Fluorosubstituted rhodacarboranes 3,3-$(R_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11-n}F_n$ (n = 1, 2, 4): synthesis, molecular structure, and catalytic properties in hydrosilylation of styrene and phenylacetylene

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Hydridorhodacarboranes 3,3-$(Ph_2RP)_2$-3-H-3,1,2-$RhC_2B_9H_{11-n}F_n$ (R = Ph, Me; n = 1, 2, 4) containing F atoms at the B atoms of the π-carborane ligand were synthesized from $(Ph_3P)_3RhCl$ or $(Ph_2MeP)_3RhCl$ and *nido*-7,8-$C_2B_9H_{12-n}F_n^-$ (n = 1, 2, 4) salts. Hydridorhodacarboranes 3,3-$(Ph_2MeP)_2$-3-H-3,1,2-$RhC_2B_9H_{11-n}F_n$ readily exchange the H atom at the Rh atom for the Cl atom under the action of CH_2Cl_2 to give 3,3-$(Ph_2MeP)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11-n}F_n$. The structures of the 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_7F_4$ and 3,3-$(Ph_2MeP)_2$-3-Cl-3,1,2-$RhC_2B_9H_9F_2$ complexes were determined by X-ray diffraction analysis. Catalytic properties of the rhodacarboranes obtained in hydrosilylation of styrene and phenylacetylene by $PhMe_2SiH$ were studied.

Key words: *B*-fluoro-*nido*-7,8-dicarbaundecaborate anions, *B*-fluororhodacarboranes, crystal structure, catalysis, hydrosilylation.

Hydridocarboranes 1-R-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{10}$ (R = H, Alk, Ar)[1] are of interest as starting compounds for the synthesis of polymetallocarborane clusters[2] and as catalysts of reactions of organic compounds.[1]

The effect of substituents linked to the boron atoms of the π-carborane ligand of hydridorhodacarboranes and on their catalytic properties is poorly known. It is shown in Ref. 3, using 6-dimethylamino- and 6-benzoylamino-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{10}$ as examples, that the substituents at the B atoms change the catalytic properties of hydridorhodacarborane 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$.

In the present work, we synthesized 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11-n}F_n$ (**4**—**6**, n = 1, 2, 4) and 3,3-$(Ph_2MeP)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11-n}F_n$ (**7**—**9**, n = 1, 2, 4) from the *nido*-7,8-$C_2B_9H_{12-n}F_n^-$ (**1**—**3**, n = 1, 2, 4) anions obtained previously.[4]

B-Fluororhodacarboranes **4**—**6** were obtained from salts **1**—**3** and $(Ph_3P)_3RhCl$ by a known scheme:[5]

Scheme 1

$$Me_3N^+H\text{-}nido\text{-}7,8\text{-}C_2B_9H_{12-n}F_n^- + (Ph_3P)_3RhCl \xrightarrow{MeOH}$$

1—**3**

$$\longrightarrow 3,3\text{-}(Ph_3P)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11-n}F_n$$

4—**6**

n = 1 (**1**, **4**), 2 (**2**, **5**), 4 (**3**, **6**)

B-Fluororhodacarboranes **7**—**9** were obtained from salts **1**—**3** and $(Ph_2MeP)_3RhCl$ by the following scheme:

Scheme 2

$$\mathbf{1}\text{—}\mathbf{3} + (Ph_2MeP)_3RhCl \xrightarrow{MeOH}$$

$$\longrightarrow 3,3\text{-}(Ph_2MeP)_2\text{-}3\text{-}H\text{-}3,1,2\text{-}RhC_2B_9H_{11-n}F_n \xrightarrow[n\text{-}C_5H_{12}]{CH_2Cl_2}$$

A

$$\longrightarrow 3,3\text{-}(Ph_2MeP)_2\text{-}3\text{-}Cl\text{-}3,1,2\text{-}RhC_2B_9H_{11-n}F_n$$

7 (n = 1); **8** (n = 2); **9** (n = 4)

Compounds **4**—**9** are first representatives of rhodacarboranes containing fluorine atoms at the boron atoms of the π-carborane ligand. Rhodacarboranes **4**—**6** are yellow substances stable in air. Compound **6** crystallizes from CH_2Cl_2—n-C_5H_{12} mixture with one CH_2Cl_2 molecule. The ability of hydridorhodacarboranes to crystallize with chlorohydrocarbons CH_2Cl_2 [6] and $ClCH_2CH_2Cl$ [7] has been reported previously. Rhodacarboranes of type **A** are also stable in air, but they were not isolated in the pure state because during crystallization from the CH_2Cl_2—n-C_5H_{12} mixture, the hydrogen atom at the rhodium atom exchanges readily for the chlorine atom to form red chlororhodacarboranes **7**—**9**. The possibility of this exchange has been shown previously[8] using 3,3-$(PhMe_2P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ as

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 570—578, March, 1997.

1066-5285/97/4603-0550 $18.00

Table 1. ^1H, ^{11}B, ^{19}F, and ^{31}P NMR spectra of 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11-n}F_n$ (n = 1, 2, 4) (**4**—**6**)

Compound	^1H δ (J/Hz)	^{11}B δ	^{19}F δ (J_{B-F}/Hz)	^{31}P δ (J/Hz)
4	8.10—6.80 (m, 30 H, Ph), 2.00 (br.s, 1 H, CH-carb.), 1.99 (br.s, 1 H, CH-carb.), −8.40 (dt, 1 H, Rh—H, J_{Rh-H} = 16, J_{P-H} = 28)	13.2 (1 B), −3.6 (2 B), −11.5 (4 B), −23.7 (2 B)	115.5 (q, 1 F, 55.0)	42.3 (RhP, J_{Rh-P} = 120), 38.6 (RhP, J_{Rh-P} = 121, J_{P-P} = 25)
5	7.60—7.10 (m., 30 H, Ph), 1.98 (br.s, 2 H, CH-carb.), −8.20 (dt, 1 H, RhH, J_{Rh-H} = 18, J_{P-H} = 28)	14.7 (1 B), 5.1 (2 B), −7.1 (1 B), −13.2 (1 B), −20.0 (2 B), −28.0 (2 B)	118.0 (q, 2 F, 55.0)	41.2 (RhP, J_{Rh-P} = 128)
6	7.30—7.10 (m, 30 H, Ph), 2.80 (br.s, 2 H, CH-carb.), −8.10 (ddt, 1 H, Rh—H, J_{Rh-H} = 10, J_{P-H} = 12.9 J_{H-F} = 9.0)	13.7 (1 B), 7.7 (2 B), 5.6 (1 B), −4.3 (1 B), −13.9 (1 B), −19.7 (1B); −22.9 (2 B)	101.5 (q, 1 F, 90.0), 119.0 (q, 1 F, 50.0), 128.5 (m, 2 F, 50.0)	40.3 (RhP, J_{Rh-P} = 144)

an example. The treatment of this compound with CH_2Cl_2 results in the formation of 3,3-$(PhMe_2P)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$. The structure of rhodacarboranes **4**—**9** is confirmed by the elemental analysis data and ^1H, ^{11}B, ^{19}F, and ^{31}P NMR spectra (Tables 1 and 2). The structure of compounds **6** and **8** was established by X-ray diffraction analysis of single crystals.

