

Isolation and characterization of the chelate *exo-nido*-ruthenacarborane intermediates formed in the thermal *exo-nido-to-closo* conversion of [*exo-nido*-5,6,10-{Cl(Ph₃P)₂Ru}-5,6,10-(μ-H)₃-10-H-7,8-R₂-7,8-C₂B₉H₆] (R = H or Me) upon the triphenylphosphine ligand displacement with the chiral (2*S*,4*S*)-(–)-2,4-bis(diphenylphosphino)pentane

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Abstract

Reactions of [*exo-nido*-5,6,10-{Cl(Ph₃P)₂Ru}-5,6,10-(μ-H)₃-10-H-7,8-R₂-7,8-C₂B₉H₆] (**1**, R = H; **2**, R = Me) with the chiral (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (**3**, *S,S*-bdpp) ligand proceed in benzene with replacement of both PPh₃ ligands on the metal center with the diphosphine affording the chelate *exo-nido* complexes [*exo-nido*-5,6,10-{Cl(*S,S*-bdpp)Ru}-5,6,10-(μ-H)₃-10-H-7,8-R₂-7,8-C₂B₉H₆] (**7**, R = H) and (**8**, R = Me), respectively. A relatively fast and irreversible rearrangement of **7** into its *closo* isomer [*closo*-3,3-(*S,S*-bdpp)-3-Cl-3-H-3,1,2-RuC₂B₉H₁₁] (**4**) occurs in solution already at room temperature. On the contrary, *exo-nido-to-closo* conversion of **8** proceeds in benzene (or much faster in toluene) only on heating and yields 17-electron paramagnetic complex [*closo*-3,3-(*S,S*-bdpp)-3-Cl-1,2-Me₂-3,1,2-RuC₂B₉H₉] (**9**). All *exo-nido*- and *closo*-ruthenacarboranes obtained were characterized by a combination of analytical, multinuclear NMR or EPR spectroscopic data and, in addition, by X-ray diffraction studies of both dimethylated complexes **8** and **9**.

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1. Introduction

In the context of our investigation on the chemical [1–3] and catalytic [4] properties of “three-bridge” *exo-nido*-metallocarboranes of ruthenium and osmium in which the exopolyhedral metal center is bonded to the cage carbo-

rane ligand via three two-electron, three-center B–H···M bonds, we became interested in extending the range of the known *exo-nido* derivatives. Such an extension could, in principle, be accomplished by varying of either the phosphine ligands attached to the metal atom or the carborane cage substituents. For this reason, we have recently examined the room-temperature phosphine–diphosphine displacement reactions of [*exo-nido*-5,6,10-{Cl(Ph₃P)₂Ru}-5,6,10-(μ-H)₃-10-H-7,8-R₂-7,8-C₂B₉H₆] (**1**, R = H; **2**,

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R = Me) using chelating diphosphines $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ and $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ [5] as well as thermal reaction of **1** with the chiral diphosphine (2*S*,4*S*)-(–)-2,4-bis(diphenylphosphino)pentane (**3**, *S,S*-bdpp) [6]. From the latter reaction, in refluxing toluene, a series of 18- and 17-electron *closo*-(*S,S*-bdpp)ruthenacarborane species were isolated, of which two were formulated as [*closo*-3,3-(*S,S*-bdpp)-3-Cl-3-H-3,1,2-RuC₂B₉H₁₁] (**4**) and [*closo*-3,3-(*S,S*-bdpp)-3-Cl-3,1,2-RuC₂B₉H₁₁] (**5**), and the third was *ortho*-cycloboronated derivative of **5**, [*closo*-3-Cl-3,3-[(*S,S*)-Ph₂PCH(CH₃)CH₂CH(CH₃)PPh₂-*ortho*-C₆H₄]-3,1,2-RuC₂B₉H₁₀] (**6**). It seemed probable that these chiral diphosphine *closo* products **4–6** could be produced either via spontaneous *exo-nido-to-closo* thermal conversion of *exo-nido* intermediate [*exo-nido*-5,6,10-{Cl(*S,S*-bdpp)Ru}-5,6,10-(μ-H)₃-10-H-7,8-C₂B₉H₈] (**7**) or, alternatively, in the course of PPh₃-diphosphine displacement reaction of *closo* precursor [*closo*-3,3-(PPh₃)₂-3-Cl-3-H-3,1,2-RuC₂B₉H₁₁] which might initially be formed from **1** at elevated temperature [7]. Of particular importance was therefore to determine the structure of real intermediate complexes of these phosphine–diphosphine displacement reactions.

