_3)
7 [b]	2.59, 2.91	4.87, 5.43	3.30 (s, 4H, CH_2), 7.25–7.4 (m, 4H, PPh_2), 7.45–7.8 (m, 12H, PPh_2), 7.85–8.05 (m, 4H, PPh_2)
9 [b]	2.73, 2.79	4.18, 4.41, 4.53, 4.98	
11a [b]	2.78, 2.85	4.86, 5.64	6.47 (bs, 5H, Cp)
11b [b]	2.32, 2.35	3.06, 3.89	1.86 (s, 15H, Cp*)

[a] In DMFA-d_7.
[b] In Me_2CO-d_6.

SMe_2-7,8-$C_2B_9H_{10}$)Rh($PPh_2CH_2CH_2PPh_2$)Cl_2 (**8**) on the basis of the ^{31}P-NMR spectrum which displays a singlet at 38 ppm and a doublet at 58.5 ppm with rhodium coupling (J(RhP) = 115 Hz). Nevertheless, we were able to obtain complex **7**BF_4 in pure form in the presence of $TlBF_4$ as a chloride-abstracting agent. In the $^{31}P\{^1H\}$-NMR spectrum of **7**, two signal sets due to inequivalent phosphorous atoms are observed at 77.16 ppm and 65.53 ppm. The former is a doublet of doublets with major Rh–P coupling (J(RhP) = 144.6 Hz) and minor P–P coupling (J(PP′) = 21.87 Hz). The latter signal is a broad doublet with Rh coupling (J(RhP) = 95.1 Hz); coupling on the phosphorous atom is not observed, probably because of quadrupole interaction with Cl atom. However, the ^{1}H-NMR spectrum of **7** shows resonance due to CH_2 groups of dppe as a singlet at 3.30 ppm, which can be attributed to the rapid bridge reversal process [21].

The structure of cation **7** is shown on Fig. 1 and selected bond lengths and angles are given in Table 2. The complex displays the expected *closo* geometry. The metal-bound ligand face C(7)–C(8)–B(9)–B(10)–B(11) is nearly planar; the maximal deviation from the mean least-square plane is 0.034(2) Å. The Rh–C_2B_3 plane distance is 1.677(1) Å. The Rh(1)–P(1) bond (2.2787(8) Å) is slightly shortened in comparison to Rh(1)–P(2) (2.3374(8) Å). This difference can be attributed both to the ligand face influence and steric effects. In fact, the P(2) atom is situated in *trans* position to B(9) atom having SMe_2 substituent, while P(1) atom is located in *trans* position to the center of C(7)–C(8) bond. The steric overcrowding leads to the presence of the unusual contact of SMe_2 group with C(17)–C(18)–C(19)–C(20)–C(21)–C(22) phenyl ring with S···C (3.257(3) ÷ 3.464(3) Å) distances considerably shorter than the sum of the respective van der Waals radii (3.94 Å). In spite of this, no change in geometry of SMe_2 moiety and Ph group was observed.

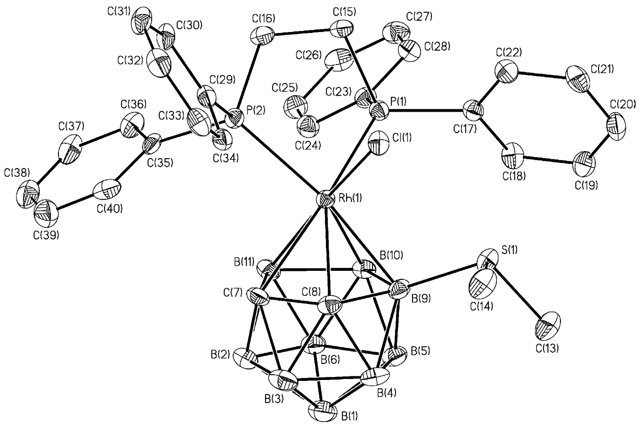


Fig. 1. Structure of cation **7**. Atoms are represented by 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