In rhodacarborane **4**, the F(9) atom is arranged asymmetrically relative to two carbon atoms of the π-carborane ligand. Its ^1H NMR spectrum contains two signals of CH with δ = 2.00 and 1.99. The number of the fluorine atoms in molecules **4**—**6** only insignificantly affects the δ value of the H atom linked with the Rh atom. In the case of rhodacarboranes **4** and **5**, the number of the F atoms also affects the coupling constant J(Rh—H). In the ^1H NMR spectrum of rhodacarborane **6**, the chemical shift of the hydrogen atom at the Rh atom is equal to −8.1 ppm. It is the doublet of the doublet of triplets with the J(Rh—H) constant that is lower than those of compounds **4** and **5**, which is caused by the interaction of the H atom at the Rh atom with the F(8) atom (J_{H-F} = 9 Hz). Due to this interaction, the coupling constant of the H(Rh) atom with the phosphorus atoms in rhodacarborane **6** is lower than in compounds **4** and **5**.

Table 2. ^{19}F and ^{31}P NMR spectra of 3,3-$(Ph_2MeP)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11-n}F_n$ (**7**—**9**) (n = 1, 2, 4)

Compound	^{19}F, δ (J_{B-F}/Hz)	^{31}P, δ (J/Hz)
7	116.5 (q, 1 F, J = 55.0)	16.5 (Rh—P, J_{Rh-P} = 125, J_{P-P} = 20), 17.0 (Rh—P, J_{Rh-P} = 120, J_{P-P} = 20)
8	117.5 (q, 2 F, J = 50.0)	17.6 (Rh—P, J_{Rh-P} = 129)
9	91.5 (q, 1 F, J = 92.0), 96.1 (q, 1 F, J = 59.0), 119.6 (m, 2 F, J = 50.0)	16.3 (Rh—P, J_{Rh-P} = 12)

In the ^{31}P NMR spectra of rhodacarboranes **4** and **7**, whose molecules are chiral, the P atoms are nonequivalent. This is evidence for restricted rotation of the $XRh(PR_3)_2$ system relative to the C_2B_3 plane of the π-carborane ligand.

The order of changing the δ values in the ^{19}F NMR spectra of rhodacarboranes **4**—**9** coincides with the order of changing the δ values in the ^{19}F NMR spectra of anions **1**—**3**.[4]

The crystallosolvate of compound **6** was obtained by crystallization from the CH_2Cl_2—C_6H_{14} system at 23 °C. The structure of crystallosolvate **6** · CH_2Cl_2 · 1/2 C_6H_{14} was confirmed by the X-ray diffraction analysis of the single crystal. The general view of molecule **6** is presented in Fig. 1, and the bond lengths and main bond angles are presented in Table 3. The Rh^{III} atom has a pseudo-octahedral ligand surrounding: the carborane ligand occupies three coordination sites; two phosphine and one hydride ligands occupy the other three sites to form a 18e-complex. The orientation of the $(Ph_3P)_2RhH$ fragment relative to the C_2B_3 face of the carborane ligand in rhodacarborane **6** is very close to that observed in the nonsubstituted analog 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ (**10**):[9] the hydride ligand is arranged in the *trans*-position relative to one of the carbon atoms (the torsion C(2)—X—Rh(3)—3H(3M) angle in com-

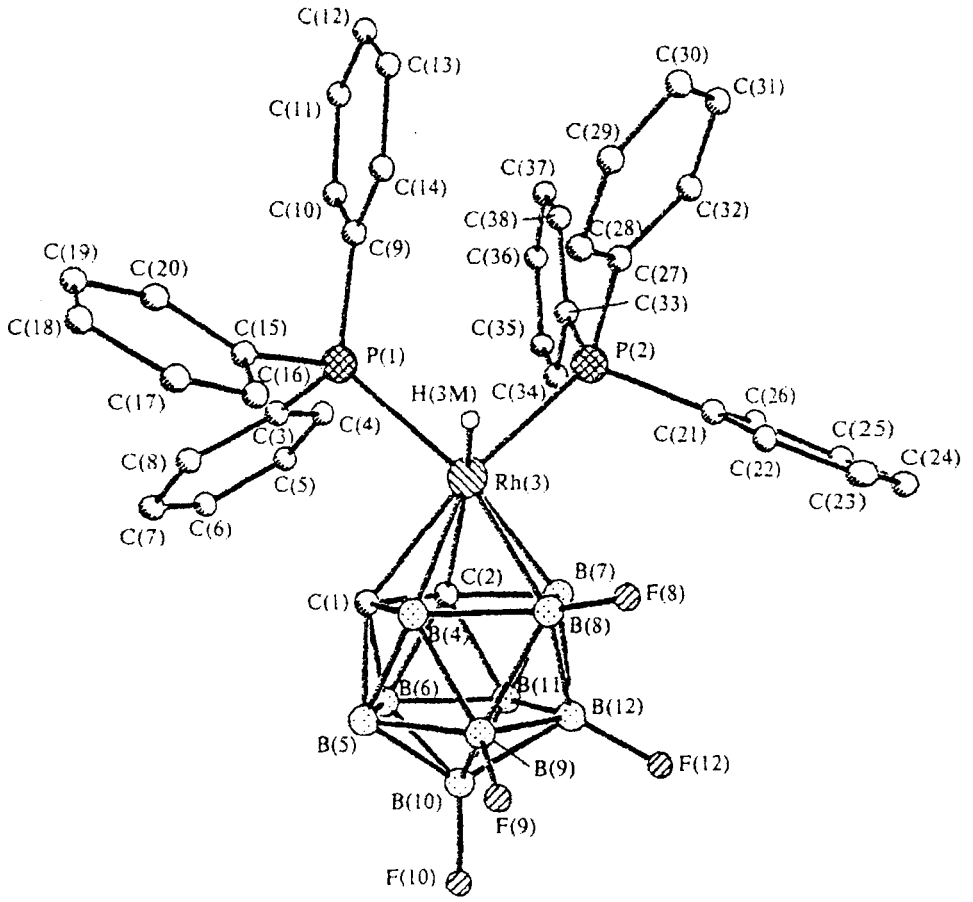


Fig. 1. Structure of 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_7F_4$ (**6**).

plex **6** is equal to 176°, where X is the center of the C_2B_3 face (Fig. 2)). It is noteworthy that the *closo*-2,2-μ-(1',2'-$CH_2C_6H_4CH_2$)-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_9$ complex (**11**)[10] has a quite different orientation of the metallophosphinehydride moiety: the hydride atom is projected on the middle of the C—C bond of the C_2B_3 face. This is most likely related to the presence of the substituents at the carborane carbon atoms and to steric hindrances for the phenyl substituents of the phosphine ligands that appear due to this reason. An interesting specific feature of complex **6** is nonequivalence of the Rh—P bonds, which is also observed for complex **10**. In both cases, the phosphorus atom that shields the carbon atom forms a longer bond with the metal atom (in compound **6**, Rh(3)—P(1) is equal to 2.377(1) Å and Rh(3)—P(2) is equal to 2.306(1) Å; in compound **10**, 2.357 and 2.301 Å, respectively). At the same time, the Rh—P bond lengths are nearly the same (2.335 and 2.324 Å) in complex **11** in which phosphine ligands are oriented symmetrically relatively to the carborane carbon atoms.

In the tetrafluorosubstituted *o*-carborane (**12**) studied previously,[11] we observed lengthening of the B—B bond involving the boron atoms linked with the electron-withdrawing substituents, fluorine atoms. It is likely that the same effect takes place in complex **6** as well. However, in this case, it is less pronounced due to the metal atom effect. Probably, both effects act in the same direction, resulting, in particular, in the fact that in the carborane polyhedron of compound **6**, the bonds involving the B(8) atom are the longest (B(8)—B(4) 1.820(5), B(8)—B(7) 1.830(6), B(8)—B(9) 1.834(5) and B(8)—B(12) 1.816(6) Å). The B—F bond lengths in molecule **6** (1.358(5)—1.381(4) Å) agree well with the values observed for compound **12** (1.358 and 1.367 Å).