Herein, we report our results for the reactions of *exo-nido* complexes **1** and **2** with the chiral (*S,S*)-bdpp ligand, focusing mainly on the isolation and the NMR spectroscopic and/or solid-state structural characterization of the chelate *exo-nido*-ruthenacarborane intermediates. In addition, thermal reactivity studies in solution of these chelate *exo-nido*-ruthenacarborane complexes with respect to *exo-nido* → *closo* conversion are reported.

2. Result and discussion

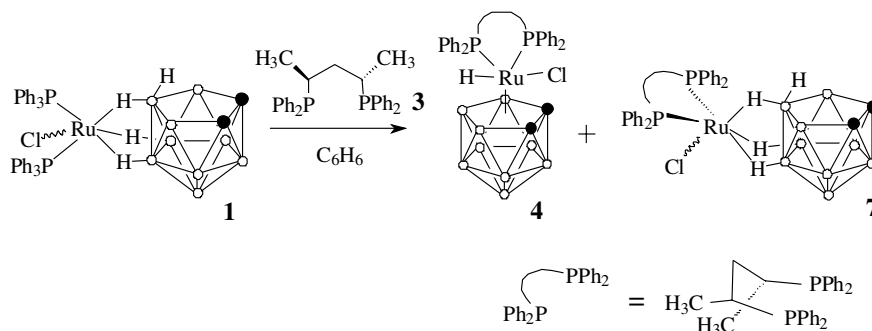
2.1. Synthesis and characterization of the chelate *exo-nido*-(**7**) and *closo*-(**4**) isomeric ruthenacarborane complexes

Previously, from the thermal PPh₃/(*S,S*)-bdpp displacement reaction of *exo-nido* complex **1** with **3** in refluxing toluene [6], we were unable to isolate the chelate *exo-nido*-ruthenacarborane complex **7**, the probable first step intermediate of this process. One may reasonably suggest that species **7** is very short-lived and quite reactive towards

exo-nido-to-closo isomerization under the thermal conditions used in the reaction. In the present work we have found that the replacement of PPh₃ ligands in **1** with diphosphine **3** to form the diamagnetic *closo* complex **4** could be achieved even at room temperature upon treatment of starting reagents in benzene for ca 2 days. Interestingly, when this reaction was monitored by TLC, an additional band of a new complex was observed after the first 2 h. The new species slowly disappeared during the conversion of **1** to **4**, exhibiting properties of an apparent intermediate. In an attempt to isolate such an intermediate complex we terminated the reaction of **1** with **3** at an earlier stage and this afforded, after column chromatography, an orange crystalline complex **7**, along with some amount of **4** (Scheme 1). The ruthenacarborane species thus isolated, on the basis of multinuclear NMR spectral data, has been identified as having an *exo-nido* cluster structure.

Interestingly, complex **7** in solution proved to be reactive toward *exo-nido-to-closo* conversion. Thus, the ¹H NMR spectrum of a pure fraction of **7**, taken for the NMR analysis immediately after the chromatographic separation, displays a sharp seven-line multiplet at δ –8.30 ppm, which is indicative of the chlorohydrido–ruthenium *closo* complex **4** [6]. The ¹H NMR spectrum of this fraction also displays in the high-field region a set of broad and partly overlapping multiplets grouped into two groups, with one of these groups between δ –0.55 and –4.75 ppm and another one at higher field between δ –14.7 and –16.8 ppm as expected [8–10] for B···H···B and B–H···Ru bonds of *exo-nido* species **7**. Note, the relative intensity of the resonance at δ –8.30 ppm is increased in time, so that after few hours complex **4** is seen in the spectrum as the predominant species. The comparison of this ¹H NMR spectrum with that initially observed for the mixture of **7** and **4** allowed us to identify all basic aliphatic resonances of the diphosphine ligand in **7** (see Section 3). Moreover, from a set of upfield B–H···Ru and B···H···B resonances it can be concluded that **7** exists in solution as a mixture of geometrical isomers [10]. Indeed, due to the chirality of (*S,S*)-bdpp ligand **3**, three geometrical isomers would have been expected to exist for the *exo-nido* complex **7** of which each has no mirror symmetry (Chart 1).