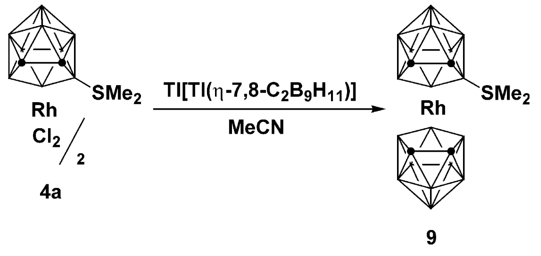
Table 2
Selected bond lengths (Å) and bond angles (°) for **7**BF_4

Bond lengths			
Rh(1)–B(11)	2.194(3)	P(1)–C(23)	1.823(3)
Rh(1)–B(10)	2.212(3)	P(1)–C(15)	1.834(3)
Rh(1)–B(9)	2.217(3)	P(2)–C(35)	1.813(3)
Rh(1)–C(8)	2.273(3)	P(2)–C(29)	1.825(3)
Rh(1)–P(1)	2.2787(8)	P(2)–C(16)	1.838(3)
Rh(1)–C(7)	2.280(3)	C(7)–C(8)	1.566(4)
Rh(1)–P(2)	2.3374(8)	C(7)–B(11)	1.743(5)
Rh(1)–Cl(1)	2.4074(8)	C(8)–B(9)	1.702(5)
S(1)–C(13)	1.795(4)	B(9)–B(10)	1.808(5)
S(1)–C(14)	1.815(3)	B(10)–B(11)	1.844(5)
S(1)–B(9)	1.921(3)	C(15)–C(16)	1.525(4)
P(1)–C(17)	1.807(3)		
Bond angles			
B(11)–Rh(1)–B(10)	49.47(13)	B(9)–Rh(1)–C(7)	74.36(12)
B(11)–Rh(1)–B(9)	81.34(13)	C(8)–Rh(1)–C(7)	40.22(11)
B(10)–Rh(1)–B(9)	48.17(13)	B(11)–Rh(1)–P(2)	95.21(10)
B(11)–Rh(1)–C(8)	75.86(12)	B(10)–Rh(1)–P(2)	135.32(9)
B(10)–Rh(1)–C(8)	77.81(12)	P(1)–Rh(1)–P(2)	83.71(3)
B(9)–Rh(1)–C(8)	44.53(12)	C(8)–Rh(1)–Cl(1)	90.84(8)
B(11)–Rh(1)–P(1)	111.94(9)	P(1)–Rh(1)–Cl(1)	82.79(3)
B(10)–Rh(1)–P(1)	86.32(9)	P(2)–Rh(1)–Cl(1)	87.08(3)
C(8)–Rh(1)–P(1)	150.59(8)	C(13)–S(1)–C(14)	100.62(18)
B(11)–Rh(1)–C(7)	45.80(12)	C(13)–S(1)–B(9)	104.07(18)
B(10)–Rh(1)–C(7)	78.30(12)	C(14)–S(1)–B(9)	105.15(17)

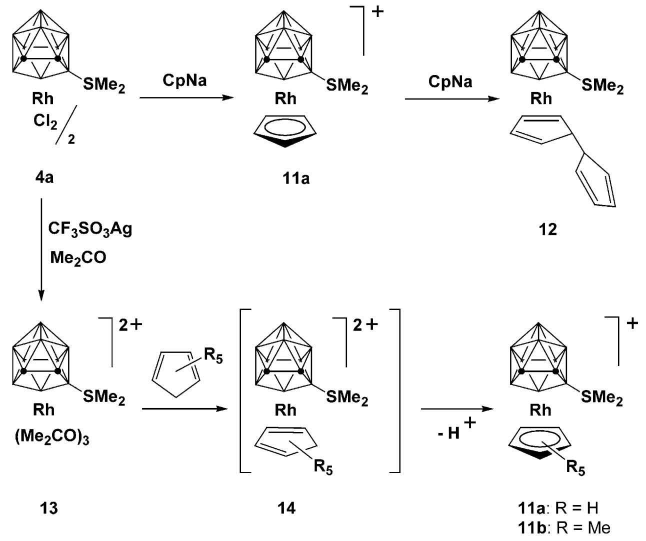
2.4. Synthesis of sandwich compounds (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(η-7,8-$C_2B_9H_{11}$) and [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(η-C_5R_5)]X (R = H, Me)