The structure of complex **8** was also established by the X-ray diffraction analysis of the single crystal. Crystals of **8** were obtained by crystallization at the interface of the CH_2Cl_2—*n*-C_5H_{12} system at room temperature. The general view of the molecule is presented in Fig. 3, and the main bond lengths and bond angles are presented in Table 4. The orientation of the metallophosphine group in complex **8**, unlike rhodacarborane **6**, is symmetric relative to the carbon atoms of the open face of the dicarbollyl ligand. In complex **8**, as in 1,2-(Me_2)-3,3-$(PMe_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_9$ (**13**)[12] and 3,3-$(PPh_3)_2$-3-Cl-3,1,2-$RhC_2B_9H_{11}$ (**14**)[13] studied previously, the Cl atom is projected approximately on

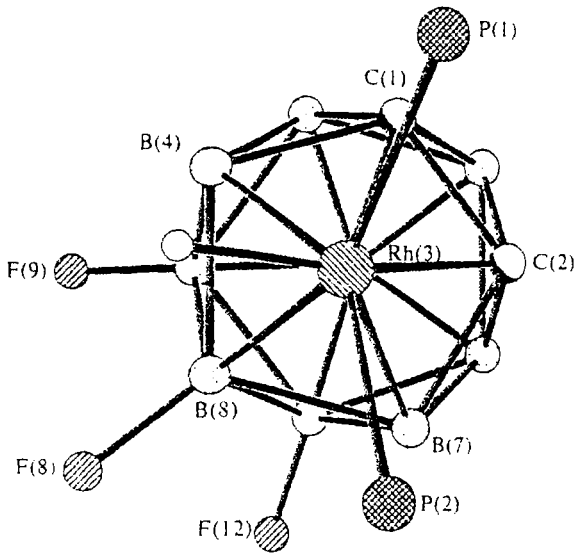


Fig. 2. Projection of molecule **6** on the plane of the "open face" of the dicarbollyl ligand.

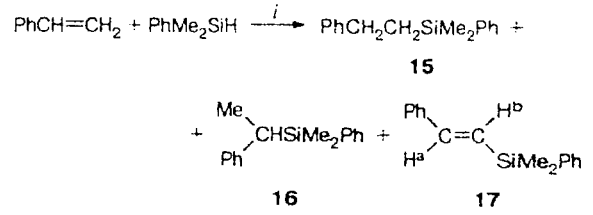
the middle of the C(1)—C(2) bond: the torsion B(8)—X—Rh(3)—Cl(1) angle is equal to 171.0° (in complexes **13** and **14**, the corresponding angles are equal to 179.1 and 167.6°). It is remarkable that in compound **8**, as in compounds **11**, **13**, and **14**, no substantial differences in the Rh—P bond lengths are observed.

It is of interest that in complex **8**, as in complex **6**, some lengthening of the B—B bonds involving the B(8) atoms is observed: B(8)—B(4) 1.805(5), B(8)—B(7) 1.826(5), B(8)—B(9) 1.802(5), B(8)—B(12) 1.807(6) Å. The B—F distances in compound **8** (B(9)—F(9) 1.365(6) and B(12)—F(12) 1.335(6) Å) do not differ within experimental errors from those determined for compound **6**.

In order to elucidate the catalytic possibilities of rhodacarboranes, we compared the selectivities of hydrosilylation of styrene and phenylacetylene by dimethylphenylsilane in the presence of *B*-fluororhodacarboranes **4**—**9**, rhodacarborane **10**, and $(Ph_3P)_3RhCl$. It is noteworthy that in compounds **4**—**10** the rhodium atom is formally trivalent, while it is monovalent in $(Ph_3P)_3RhCl$.

B-Fluororhodacarboranes **5**, **6**, and **8** were used as the catalysts in hydrosilylation of styrene, and $(Ph_3P)_3RhCl$ and rhodacarborane **10** were used for comparison. The reaction in a solution of benzene and THF was established to occur *via* the following scheme:

Scheme 3



i. Rh-catalyst, C_6H_6 or THF.

The data on the composition of the products of hydrosilylation of styrene are presented in Table 5. The structures of the products of styrene hydrosilylation were confirmed by comparison with the authentic compounds. The structures of compounds **15** and **17** were additionally confirmed by ^1H NMR spectroscopy.

Table 3. Main bond lengths (*d*) and bond angles (ω) of molecule **6**

Bond	*d*/Å	Angle	ω/deg	Bond	*d*/Å	Angle	ω/deg
Rh(3)—P(1)	2.377(1)	P(1)—Rh(3)—P(2)	95.5(1)	C(2)—B(6)	1.718(5)	B(7)—Rh(3)—B(8)	48.2(2)
Rh(3)—P(2)	2.306(1)	P(1)—Rh(3)—C(1)	89.3(1)	C(2)—B(7)	1.688(5)	Rh(3)—P(1)—C(3)	106.4(1)
Rh(3)—C(1)	2.231(3)	P(1)—Rh(3)—H(3M)	77(2)	C(2)—B(11)	1.698(5)	Rh(3)—P(1)—C(9)	124.9(1)
Rh(3)—C(2)	2.290(4)	P(2)—Rh(3)—H(3M)	83(2)	B(4)—B(5)	1.793(6)	C(3)—P(1)—C(9)	105.8(2)
Rh(3)—B(4)	2.247(4)	P(2)—Rh(3)—C(1)	156.8(1)	B(4)—B(8)	1.820(5)	Rh(3)—P(1)—C(15)	115.3(1)
Rh(3)—B(7)	2.245(4)	P(1)—Rh(3)—C(2)	105.3(1)	B(4)—B(9)	1.778(6)	C(3)—P(1)—C(15)	104.6(2)
Rh(3)—B(8)	2.239(3)	P(2)—Rh(3)—C(2)	115.1(1)	B(5)—B(6)	1.789(8)	C(9)—P(1)—C(15)	97.9(2)
Rh(3)—H(3M)	1.51(5)	C(1)—Rh(3)—C(2)	42.0(1)	B(5)—B(9)	1.764(6)	Rh(3)—P(2)—C(21)	116.7(1)
P(1)—C(3)	1.829(4)	P(1)—Rh(3)—B(4)	109.5(1)	B(5)—B(10)	1.781(6)	Rh(3)—P(2)—C(27)	118.8(1)
P(1)—C(9)	1.835(3)	P(2)—Rh(3)—B(4)	149.6(1)	B(6)—B(10)	1.765(6)	C(21)—P(2)—C(27)	97.5(2)
P(1)—C(15)	1.835(4)	C(1)—Rh(3)—B(4)	44.5(2)	B(6)—B(11)	1.753(6)	Rh(3)—P(2)—C(33)	111.6(1)
P(2)—C(21)	1.843(3)	C(2)—Rh(3)—B(4)	75.6(2)	B(7)—B(8)	1.830(6)	C(21)—P(2)—C(33)	103.4(2)
P(2)—C(27)	1.829(4)	P(1)—Rh(3)—B(7)	145.8(1)	B(7)—B(11)	1.818(6)	C(27)—P(2)—C(33)	106.9(2)
P(2)—C(33)	1.840(4)	P(2)—Rh(3)—B(7)	89.1(1)	B(7)—B(12)	1.785(5)	C(2)—C(1)—B(4)	113.9(3)
F(8)—B(8)	1.376(5)	C(1)—Rh(3)—B(7)	74.6(1)	B(8)—B(9)	1.834(5)	C(1)—C(2)—B(7)	110.1(3)
F(9)—B(9)	1.358(5)	C(2)—Rh(3)—B(7)	43.7(1)	B(8)—B(12)	1.816(6)	C(1)—B(4)—B(8)	104.5(3)
F(10)—B(10)	1.367(5)	B(4)—Rh(3)—B(7)	80.1(1)	B(9)—B(10)	1.805(8)	C(2)—B(7)—B(8)	106.6(3)
F(12)—B(12)	1.381(4)	P(1)—Rh(3)—B(8)	156.6(1)	B(9)—B(12)	1.800(6)	B(4)—B(8)—B(7)	104.8(3)
C(1)—C(2)	1.623(6)	P(2)—Rh(3)—B(8)	104.6(1)	B(10)—B(11)	1.763(6)		
C(1)—B(4)	1.695(7)	C(1)—Rh(3)—B(8)	76.9(1)	B(10)—B(12)	1.799(5)		
C(1)—B(5)	1.702(5)	C(2)—Rh(3)—B(8)	77.1(1)	B(11)—B(12)	1.772(7)		
C(1)—B(6)	1.752(7)	B(4)—Rh(3)—B(8)	47.9(1)				