Owing to the observed overlapping of principal resonances in the high-field region of the ¹H NMR spectrum



Scheme 1.

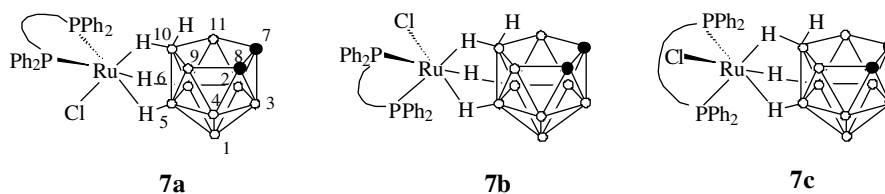


Chart 1.

of **7**, the exact assignment of isomers could not confidently be made. However, this was readily distinguishable from the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the mixture of **7** and **4**, where a set of nicely resolved and well-separated doublet resonances for each species was observed. In particular, one pair of doublets at δ 51.0 and 29.2 ppm with small coupling constant $^2J(\text{P},\text{P}) = 9.5$ Hz was assigned, on the comparison with the authentic sample [6], to diphosphine PPh_2 groups of *closo* complex **4**, while other three pairs of doublets at δ 65.7 and 51.6 ppm with $^2J(\text{P},\text{P}) = 48.2$ Hz, and at δ 38.1 and 34.4 ppm with $^2J(\text{P},\text{P}) = 69.8$ Hz, then at δ 61.7 and 54.4 with $^2J(\text{P},\text{P}) = 51.0$ Hz were tentatively attributed to the coordinated diphosphine ligands of isomeric *exo-nido* species **7a–c**, respectively. The relative peak integrals suggest a ratio of isomers **7a–c** of 1.25:1:0.3, respectively.

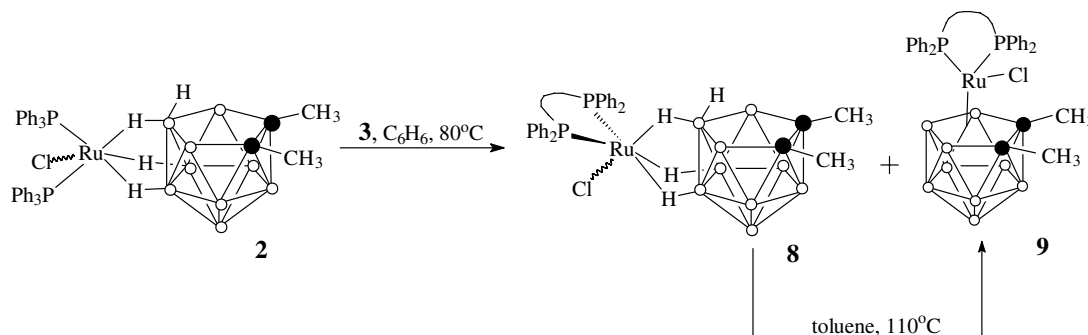
2.2. Synthesis and characterization of the chelate C,C'-dimethylated *exo-nido* complex (**8**) and the product of its *exo-nido-to-closo* conversion, paramagnetic complex (**9**)