The reaction of **4a** with Tl[Tl(η-7,8-$C_2B_9H_{11}$)] in MeCN produces (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(η-7,8-$C_2B_9H_{11}$) (**9**) in a good yield (Scheme 4). This reaction is quite similar to the reaction of [Cp*$RhCl_2$]$_2$ with Tl[Tl(η-7,8-$C_2B_9H_{11}$)], that affords Cp*Rh(η-7,8-$C_2B_9H_{11}$) (**10**) [22]. The ^{1}H-NMR spectrum of **9** displays four resonances due to CH-protons of two carborane cages. The inequivalency of CH-protons of 7,8-$C_2B_9H_{11}$ ligand suggests that there is no rotation of carborane ligands or at least it is very slow in the NMR time scale.

In order to synthesize complex [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)RhCp]$^+$ (**11a**), which can be considered as metallacarborane analogue of rhodocenium cation, we studied the reaction of **4a** with CpNa (Scheme 5). However, this reaction gave a mixture of products. Although this mixture was not separated, we can



Scheme 4.



Scheme 5.

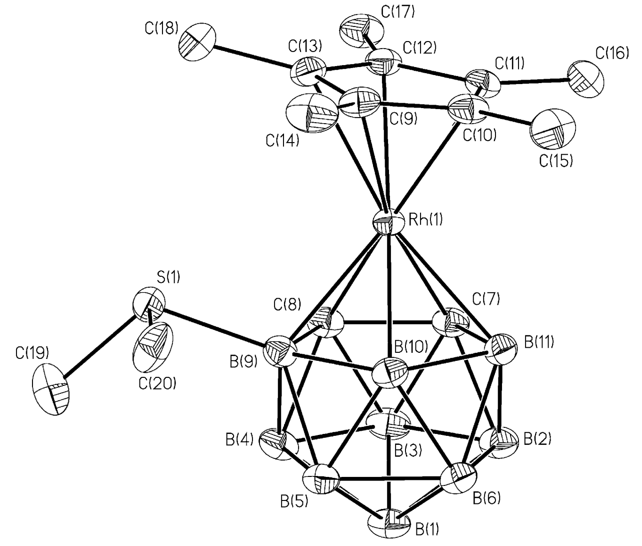
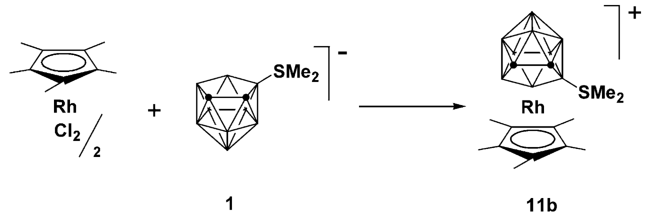


Fig. 2. Structure of cation **11b** (for one of two independent molecules). Atoms are represented by 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

propose that cation **11a** reacts further with Cp^- to give diene complexes: **12** and its Diels–Alder dimer, quite similar to the reaction of $[Cp_2Rh]^+$ with Cp^- [23]. The formation of diene complexes was indirectly confirmed by the formation of the bromide complex **4b** as a result of treatment of the mixture with HBr (cf. with synthesis of **4b** described above). Nevertheless, we were able to synthesize **11a** by a two-step method. The reaction of **4a** with silver triflate in acetone produces a yellow–green solution, which presumably contains solvate complex **13**. Subsequent addition of cyclopentadiene leads to **11a** via intermediate formation of strongly acidic diene dication **14**. The addition of C_5Me_5H instead of C_5H_6 yields pentamethyl-substituted complex $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})RhCp^*]^+$ (**11b**); the reaction is analogous to the synthesis of decamethylrhodocenium cation [24]. The yields of **11a** and **11b**, prepared by this method, are about 50%. Complex **11b** was prepared in even higher yield (97%) by reaction of anion **1** with $[Cp^*RhCl_2]_2$ (Scheme 6). Signals of CH-protons of carborane ligand of **11a** (5.64 and 4.86 ppm) are significantly down-field shifted as compared with the corresponding signals of methylated analogue **11b** (3.89 and 3.06 ppm), which may be attributed to the strong electron-donating effect of C_5Me_5 ring. The same is true for signals of SMe_2 groups, which are observed at 2.85, 2.78 ppm for **11a**, and at 2.35, 2.32 ppm for **11b**.