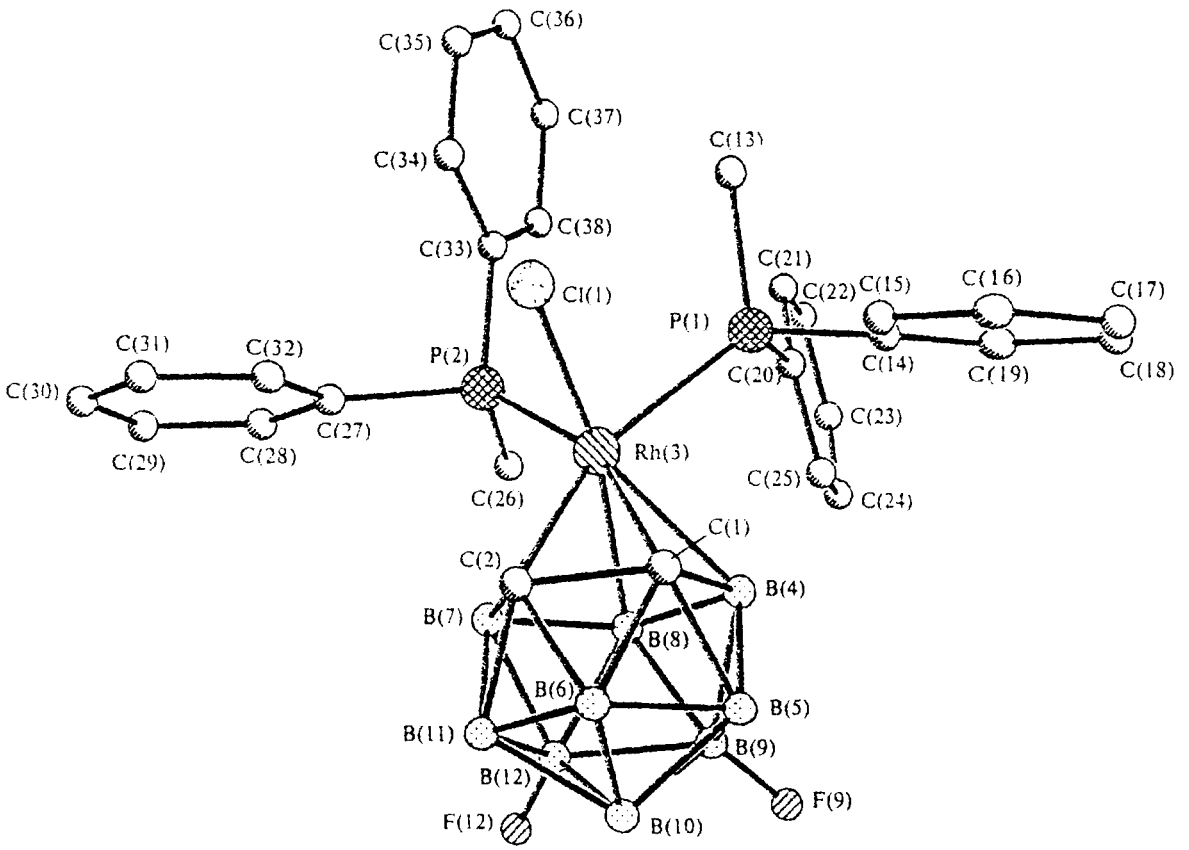


Fig. 3. Structure of 3,3-$(Ph_2MeP)_2$-3-Cl-3,1,2-$RhC_2B_9H_9F_2$ (**8**).

Table 4. Main bond lengths (d) and bond angles (ω) of molecule **8**

Bond	d/Å	Angle	ω/deg	Bond	d/Å	Angle	ω/deg
Rh(3)—C(1)	2.205(3)	C(1)—Rh(3)—B(4)	45.18(12)	B(4)—B(8)	1.805(5)	C(2)—Rh(3)—Cl(1)	87.13(8)
Rh(3)—B(4)	2.218(3)	C(1)—Rh(3)—C(2)	43.15(12)	B(5)—B(6)	1.752(6)	B(8)—Rh(3)—Cl(1)	164.43(10)
Rh(3)—C(2)	2.218(3)	B(4)—Rh(3)—C(2)	76.38(12)	B(5)—B(10)	1.771(6)	B(7)—Rh(3)—Cl(1)	118.38(10)
Rh(3)—B(8)	2.242(3)	C(1)—Rh(3)—B(8)	77.97(12)	B(5)—B(9)	1.778(6)	P(2)—Rh(3)—Cl(1)	92.41(3)
Rh(3)—B(7)	2.258(4)	B(4)—Rh(3)—B(8)	47.73(14)	B(6)—B(11)	1.746(6)	P(1)—Rh(3)—Cl(1)	87.75(3)
Rh(3)—P(2)	2.3349(10)	C(2)—Rh(3)—B(8)	77.41(13)	B(6)—B(10)	1.766(6)	C(20)—P(1)—C(13)	105.3(2)
Rh(3)—P(1)	2.3406(10)	C(1)—Rh(3)—B(7)	76.30(12)	B(7)—B(12)	1.757(5)	C(20)—P(1)—C(14)	106.9(2)
Rh(3)—Cl(1)	2.4178(9)	B(4)—Rh(3)—B(7)	80.32(13)	B(7)—B(11)	1.793(5)	C(13)—P(1)—C(14)	97.4(2)
P(1)—C(20)	1.817(3)	C(2)—Rh(3)—B(7)	44.29(13)	B(7)—B(8)	1.826(5)	C(20)—P(1)—Rh(3)	113.66(11)
P(1)—C(13)	1.825(3)	B(8)—Rh(3)—B(7)	47.88(14)	B(8)—B(9)	1.802(5)	C(13)—P(1)—Rh(3)	118.39(12)
P(1)—C(14)	1.828(3)	C(1)—Rh(3)—P(2)	159.25(9)	B(8)—B(12)	1.807(6)	C(14)—P(1)—Rh(3)	113.37(11)
P(2)—C(26)	1.818(3)	B(4)—Rh(3)—P(2)	136.81(9)	B(9)—F(9)	1.365(6)	C(26)—P(2)—C(33)	103.2(2)
P(2)—C(33)	1.824(3)	C(2)—Rh(3)—P(2)	116.94(9)	B(9)—B(10)	1.785(6)	C(26)—P(2)—C(27)	104.5(2)
P(2)—C(27)	1.826(3)	B(8)—Rh(3)—P(2)	92.91(10)	B(9)—B(12)	1.789(6)	C(33)—P(2)—C(27)	100.2(2)
C(1)—C(2)	1.627(5)	B(7)—Rh(3)—P(2)	83.74(9)	B(10)—B(11)	1.770(6)	C(26)—P(2)—Rh(3)	113.18(12)
C(1)—B(4)	1.699(5)	C(1)—Rh(3)—P(1)	108.01(9)	B(10)—B(12)	1.780(6)	C(33)—P(2)—Rh(3)	118.60(10)
C(1)—B(5)	1.699(5)	B(4)—Rh(3)—P(1)	84.97(10)	B(11)—B(12)	1.778(6)	C(27)—P(2)—Rh(3)	115.23(11)
C(1)—B(6)	1.731(5)	C(2)—Rh(3)—P(1)	150.39(9)	B(12)—F(12)	1.335(6)	C(2)—C(1)—B(4)	111.1(2)
C(2)—B(11)	1.685(5)	B(8)—Rh(3)—P(1)	106.63(10)			C(1)—C(2)—B(7)	112.6(2)
C(2)—B(7)	1.688(5)	B(7)—Rh(3)—P(1)	153.65(10)			C(1)—B(4)—B(8)	106.0(2)
C(2)—B(6)	1.730(5)	P(2)—Rh(3)—P(1)	92.40(3)			C(2)—B(7)—B(8)	105.0(2)
B(4)—B(9)	1.771(5)	C(1)—Rh(3)—Cl(1)	92.10(8)			B(4)—B(8)—B(7)	105.3(2)
B(4)—B(5)	1.795(5)	B(4)—Rh(3)—Cl(1)	130.39(9)				