It has earlier been demonstrated that the bulkiness of the substituents at the cage carbon atoms is an important factor to define the stability of the “two-bridge” *exo-nido*-bis(triphenylphosphine)rhodacarborane complexes relative to their *closo* tautomers [8]. We therefore assumed that there might be some similarity in derivative chemistry between “two-bridge” and “three-bridge” *exo-nido*-metallacarboranes, and that the introduction of substituents at the cage carbon positions of the {*nido*- C_2B_9 } framework would enhance the stability of the chelate “three-bridge” *exo-nido*-{ $\text{MCl}(\text{P}-\text{P})$ }-metallacarboranes. Accordingly, we attempted to synthesize such a chelate *exo-nido* complex [*exo-nido*-5,6,10- $\{\text{Cl}(\text{S}, \text{S}-\text{bdpp})\text{Ru}\}$ -5,6,10- μ -(H) $_3$ -10-H-

7,8- Me_2 -7,8- $\text{C}_2\text{B}_9\text{H}_6$] (**8**) starting from the C,C'-dimethylated *exo-nido* complex **2** [1] and the diphosphine **3**.

However, in contrast to the reaction of **1** with **3** which at room temperature afforded mixture of complexes **7** and **4**, the exchange reaction of the C,C'-dimethylated complex **2** with the diphosphine **3** under exactly the same conditions failed. Only when gently refluxed in benzene for ca. 2 days, complex **2** has been found to react with **3** to afford the desired *exo-nido* complex **8**, along with the new paramagnetic species [*closo*-3,3-(*S,S*-bdpp)-3-Cl-1,2- Me_2 -3,1,2- $\text{RuC}_2\text{B}_9\text{H}_9$] (**9**). Both complexes **8** and **9** were isolated, after column chromatography, as air-stable crystalline solids in 48% and 27% yields, respectively. It is apparent that the paramagnetic complex **9** is not the first step product of this thermal reaction. It is likely that the initially formed complex **8** could be further transformed, via *exo-nido-to-closo* rearrangement, into an 18-electron *closo* complex [*closo*-3,3-(*S,S*-bdpp)-3-Cl-3-H-1,2- Me_2 -3,1,2- $\text{RuC}_2\text{B}_9\text{H}_9$] (**10**). This sterically crowded C,C'-dimethylated *closo* Ru(IV) cluster **10** would be expected to lose a metal-hydride under thermal conditions affording thermodynamically more stable paramagnetic Ru(III) complex **9**. It has also been found that under more severe conditions, in refluxing toluene for 3.5 h, *exo-nido* complex **8** could be converted into **9** in 61% yield (see Scheme 2).

In agreement with the paramagnetic structure of 17-electron complex **9**, we have observed its EPR spectrum in frozen dichloromethane solution at 77 K (Fig. 1). As expected, the EPR spectrum of **9** proved to be quite similar to that observed earlier for the C,C'-unsubstituted analogue **5** [6]. It exhibited rhombic g component patterns with $g_1 = 2.40$, $g_2 = 2.06$, $g_3 = 1.97$ which are typical of a low-spin Ru(III) $3d^5$ complexes [11]. Moreover, since the paramagnetic complex **9** is, in fact, optically active compound,



Scheme 2.

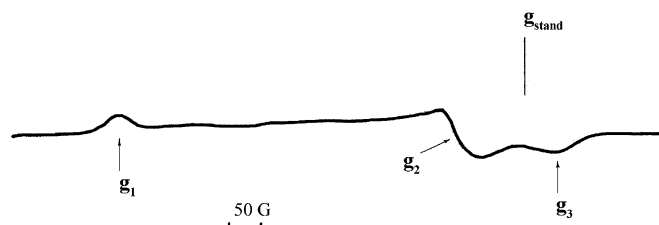


Fig. 1. EPR spectrum of **9** in frozen CH_2Cl_2 at 77 K ($g_{\text{standard}} = 2.003$).

due to the chirality of the diphosphine ligand at the metal vertex, we have also studied its chiroptical properties. This complex is characterized by rather high value of optical rotation angle, ($\alpha_D^{20} - 852^\circ$) and exhibits CD spectrum shown in Fig. 2.