Scheme 6.

2.5. Structure of $[(\eta\text{-}9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10})RhCp^*]PF_6$

The structure of cation **11b** is shown in Fig. 2 and selected bond lengths and angles are given in Table 3. The crystallographic cell contains two independent molecules. The cation **11b** has the expected *closo*-MC_2B_9 geometry. The maximal deviation from the best least-squares plane passing through metal-bound ligand face C(7)–C(8)–B(9)–B(10)–B(11) is 0.015(1) Å. The $Rh–C_2B_3$ plane distance (1.625(1) Å) is slightly shorter than in cation **7** (1.677(1) Å). Related Rh–C and Rh–B distances in **11b** and the uncharged complex $Cp^*Rh(\eta\text{-}7,8\text{-}C_2B_9H_{11})$ (**10**) [22] are approximately equal, except Rh(1)–B(10) bond, which is significantly longer in **11b** (2.226(2) Å) than in **10** (2.173 Å). Remarkably the dihedral angle between C_5 and C_2B_3 planes in **11b** is 7.9°, almost the same as in **10** (7.6°). The structural similarity between **10** and **11b** suggests that there are no significant differences in bonding characteristics between dianion $[\eta\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ and charge-compensated monoanion **1**.

3. Conclusion

The results presented here demonstrate that reactions of (rhodacarborane)halide complexes **4** are similar to those of $[Cp^*RhX_2]_2$, giving additional confirmation of the isolobal analogy between $9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}$ and Cp* ligands.

Table 3
Selected bond lengths (Å) and bond angles (°) for **11b**PF_6 (for one of two independent molecules)