Table 5. Distribution of products of hydrosilylation of styrene (**15**—**17**) by dimethylphenylsilane (%)

Catalyst	15		16		17	
	A	B	A	B	A	B
$(Ph_3P)_3RhCl$	83	70	8	8	9	22
10	—	60	—	22	—	18
5	43	47	18	24	39	29
6	26	23	36	27	38	50
8	24	—	53	—	23	—

Note. Solvent C_6H_6 (A), THF (B).

The influence of different Rh^I complexes on hydrosilylation of styrene has been studied in several works.[15—17] It has been shown that the reaction results in the formation of two isomeric silanes $PhCH_2CH_2SiR_3$ and $PhCH(Me)SiR_3$. However, our data on the hydrosilylation of styrene by $PhMe_2SiH$ catalyzed by rhodacarboranes **5**, **6**, **8**, **10**, and $(Ph_3P)_3RhCl$ do not agree with the data in Refs. 15—17 but are in agreement with the data in Ref. 19 according to which the hydrosilylation of styrene in the presence of the Rh(I) complexes results in the formation of the product of dehydrosilylation $PhCH{=}CHSiR_3$ along with the silanes mentioned. The amount of $PhCH{=}CHSiR_3$ depends on the catalyst : silane ratio.

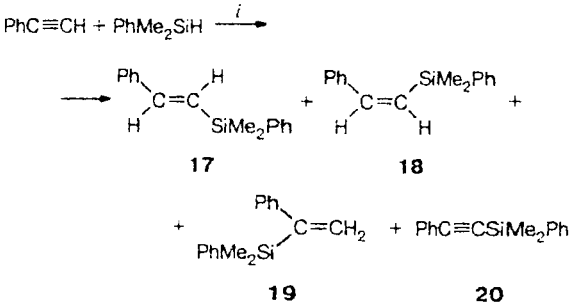
It follows from the data in Table 5 that the hydrosilylation of styrene by $PhMe_2SiH$ catalyzed by *B*-fluororhodacarboranes **5**, **6**, and **8** proceeds with almost the same selectivity as in the case of $(Ph_3P)_3RhCl$. In the series of rhodacarboranes, hydridorhodacarborane **10** exhibits a higher selectivity in the formation of **15** than *B*-fluororhodacarboranes. The effect of the solvent (benzene or THF) somewhat changes the ratio of the reaction products, which is especially pronounced in the catalysis by rhodacarborane **6**. In the case of the reaction in THF, the amount of product **16** is 1.3 times less, and the product of dehydrosilylation **17** is formed in 1.3 times greater amount. The comparison of the catalytic properties of compounds **5** and **8** (Table 5) shows that they differ somewhat in selectivity. In the case of **5**, the ratio of the **15** : **16** yields is equal to 2.4, while in the case of **8**, it is equal to 0.45. The reason for this difference is not quite clear. Probably, this is related to the effect of various phosphine ligands at the Rh atom rather than to the existence of the Cl atom at the rhodium atom in compound **8**.

Rhodacarboranes **4**—**8**, **10**, and $(Ph_3P)_3RhCl$ were used as the catalysts in the hydrosilylation of phenylacetylene by dimethylphenylsilane. The reaction in a benzene solution occurs *via* Scheme 4.

The ratios of the products of the hydrosilylation of phenylacetylene are presented in Table 6.

When phenylacetylene was hydrosilylated by $PhMe_2SiH$ in the presence of $(Ph_3P)_3RhCl$, the ratio of the products was the same as in Ref. 18. Unlike $(Ph_3P)_3RhCl$, when the hydrosilylation of phenylacetylene was catalyzed by *B*-fluororhodacarboranes, the hydrogen atom is substituted to a small extent by the silyl group.

Схема 4



i. Rh-catalyst.

Table 6. Distribution of products of hydrosilylation of phenylacetylene (**17**—**20**) by dimethylphenylsilane (%)

Catalyst	17	18	19	20
$(Ph_3P)_3RhCl$	21	75	4	—
10	68	9	19	4
4	23	53	16	8
5	32	42	18	8
6	51	14	29	6
7	61	12	20	7
8	50	15	29	6

The structure of hydrosilylation products was proved by comparison with authentic samples. The structure of product **20** was supported by its synthesis from lithium phenylacetylide and chlorodimethylphenylsilane. In the catalysis of hydrosilylation of phenylacetylene, *B*-fluororhodacarboranes are less selective than $(Ph_3P)_3RhCl$, since α-silyl isomer **19** is formed in a considerable amount.

The difference in the catalytic activity of hydridorhodacarboranes **4**—**6** and chlororhodacarboranes **7** and **8** is insignificant.

Thus, *B*-fluororhodacarboranes are low-selective catalysts of hydrosilylation of styrene and phenylacetylene. Unsubstituted hydridorhodacarborane **10** exhibits a somewhat higher selectivity than *B*-fluororhodacarboranes. It is of interest that complex **6** catalyzes to a great extent the reaction of dehydrosilylation in the hydrosilylation of styrene by diphenylmethylsilane.