The ^1H NMR spectrum of **8** in the upfield region shows a set of quadruplet-like multiplets, diagnostic of the presence of $\text{B}\cdots\text{H}\cdots\text{B}$ and $\text{B}\text{--}\text{H}\cdots\text{M}$ groups [8–10]. In contrast to the ^1H NMR spectrum of **7**, the high-field resonances in the spectrum of **8** are distinctively separated within three negative zones from ca. $\delta -1.0$ to -2.0 ppm, then in the

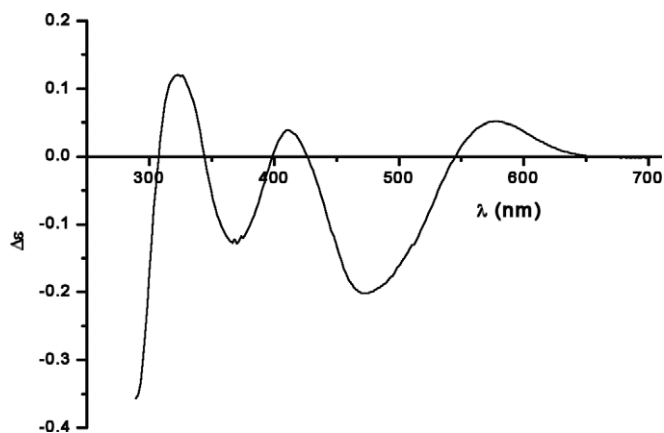


Fig. 2. CD spectrum of **9** in CH_2Cl_2 at 25 °C (c , 0.001 M).

range between -2.0 and -6.0 ppm, and from $\delta -16.0$ to -18.0 ppm. From the ^1H NMR spectrum of **8** it was clear that there is one major (**8a**) and two minor (**8b,c**) isomeric species in solution. Again, owing to the high degree of overlapping of main isomer resonances with those weaker signals arising from minor isomers, to determine their ratios via integration could not be achieved. However, this was successfully accomplished from a fully boron-decoupled $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **8a–c** (Fig. 3), where integration of the major isomer resonances with respect to those of minor isomers estimates their ratio is ca. 10:1:0.3, respectively.

In the boron-decoupled $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of **8** resonances corresponding to *endo*-hydrogen atoms were revealed for all three isomers **8a–c**: at $\delta -1.14$ (**8b**), -1.49 (**8a**) and -1.83 ppm (**8c**), and these all were doublets with very close geminal coupling constants $^2J(\text{H,H-endo})$ ranging from 11 to 13 Hz. This can be used as a good evidence for the presence of the BH_2 fragments in each isomers **8a–c**. Of a set of resonances originating from the $\text{B}\text{--}\text{H}\cdots\text{Ru}$ bridges of all three isomers, only one resonance at $\delta -17.6$ ppm exhibits an apparent quadruplet-like multiplicity (actually an overlapping doublet of doublets of doublets) with $\Delta\delta$ value of 8–10.5 Hz that is comparable to the value of geminal $^2J(\text{H,H})$ coupling. The unique resonance at $\delta -17.6$ ppm is therefore best attributed to the $\text{B}\text{--}\text{H}\cdots\text{Ru}$ bridging hydrogen H(10) lying *cis* to both PPh_2 groups of the diphosphine ligand and *trans* to the Cl ligand in **8a**. The remaining two doublets observed at $\delta -3.00$ and -4.20 ppm with *trans* coupling $^2J(\text{H,P})$ of 35.4 and 40.4 Hz, respectively, can thus be assigned to the $\text{B}\text{--}\text{H}\cdots\text{Ru}$ bridging hydrogens H(5) and H(6) of **8a** or vice versa.

The proton resonances of minor isomers **8b,c** which are revealed at $\delta -16.28$ (**8b**) and -16.38 ppm (**8c**) display a triplet-like structure. Taking into account the observed multiplicity of these resonances, and based upon their positions in the spectrum these appear to be best attributed to