	Molecule A	Molecule B
Bond lengths		
Rh(1)–C(10)	2.169(2)	2.157(2)
Rh(1)–C(7)	2.177(2)	2.169(2)
Rh(1)–C(11)	2.177(2)	2.174(2)
Rh(1)–C(8)	2.186(2)	2.178(2)
Rh(1)–B(9)	2.189(2)	2.181(2)
Rh(1)–C(9)	2.190(2)	2.184(2)
Rh(1)–B(11)	2.198(2)	2.190(3)
Rh(1)–C(12)	2.203(2)	2.213(2)
Rh(1)–B(10)	2.226(2)	2.218(2)
Rh(1)–C(13)	2.235(2)	2.225(2)
S(1)–C(20)	1.799(3)	1.795(3)
S(1)–C(19)	1.803(3)	1.801(3)
S(1)–B(9)	1.909(3)	1.915(2)
C(7)–C(8)	1.622(3)	1.634(3)
C(7)–B(11)	1.729(3)	1.727(4)
C(8)–B(9)	1.717(3)	1.704(3)
B(9)–B(10)	1.797(3)	1.793(4)
B(10)–B(11)	1.811(3)	1.824(4)
C(9)–C(13)	1.424(3)	1.434(3)
C(9)–C(10)	1.439(3)	1.446(3)
C(9)–C(14)	1.499(3)	1.495(3)
C(10)–C(11)	1.437(3)	1.433(3)
C(10)–C(15)	1.497(3)	1.495(3)
C(11)–C(12)	1.435(3)	1.437(3)
C(11)–C(16)	1.504(3)	1.486(4)
C(12)–C(13)	1.428(3)	1.436(3)
C(12)–C(17)	1.490(3)	1.491(3)
C(13)–C(18)	1.495(3)	1.492(3)
Bond angles		
C(10)–Rh(1)–C(9)	38.56(9)	39.02(9)
C(7)–Rh(1)–C(8)	43.64(8)	44.15(8)
C(7)–Rh(1)–B(9)	77.53(9)	77.77(9)
C(8)–Rh(1)–B(9)	46.23(9)	46.03(9)
C(10)–Rh(1)–C(11)	38.63(8)	38.54(9)
C(11)–Rh(1)–C(9)	64.18(9)	64.57(9)
C(7)–Rh(1)–B(11)	46.56(9)	46.70(10)
C(8)–Rh(1)–B(11)	78.80(9)	79.38(9)
B(9)–Rh(1)–B(11)	81.39(9)	81.79(10)
C(10)–Rh(1)–C(12)	64.16(8)	64.23(8)
C(9)–Rh(1)–C(12)	63.47(8)	63.98(8)
C(11)–Rh(1)–C(12)	38.24(8)	38.13(8)
C(7)–Rh(1)–B(10)	79.54(8)	80.08(9)
C(8)–Rh(1)–B(10)	79.99(8)	80.26(9)
B(9)–Rh(1)–B(10)	48.05(9)	48.08(10)
B(11)–Rh(1)–B(10)	48.33(9)	48.89(10)
C(10)–Rh(1)–C(13)	63.56(8)	64.13(8)
C(9)–Rh(1)–C(13)	37.52(8)	38.03(8)
C(11)–Rh(1)–C(13)	63.36(8)	63.61(9)
C(12)–Rh(1)–C(13)	37.53(8)	37.75(8)
C(20)–S(1)–C(19)	100.12(17)	102.09(13)
C(20)–S(1)–B(9)	100.40(12)	109.12(12)
C(19)–S(1)–B(9)	108.59(14)	101.60(12)
C(8)–C(7)–B(11)	112.27(16)	112.13(17)
C(8)–C(7)–Rh(1)	68.50(11)	68.21(11)
B(11)–C(7)–Rh(1)	67.36(11)	67.28(12)
C(7)–C(8)–B(9)	109.85(16)	109.78(17)
C(7)–C(8)–Rh(1)	67.86(11)	67.63(11)
B(9)–C(8)–Rh(1)	66.95(11)	67.09(11)
C(8)–B(9)–B(10)	107.55(16)	108.23(17)
C(8)–B(9)–S(1)	121.85(15)	120.28(16)
B(10)–B(9)–S(1)	124.48(16)	124.49(16)
S(1)–B(9)–Rh(1)	109.30(11)	107.89(11)
B(9)–B(10)–B(11)	104.86(16)	104.58(17)
B(9)–B(10)–Rh(1)	64.90(10)	64.88(10)
C(7)–B(11)–B(10)	105.41(16)	105.24(17)
C(13)–C(9)–C(10)	108.2(2)	107.7(2)

4. Experimental

4.1. General

All reactions were carried out under an inert atmosphere in dry solvents, unless otherwise stated. The products were isolated in air. The ^1H-, ^{11}B-, and ^{31}P-NMR spectra were recorded on a Bruker AMX-400 spectrometer (^1H 400.13 MHz; ^{11}B 128.38 MHz; ^{31}P 161.98 MHz) relative to residual protons of the solvents (^1H) or $BF_3 \cdot Et_2O$ and 80% H_3PO_4 (external standards for ^{11}B and ^{31}P, respectively). Mass spectra were recorded on a MS-890 “Kratos” spectrometer by electron impact ionization (70 eV). Complex (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(cod) [5] and a solution Na[9-SMe_2-7,8-$C_2B_9H_{10}$] [6] were prepared according to the literature methods.

4.2. Synthesis of [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)RhX_2]$_2$ (**4a–c**)

4.2.1. Method 1

Conc. aqueous HBr (0.6 ml) was added to (η-9-SMe_2-7,8-$C_2B_9H_{10}$)Rh(cod) (40 mg, 0.1 mmol) in Me_2CO (5 ml) (an inert atmosphere is not necessary). The reaction mixture was stirred for 12 h and the solvent was removed in vacuo. The residue was washed several times with small portions of 2-propanol and ether and dried in vacuo. Yield of **4b**: 36 mg (79%). Compounds **4a** (76%) and **4c** (80%) were obtained similarly using conc. aqueous HCl and HI, respectively. In the case of **4c**, the reaction time was 48 h.