Experimental

^1H, ^{11}B, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker WP-200 SY instrument. Starting salts **1**—**3** were prepared by a known procedure.[4] The course of reactions was monitored by TLC on Silufol plates. The ratio of hydrosilylation products was determined by GLC on an LKhM-8MD chro-

Table 7. Coordinates of atoms ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) of molecule **6**

Atom	*x*	*y*	*z*	*U*(eq)	Atom	*x*	*y*	*z*	*U*(eq)
Rh(3)	−2209(1)	6298(1)	7714(1)	19(1)	B(9)	−69(5)	3515(3)	8192(2)	36(2)
P(1)	−4119(1)	7539(1)	8356(1)	22(1)	B(10)	−1285(5)	2733(3)	8075(2)	39(2)
P(2)	−2041(1)	7622(1)	6680(1)	22(1)	B(11)	−2238(5)	3573(3)	7401(2)	33(1)
F(8)	1110(2)	5126(2)	7261(1)	38(1)	B(12)	−384(4)	3577(3)	7326(2)	29(1)
F(9)	1237(3)	2970(2)	8392(1)	55(1)	Cl(1)	4483(2)	2876(2)	5622(1)	132(1)
F(10)	−937(3)	1560(2)	8194(1)	58(1)	Cl(2)	4784(2)	4617(2)	6264(1)	121(1)
F(12)	719(2)	3051(2)	6847(1)	37(1)	C(39)	3638(7)	3851(5)	6156(4)	77(3)
C(1)	−2857(4)	4791(3)	8462(2)	32(1)	C(1S)	−9190(17)	9349(20)	9552(8)	201(12)
C(2)	−3159(4)	4811(3)	7691(2)	29(1)	C(2S)	−10064(28)	10138(15)	9661(8)	272(13)
C(3)	−5694(4)	6901(3)	8583(2)	31(1)	C(3S)	−9315(15)	8917(9)	9229(6)	147(6)
C(4)	−6366(4)	6868(4)	8044(2)	44(2)	H(3M)	−1411(47)	7008(37)	7933(23)	58(13)
C(5)	−7415(5)	6249(5)	8178(3)	69(3)	H(1)	−3606(39)	5052(28)	8754(19)	22(9)
C(6)	−7804(6)	5661(6)	8838(4)	79(3)	H(2)	−4120(44)	5102(32)	7622(19)	34(10)
C(7)	−7165(6)	5686(5)	9381(3)	65(2)	H(4)	−6119(43)	7269(33)	7631(22)	34(11)
C(8)	−6126(4)	6316(3)	9259(2)	41(2)	H(5)	−7757(57)	6192(44)	7789(28)	74(16)
C(9)	−4827(4)	9073(3)	8036(2)	29(1)	H(6)	−8425(57)	5307(43)	8923(27)	64(15)
C(10)	−6228(5)	9552(4)	7900(2)	45(2)	H(7)	−7328(60)	5205(46)	9781(30)	74(17)
C(11)	−6708(7)	10737(4)	7727(3)	64(2)	H(8)	−5757(43)	6362(33)	9631(22)	38(11)
C(12)	−5818(7)	11424(4)	7678(2)	67(2)	H(10)	−6887(46)	9111(36)	7930(22)	46(12)
C(13)	−4410(7)	10965(4)	7802(2)	58(2)	H(11)	−7585(61)	11064(47)	7678(28)	73(17)
C(14)	−3928(5)	9787(3)	7988(2)	38(1)	H(12)	−6265(55)	12319(47)	7566(27)	77(15)
C(15)	−3785(4)	7651(3)	9204(2)	29(1)	H(13)	−3790(53)	11428(44)	7788(26)	64(15)
C(16)	−2417(5)	7237(3)	9389(2)	40(2)	H(14)	−3075(48)	9507(36)	8079(22)	41(12)
C(17)	−2196(6)	7410(4)	10015(3)	60(2)	H(16)	−1646(44)	6845(33)	9115(21)	37(10)
C(18)	−3328(6)	8000(4)	10453(2)	58(2)	H(17)	−1487(73)	7177(59)	10151(37)	107(25)
C(19)	−4675(6)	8412(4)	10270(2)	47(2)	H(18)	−3197(51)	8080(39)	10886(26)	63(14)
C(20)	−4924(5)	8257(3)	9646(2)	36(1)	H(19)	−5296(47)	8745(37)	10495(23)	42(13)
C(21)	−815(3)	7097(3)	5906(2)	23(1)	H(20)	−5840(40)	8587(29)	9505(18)	25(9)
C(22)	675(4)	6857(3)	5888(2)	32(1)	H(22)	1026(40)	6944(31)	6255(21)	33(10)
C(23)	1659(4)	6482(3)	5314(2)	39(1)	H(23)	2688(44)	6321(31)	5317(20)	35(10)
C(24)	1156(5)	6321(3)	4759(2)	39(1)	H(24)	1838(51)	6053(38)	4370(25)	59(13)
C(25)	−312(4)	6560(3)	4773(2)	37(1)	H(25)	−741(44)	6365(34)	4397(22)	47(11)
C(26)	−1301(4)	6959(3)	5335(2)	32(1)	H(26)	−2271(41)	7157(28)	5323(17)	22(9)
C(27)	−1291(4)	8844(3)	6638(2)	29(1)	H(28)	−624(41)	8444(33)	7561(21)	32(10)
C(28)	−631(4)	8934(3)	7164(2)	34(1)	H(29)	354(46)	9900(36)	7451(23)	46(12)
C(29)	−18(5)	9855(3)	7092(3)	45(2)	H(30)	281(50)	11346(41)	6488(24)	62(13)
C(30)	−77(5)	10694(3)	6501(3)	50(2)	H(31)	−680(50)	11193(40)	5566(25)	59(13)
C(31)	−682(5)	10600(3)	5966(2)	51(2)	H(32)	−1566(46)	9625(35)	5649(23)	46(12)
C(32)	−1267(5)	9678(3)	6026(2)	41(2)	H(34)	−4031(44)	6630(37)	6370(21)	41(11)
C(33)	−3814(4)	8210(3)	6389(2)	30(1)	H(35)	−6229(49)	7298(37)	6002(23)	46(13)
C(34)	−4503(4)	7414(4)	6299(2)	38(1)	H(36)	−7488(57)	9163(43)	5803(26)	72(15)
C(35)	−5828(5)	7772(5)	6074(2)	51(2)	H(37)	−6374(53)	10473(43)	5992(25)	62(14)
C(36)	−6502(5)	8912(5)	5946(2)	60(2)	H(38)	−4085(43)	9905(34)	6376(21)	43(11)
C(37)	−5843(6)	9708(5)	6048(3)	63(2)	H(4B)	−843(38)	5115(30)	8902(19)	34(10)
C(38)	−4511(4)	9362(3)	6270(2)	42(2)	H(5B)	−1882(43)	3167(34)	9306(22)	46(11)
B(4)	−1123(5)	4816(3)	8467(2)	32(1)	H(6B)	−4084(49)	3308(37)	8544(24)	55(12)
B(5)	−1750(6)	3520(3)	8771(2)	42(2)	H(7B)	−1751(35)	5205(27)	6572(18)	21(8)
B(6)	−3092(6)	3539(4)	8283(3)	44(2)	H(11B)	−2646(44)	3310(35)	7038(22)	49(11)
B(7)	−1643(4)	4904(3)	7081(2)	25(1)	H(39A)	3152(70)	3277(60)	6615(38)	120(22)
B(8)	−219(4)	4868(3)	7553(2)	26(1)	H(39B)	2894(100)	4415(81)	5885(49)	208(37)

matograph in a helium flow on a column 1600×2 mm with the phase 5% SE-30 on Chromaton N-A at 200 °C. Prior to use, styrene and phenylacetylene were distilled and stabilized by hydroquinone. All reactions were performed in an argon flow. Hydrosilylation was mainly performed by a known procedure.[3] $PhMe_2SiH$ was obtained by the reduction of chlorodimethylphenylsilane by $LiAlH_4$ and was distilled prior to use.