4.2.2. Method 2. One-pot synthesis of **4a**

Complex [(cod)RhCl]$_2$ (99 mg, 0.2 mmol) was dissolved in THF (6 ml) and a solution of Na[9-SMe_2-7,8-$C_2B_9H_{10}$] in THF (2 ml of 0.21 M solution, 0,42 mmol) was added. The reaction mixture was stirred for 6 h and conc. aqueous HCl (2 ml, excess) was added. The solution was stirred overnight resulting in color change from yellow–brown to bright red. Water (30 ml) was added to precipitate the product, which was filtered off, washed with water, 2-propanol, and ether, and dried in vacuo. Yield 132 mg (84%).

4.3. Synthesis of (η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)Rh(CO)I$_2$ (**5**)

Carbon monoxide was bubbled through a suspension of [(η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)RhI$_2$]$_2$ (55 mg, 0.05 mmol) in THF (5 ml) for 2 h leading to dissolution of the starting material and color change from purple to brown. After filtration, petroleum ether was added to precipitate the product, which was washed with petroleum ether and dried in vacuo. Yield 51 mg (89%). The ^{1}H- and ^{11}B-NMR spectroscopy confirmed the identity and purity of **5** [10].

4.4. Synthesis of (η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)Rh(PPh$_3$)Cl$_2$ (**6a**)

A suspension of [(η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)RhCl$_2$]$_2$ (37 mg, 0.05 mmol) and PPh$_3$ (27 mg, 0.1 mmol) in CH$_2$Cl$_2$ (10 ml) was stirred overnight. The red solution was filtered and petroleum ether was added to precipitate the crude product as a microcrystalline solid, which was filtered off, washed with ether and dried in vacuo. An analytically pure sample was obtained by reprecipitation of the crude product by petroleum ether from CH$_2$Cl$_2$. Yield 57 mg (90%). Anal. Calc. for C$_{22}$H$_{31}$B$_9$Cl$_2$PRhS: C, 41.97; H, 4.96; B, 15.45. Found: C, 42.10; H, 5.18; B, 15.30%. ^{11}B{^{1}H}-NMR δ/ppm ((CD$_3$)$_2$CO): $\delta =$ −20.39 (bs, 2B), −14.79 (bs, 1B), −8.85 (bs, 1B), −4.82 (bs, 1B), −0.79 (bs, 2B), 4.18 (bs, 1B), 6.26 (bs, 1B). ^{31}P-NMR δ/ppm ((CD$_3$)$_2$CO): $\delta = 35.41$, 34.66 (d, 1P, $J = 121.1$ Hz, Rh).

4.5. Synthesis of [(η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)Rh(dppe)Cl]BF$_4$ (**7**BF$_4$)

MeCN (5 ml) was added to a mixture of [(η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)RhCl$_2$]$_2$ (37 mg, 0,05 mmol), TlBF$_4$ (29 mg, 0.1 mmol) and PPh$_2$CH$_2$CH$_2$PPh$_2$ (40 mg, 0.1 mmol). An immediate precipitation of TlCl occurs. The reaction mixture was stirred overnight. After filtration solvent was removed in vacuo and the residue was recrystallized from hot methanol–benzene mixture to give 45 mg (55%) of orange crystals. Anal. Calc. for C$_{30}$H$_{40}$B$_{10}$ClF$_4$P$_2$RhS: C, 44.10; H, 4.93; B, 13.23. Found: C, 43.88; H, 5.29; B, 13.10%. ^{11}B{^{1}H}-NMR δ/ppm ((CD$_3$)$_2$CO): $\delta = -24.68$ (bs, 1B), −12.40 (bs, 1B), −7.70 (bs, 3B), −5.58 (bs, 2B), −0.15 (bs, 1B, BF$_4^-$), 3.86 (bs, 1B), 8.24 (bs, 1B). ^{31}P-NMR δ/ppm ((CD$_3$)$_2$CO): $\delta = 65.24$, 65.82 (d, 1P, $J = 95.1$ Hz, Rh). 76.65, 76.78, 77.54, 77.67 (d of d, 1P, $J = 144.6$ Hz, Rh; $J = 21.87$ Hz, P).

4.6. Synthesis of (η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)Rh(η-7,8-C$_2$B$_9$H$_{11}$) (**9**)

MeCN (5 ml) was added to a mixture of [(η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)RhCl$_2$]$_2$ (74 mg, 0,1 mmol) and Tl[Tl(η-7,8-C$_2$B$_9$H$_{11}$)] (135 mg, 0.25 mmol), and the reaction mixture was stirred for 48 h. After filtration, solvent was removed in vacuo and the residue was dissolved in acetone and filtered through a short layer (5 cm) of Al$_2$O$_3$. The resulting solution was reduced in volume to ca. 2 ml and ether was added to precipitate white solid, which was filtered off, washed with ether and dried in vacuo. Yield 67 mg (78%). MS (several sets of peaks corresponding to the isotopic distribution were observed; only the highest peaks are given): $m/z = 429$ [M$^+$], 297 ([M−C$_2$B$_9$H$_{11}$]$^+$), 234 ([M−SMe$_2$−C$_2$B$_9$H$_{10}$]$^+$). Anal. Calc. for C$_6$H$_{27}$B$_{18}$RhS: C, 16.80; H, 6.35; B, 45.38. Found: C, 16.67; H, 6.63; B, 45.60%. ^{11}B{^{1}H}-NMR δ/ppm ((CD$_3$)$_2$CO): $\delta = -22.03$ (bs, 1B), −21.04 (bs, 1B), −18.16 (bs, 1B), −17.26 (bs, 1B), −15.44 (bs, 1B), −14.74 (bs, 1B), −9.29 (bs, 1B), −5.51 (bs, 2B), −4.60 (bs, 3B), −2.96 (bs, 1B), −1.47 (bs, 1B), 0.74 (bs, 1B), 4.33 (bs, 1B), 5.51 (bs, 1B), 8.49 (bs, 1B).

4.7. Synthesis of [CpRh(η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)]CF$_3$SO$_3$ (**11a**CF$_3$SO$_3$)

Acetone (10 ml) was added to a mixture of [(η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)RhCl$_2$]$_2$ (73 mg, 0.1 mmol) and CF$_3$SO$_3$Ag (103 mg, 0.4 mmol). An immediate precipitation of AgCl occurs. The suspension was stirred for 1 h and cyclopentadiene (0.3 ml, excess) was added. The reaction mixture was stirred overnight. After filtration solvent was removed in vacuo and the residue was reprecipitated twice by ether from CH$_2$Cl$_2$ to give 53 mg (52%) of very pale yellow microcrystalline solid. Anal. Calc. for C$_{10}$H$_{21}$B$_9$F$_3$O$_3$RhS$_2$: C, 23.52; H, 4.15; B, 19.06. Found: C, 23.78; H, 4.22; B, 19.01%. ^{11}B{^{1}H}-NMR δ/ppm ((CD$_3$)$_2$CO): $\delta = -22.26$ (bs, 1B), −18.27 (bs, 1B), −16.82 (bs, 1B), −9.79 (bs, 1B), −5.76 (bs, 1B), −3.48 (bs, 1B), 1.23 (bs, 1B), 2.87 (bs, 1B), 4.85 (bs, 1B).

4.8. Synthesis of [Cp*Rh(η-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)]X (**11b**X)

4.8.1. Method 1, X = PF$_6$

[Cp*RhCl$_2$]$_2$ (56 mg, 0.09 mmol) was dissolved in THF (5 ml) and a solution of Na[9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$] in THF (1.2 ml of 0.17 M solution, 0.2 mmol) was added. The reaction mixture was stirred overnight. After the solvent was removed in vacuo, the residue was dissolved in H$_2$O (3 ml) and filtered. Excess of a solution of NH$_4$PF$_6$ in water was added to precipitate white solid, which was filtered off, washed with water, and dried in vacuo. Reprecipitation by ether from CH_2Cl_2 gave 101 mg (97%) of **11b**PF_6. Anal. Calc. for $C_{14}H_{31}B_9F_6PRhS$: C, 29.16; H, 5.42; B, 16.87. Found: C, 29.26; H, 5.40; B, 16.92%. $^{11}B\{^1H\}$-NMR δ/ppm (CF_3COOD): $\delta = -23.88$ (bs, 1B), -20.45 (bs, 1B), -18.52 (bs, 1B), -11.74 (bs, 1B), -7.67 (bs, 1B), -4.51 (bs, 1B), -2.15 (bs, 2B), 4.45 (bs, 1B).