***Closo*-9-fluoro-bis(triphenylphosphine)-3-hydride-3,1,2-rhodacarborane (4).** A solution of compound **1** (0.45 g, 2.1 mmol) in MeOH (20 mL) was added to a suspension of $(Ph_3P)_3RhCl$ (1.7 g, 1.83 mmol) in MeOH (30 mL). The reaction mixture was boiled for 3 h until $(Ph_3P)_3RhCl$ disappeared (monitoring by TLC in CH_2Cl_2). When the reaction was complete, the mixture was cooled and filtered. The residue on the filter was washed with MeOH (50 mL), dried *in vacuo* with P_2O_5, and crystallized from the CH_2Cl_2—*n*-C_5H_{12} (1 : 5) mixture. Compound **4** (yellow crystals) was obtained (1.2 g, 89%) with m.p. 214—215 °C. Found (%): C, 59.18; H, 5.27; P, 7.19. $C_{38}H_{41}B_9FP_2Rh$. Calculated (%): C, 59.61; H, 5.26; P, 7.79.

Table 8. Coordinates of atoms ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) of molecule **8**

Atom	x	y	z	U(eq)
Rh(3)	1256(1)	8541(1)	6229(1)	13(1)
Cl(1)	924(1)	8692(1)	4950(1)	20(1)
P(1)	3436(1)	8807(1)	6252(1)	17(1)
P(2)	1548(1)	7102(1)	6165(1)	15(1)
C(1)	300(3)	9739(2)	6354(2)	18(1)
C(2)	−744(3)	8991(2)	6164(2)	20(1)
B(4)	1425(3)	9498(2)	7079(2)	18(1)
B(5)	140(4)	10212(2)	7128(2)	24(1)
B(6)	−1230(4)	9898(3)	6527(2)	24(1)
B(7)	−438(4)	8178(2)	6731(2)	21(1)
B(8)	993(4)	8482(2)	7366(2)	21(1)
B(9)	546(4)	9419(3)	7780(2)	24(1)
F(9)	1105(5)	9571(3)	8470(2)	90(1)
B(10)	−1097(4)	9661(3)	7440(2)	27(1)
B(11)	−1693(4)	8914(3)	6779(2)	24(1)
B(12)	−607(4)	8601(2)	7557(2)	24(1)
F(12)	−960(5)	8127(3)	8062(2)	94(1)
C(13)	4115(3)	8533(2)	5471(2)	23(1)
C(14)	3825(3)	9918(2)	6270(2)	23(1)
C(15)	3075(4)	10441(2)	5774(2)	29(1)
C(16)	3382(5)	11274(3)	5738(2)	37(1)
C(17)	4442(5)	11600(2)	6179(2)	37(1)
C(18)	5188(4)	11097(3)	6668(3)	38(1)
C(19)	4900(4)	10248(3)	6721(2)	31(1)
C(20)	4494(3)	8330(2)	7001(2)	21(1)
C(21)	5438(3)	7767(2)	6894(2)	25(1)
C(22)	6177(4)	7343(3)	7465(2)	32(1)
C(23)	5967(4)	7479(3)	8151(2)	34(1)
C(24)	5044(4)	8049(3)	8264(2)	36(1)
C(25)	4316(4)	8475(3)	7702(2)	31(1)
C(26)	2051(4)	6618(2)	7031(2)	24(1)
C(27)	127(3)	6514(2)	5755(2)	21(1)
C(28)	−66(4)	5711(3)	5993(3)	44(1)
C(29)	−1111(5)	5241(3)	5653(4)	57(2)
C(30)	−1937(4)	5557(3)	5076(3)	42(1)
C(31)	−1769(4)	6352(3)	4841(2)	35(1)
C(32)	−738(3)	6834(2)	5185(2)	27(1)
C(33)	2712(3)	6709(2)	5650(2)	17(1)
C(34)	2433(3)	6782(2)	4905(2)	20(1)
C(35)	3306(4)	6503(2)	4495(2)	24(1)
C(36)	4460(4)	6150(2)	4819(2)	27(1)
C(37)	4738(3)	6067(2)	5552(2)	27(1)
C(38)	3865(3)	6340(2)	5971(2)	21(1)
H(1)	444(51)	10047(34)	5981(29)	45(14)
H(2)	−1036(40)	8987(27)	5667(23)	23(10)
H(4)	2339(40)	9763(27)	7171(22)	22(10)
H(5)	327(44)	10818(30)	7195(25)	32(12)
H(6)	−1750(38)	10360(26)	6171(22)	20(10)
H(7)	−771(41)	7621(29)	6608(23)	26(11)
H(8)	1635(43)	8090(29)	7745(23)	29(11)
H(10)	−1784(43)	9882(29)	7735(24)	31(12)
H(11)	−2661(39)	8726(25)	6616(22)	17(9)
H(13A)	3628(67)	8761(45)	5022(39)	77(21)
H(13B)	4107(39)	7961(27)	5385(22)	19(10)
H(13C)	4919(46)	8761(29)	5538(25)	27(11)
H(15)	2370(43)	10256(29)	5463(24)	26(11)
H(16)	2790(45)	11686(31)	5322(25)	32(12)
H(17)	4671(56)	12175(37)	6196(31)	58(17)
H(18)	5954(69)	11354(41)	6965(39)	73(21)
H(19)	5381(45)	9946(31)	7051(25)	32(12)
H(21)	5531(38)	7705(25)	6446(21)	16(9)
H(22)	6848(49)	6860(35)	7368(27)	43(14)
H(23)	6430(45)	7170(29)	8572(25)	31(12)
H(24)	4961(49)	8119(35)	8685(29)	42(14)
H(25)	3634(41)	8923(27)	7797(23)	24(10)
H(26A)	2100(57)	5997(40)	6875(32)	63(18)
H(26B)	1359(37)	6678(24)	7287(20)	12(9)
H(26C)	2790(51)	6964(35)	7253(28)	44(14)
H(28)	715(57)	5508(37)	6442(31)	58(17)
H(29)	−1306(52)	4697(36)	5810(29)	48(15)
H(30)	−2679(51)	5255(34)	4868(28)	43(14)
H(31)	−2403(71)	6622(46)	4419(40)	83(23)
H(32)	−724(51)	7428(36)	5044(28)	47(15)
H(34)	1659(41)	7003(27)	4702(22)	21(10)
H(35)	3223(45)	6540(27)	4099(27)	25(11)
H(36)	5065(40)	5994(26)	4558(22)	21(10)
H(37)	5533(59)	5865(38)	5769(33)	60(17)
H(38)	4120(36)	6217(24)	6491(21)	13(9)

***Closo*-9,12-difluoro-bis(triphenylphospine)-3-hydride-3,1,2-rhodacarborane (5).** Compound **5** (1.2 g, 85%, yellow crystals, m.p. 252 °C) was obtained similarly to the previous compound from $(Ph_3P)_3RhCl$ (1.57 g, 1.78 mmol) and compound **2** (0.46 g, 2.0 mmol) in MeOH (50 mL) by boiling for 4 h and crystallization from CH_2Cl_2–*n*-C_5H_{12} (1 : 4). Found (%): C, 55.67; H, 4.81; P, 7.50; Rh, 11.84. $C_{38}H_{40}B_9F_2P_2Rh$. Calculated (%): C, 57.27; H, 5.02; P, 7.79; Rh, 12.04.