4.8.2. *Method 2, X = CF_3SO_3*

Acetone (10 ml) was added to a mixture of [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)$RhCl_2$]$_2$ (73 mg, 0.1 mmol) and CF_3SO_3Ag (103 mg, 0.4 mmol). The suspension was stirred for 1 h and pentamethylcyclopentadiene (0.2 ml, excess) was added. The reaction mixture was stirred overnight. After filtration solvent was removed in vacuo and the residue was reprecipitated twice by ether from CH_2Cl_2 to give 64 mg (55%) of **11b**CF_3SO_3, which has the same ^1H- and ^{11}B-NMR spectra as **11b**PF_6.

4.9. *Reaction of [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)$RhCl_2$]$_2$ with CpNa*

A solution of CpNa in THF (0.1 ml of 2.2 M solution, 0.22 mmol) was added to a stirred suspension of [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)$RhCl_2$]$_2$ (74 mg, 0.1 mmol) in THF (5 ml). The solution turned rapidly from red to brown–yellow. The reaction mixture was stirred overnight and filtered. All attempts to isolate and identify the products failed to give any reproducible result. If conc. aqueous HBr (1 ml, excess) was added to the resulting solution, the reaction mixture turned from brown–yellow to red. Water was added to precipitate red solid, which was filtered off, washed with water, 2-propanol and ether; the solid was identified as [(η-9-SMe_2-7,8-$C_2B_9H_{10}$)$RhBr_2$]$_2$ (32 mg, 36%).

4.10. *X-ray crystallography*

Crystals of **7**BF_4 and **11**PF_6 were obtained by slow diffusion of ether and CH_2Cl_2 solutions of complexes. Crystallographic data for **7**BF_4 and **11b**PF_6 and parameters of the refinement are given in Table 4. The experimental data were collected at 110 K on Bruker SMART 1000 CCD area detector using graphite monochromated Mo–K_α ($\lambda = 0.71072$ Å, ω-scans with 0.3° step in ω and 10 s per frame exposure). The absorption correction was applied semi-empirically from equivalents. Structures were solved by direct method and refined by full-matrix least-squares against F^2 in the anisotropic (H-atoms isotropic) approximation using SHELXTL 5.1 package [25]. The analysis of the Fourier density synthesis has revealed that BF_4 in **7**BF_4 is disordered by two positions. All hydrogen atoms were located from the Fourier synthesis and were included in the refinement in isotropic approximation.

Table 4
Summary of crystallographic data for **7**BF_4 and **11b**PF_6

	7BF_4	**11b**PF_6
Empirical formula	$C_{31}H_{42}B_{10}Cl_3F_4P_2RhS$	$C_{14}H_{31}B_9F_6PRhS$
Formula weight	902.01	576.62
Crystal system, space group	Orthorhombic, *Pbca*	Monoclinic, $P2_1/c$
Crystal form, color	Plate, orange	Prism, colorless
Crystal size (mm)	0.43 × 0.36 × 0.21	0.18 × 0.10 × 0.08
a (Å)	14.716(2)	13.5151(8)
b (Å)	20.558(2)	16.1000(9)
c (Å)	25.900(3)	22.4871(13)
β (°)		96.0580(10)
V (Å^3)	7835.7(18)	4865.7(5)
Z	8	8
D_{calc} (Mg m^{-3})	1.529	1.574
Radiation type	Mo–K_α	Mo–K_α
μ (cm^{-1})	8.20	9.01
$F(000)$	3648	2320
T_{min}/T_{max}	0.598/0.855	0.717/1.000
θ_{max} (°)	30.01	30.04
Number of measured, independent and observed reflections	56 920, 11 313, 7544	50 491, 14 080, 12 287
R_{int}	0.0570	0.0201
Number of parameters used in refinement	669	825
wR_2 for all data	0.1021	0.1130
R for observed data (against F_{hkl})	0.0486	0.0385
S	1.082	1.014
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.656, -0.680	2.613, -0.925

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 169559 for **7**BF_4, and no. 169560 for **11b**PF_6. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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