***Closo*-8,9,10,12-tetrafluoro-bis(triphenylphosphine)-3-hydride-3,1,2-rhodacarborane (6).** Compound **6** (1.1 g, 82%, yellow crystals, m.p. 224 °C) was obtained similarly to the previous compound from $(Ph_3P)_3RhCl$ (1.48 g, 1.6 mmol) and compound **3** (0.5 g, 1.8 mmol) in MeOH (60 mL) by boiling for 6 h and crystallization from CH_2Cl_2–*n*-C_5H_{12} (1 : 3). Found (%): C, 49.70; H, 4.28; B, 10.10; F, 8.05; Rh, 10.87. $C_{38}H_{38}B_9F_4P_2Rh \cdot CH_2Cl_2$. Calculated (%): C, 50.99; H, 4.36; B, 10.57; F, 8.29; Rh, 11.23.

X-ray diffraction analysis of compound 6. Crystals are triclinic, at −80 °C $a = 9.704(3)$, $b = 12.354(4)$, $c = 19.908(6)$ Å, $\alpha = 76.14(2)$, $\beta = 76.48(2)$, $g = 73.66(2)°$, $V = 2188(1)$ Å^3, $Z = 2$, $d_{calc} = 1.448$ g cm^{-3}, space group $P\bar{1}$. Unit cell parameters and intensities of 7381 reflections were measured on a Syntex $P2_1$ four-circle diffractometer (Mo-Kα radiation, graphite monochromator, $\theta/2\theta$-scanning, $0 \leq 25°$). The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation. Hydrogen atoms were revealed in the differential Fourier synthesis and included into the refinement in the isotropic approximation. All calculations were performed by the SHELXTL PLUS programs[14] on an IBM PC. The final divergence factors $R_1 = 0.0369$ and $wR_1 = 0.0485$ (by F for 6011 reflections with $I > 3\sigma(I)$). The coordinates of the atoms and their temperature factors in the structure of **6** are presented in Table 7.

***Closo*-9-fluoro-bis(diphenylmethylphosphine)-3-chloro-3,1,2-rhodacarborane (7).** A solution of **1** (0.42 g, 2.0 mmol) in MeOH (25 mL) was added to a suspension of $(Ph_2MeP)_3RhCl$ (1.33 g, 1.8 mmol) in MeOH (20 mL). The reaction mixture was boiled until $(Ph_2MeP)_2RhCl$ disappeared (TLC monitoring in CH_2Cl_2). When the reaction was complete, the reaction mixture was cooled and filtered. The precipitate on the filter was washed with MeOH (50 mL). Orange

crystals were obtained. Crystallization of the orange crystals from the CH_2Cl_2—*n*-C_5H_{12} mixture gave red crystals of compound **7** (1.0 g, 77%, m.p. 220 °C). Found (%): C, 50.41; H, 6.20; Cl, 5.21. $C_{28}H_{36}B_9FClP_2Rh$. Calculated (%): C, 48.79; H, 5.27; Cl, 5.15.

***Closo*-9,12-difluoro-bis(diphenylmethylphosphine)-3-chloro-3,1,2-rhodacarborane (8).** Red crystals of compound **8** (0.55 g, 70%, m.p. 221 °C) were obtained similarly to the previous compound from $(Ph_2MeP)_3RhCl$ (0.8 g, 1.1 mmol) and compound **2** (0.3 g, 1.3 mmol) in MeOH (30 mL). Found (%): C, 46.83; H, 5.41; F, 4.35; Cl, 5.99. $C_{28}H_{35}B_9F_2ClP_2Rh$. Calculated (%): C, 47.57; H, 4.95; F, 5.33; Cl, 5.99.

X-ray diffraction analysis of compound 8. Crystals are monoclinic, at −85 °C a = 10.588(3), b = 16.040(4), c = 19.115(4) Å, β = 100.53(2)°, V = 3192(1) Å^3, Z = 4, d_{calc} = 1.472 g cm^{-3}, space group $P2_1/n$. Unit cell parameters and intensities of 10074 reflections were measured on a Syntex $P2_1$ four-circle diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ-scanning, θ ≤ 30°). The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation. Hydrogen atoms were revealed in the differential Fourier synthesis and included into the refinement in the isotropic approximation. All calculations were performed by the SHELXTL PLUS 5 programs (gamma-version) on an IBM PC. The final divergence factors R_1 = 0.0500 (by F for 7556 reflections with $I > 2\sigma(I)$) and wR_2 = 0.1489 (by F^2 for all 9572 independent reflections). The coordinates of the atoms and their temperature factors in the structure of **8** are presented in Table 8.

***Closo*-8,9,10,12-tetrafluoro-bis(diphenylmethylphosphine)-3-chloro-3,1,2-rhodacarborane (9).** Red crystals of compound **9** (0.50 g, 70%, decomp. 222 °C) were obtained similarly to the previous compound from $(Ph_2MeP)_3RhCl$ (0.66 g, 0.9 mmol) and compound **3** (0.26 g, 1.0 mmol) in MeOH (30 mL). Found (%): C, 44.98; H, 4.44; P, 8.02. $C_{28}H_{33}B_9F_4ClP_2Rh$. Calculated (%): C, 45.24; H, 4.58; P, 8.34.

Hydrosilylation of styrene by $PhMe_2SiH$ in the presence of $(Ph_3P)_3RhCl$. A mixture of PhCH=CH (2.7 g, 0.027 mol), $PhMe_2SiH$ (3.8 g, 0.028 mol), and $(Ph_3P)_3RhCl$ (2.4 mg, $2.7 \cdot 10^{-6}$ mol) was heated in benzene at 80 °C for 5 h. The reaction mixture was filtered, and benzene was distilled off from the filtrate. The residue was distilled *in vacuo*: b.p. 135—150 °C (2 Torr). A mixture of products (3.8 g) was obtained. It was determined by GLC and ^{1}H NMR spectra that the mixture contained compound **15** (83%); ^{1}H NMR, $CDCl_3$, δ: 0.25 (s, 6 H, 2 Me); 1.07 (m, 2 H, CH_2Si); 2.70 (m, 2 H, $PhC\underline{H}_2$); compound **16** (8%) and compound **17** (9%); ^{1}H NMR, $CDCl_3$, δ: 0.44 (s, 6 H, 2 Me); 6.60 (m, H_a, J = 19 Hz); 6.95 (m, H_b, J = 19 Hz).

Hydrosilylation of styrene in the presence of complexes 5, 6, 8, and 10 (general procedure). a. In benzene. The catalyst ($2 \cdot 10^{-5}$ mol) was added to a mixture of $PhCH=CH_2$ (0.21 g, 2.0 mmol) and $PhMe_2SiH$ (0.28 g, 2.1 mmol) in anhydrous C_6H_6 (1.25 mL). The reaction mixture was boiled for 5 h, cooled, and analyzed by GLC.

b. In THF. A mixture of $PhCH=CH_2$ (0.21 g, 2.0 mmol), $PhMe_2SiH$ (0.28 g, 2.1 mmol), and catalyst ($2 \cdot 10^{-5}$ mmol) was boiled for 5 h in anhydrous THF (1.25 mL), cooled, and analyzed by GLC.

Hydrosilylation of phenylacetylene in the presence of complexes 4—8, 10, and $(Ph_3P)_3RhCl$ (general procedure). A mixture of PhC≡CH (0.40 g, 4.0 mmol), $PhMe_2SiH$ (0.57 g, 4.2 mmol), and catalyst ($4 \cdot 10^{-5}$ mol) was boiled for 5 h in anhydrous C_6H_6 (2.5 mL). The reaction mixture was cooled and analyzed by GLC.

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Received August 1, 1996;
in revised form January 10, 1997