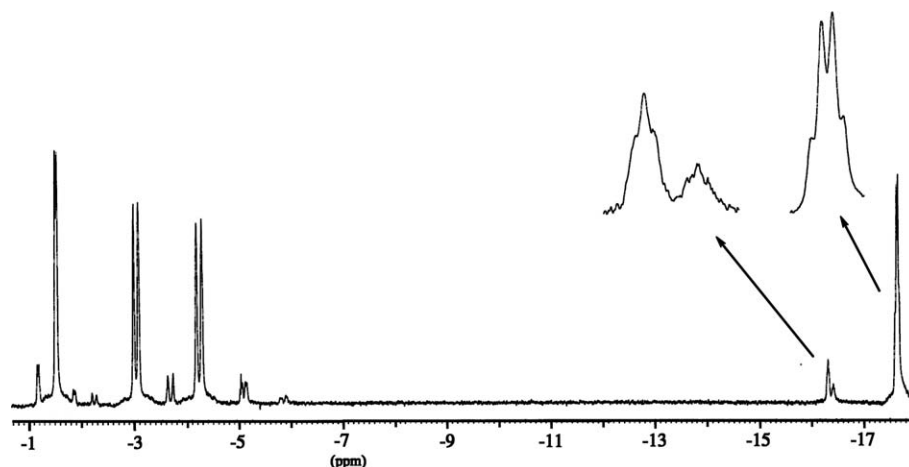


Fig. 3. 400.13 MHz $^1\text{H}\{^{11}\text{B}\}$ spectrum for **8** (22 °C, CD_2Cl_2) in the upfield region from -1.0 to -17.5 ppm (aromatic and aliphatic regions of the spectrum are not displayed).

the low B₅-belt bridging hydrogen atoms H(5) in **8b** and H(6) in **8c**. The resonances observed at δ –2.21 (**8c**) and –3.65 ppm (**8b**), due to their doublet multiplicity and *trans* $^2J(\text{H},\text{P})$ coupling of 30.5 and 38.4 Hz, were thus attributed to the bridging B–H···Ru hydrogens H(6) (**8b**) and H(5) (**8c**), respectively. It is of interest that none of these resonances displays *cis* $^2J(\text{H},\text{P})$ coupling, presumably, due to their very small magnitude. The remaining two resonances derived from the bridging H(10) hydrogen atom of minor isomers revealed at δ –5.05 (**8b**) and –5.82 ppm (**8c**) and, in the first approximation, were doublet of doublets exhibiting the *trans* coupling $^2J(\text{H},\text{P})$ of 35.5 and 43.5 Hz and the geminal coupling $^2J(\text{H},\text{H-endo})$ of 13.3 and 10.5 Hz, respectively. These H(10) resonances of **8b,c** as well as resonances originating from the low-belt bridging hydrogens, H(6) (**8b**) and H(5) (**8c**), do not display the *cis* $^2J(\text{H},\text{P})$ coupling. In this respect it should be noted that in the $^1\text{H}\{^{11}\text{B}\}$ NMR spectrum of the related “three-bridge” osmium complex [*exo-nido*-(Cl(Ph₃P)₂Os)-(μ-H)₃-10-H-7,8-(PhCH₂)₂-7,8-C₂B₉H₆] (**11**, an asymmetric isomer [3]) the multiplicity observed for the bridging B–H(10)···M resonance at δ –8.20 ppm, in contrast to those of **8b,c**, has doublet of triplets structure with the *trans* $^2J(\text{H},\text{P}_1) = 44.2$, *cis* $^2J(\text{H},\text{P}_2) = 10.0$ and the geminal coupling $^2J(\text{H},\text{H-endo}) = 12.5$ Hz, while other two low-belt bridging hydrogens involving in the B–H···Os interaction show similar multiplicity to that observed for H(5) or H(6) in **8b,c**, a doublet at δ –5.40 ppm with the *trans* $^2J(\text{H},\text{P}) = 40$ Hz and a triplet-like signal at δ –15.6 ppm with *cis* $^2J(\text{H},\text{P}_1) \sim ^2J(\text{H},\text{P}_2)$ of 10.5 Hz.

As expected, in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **8** there are three pairs of doublet resonances due to isomers **8a–c** with $^2J(\text{P},\text{P})$ coupling ranged from 40 to 50 Hz. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **8** consisted of a set of eight peaks of the major isomer **8a**, with one of double intensity, and only four resonances were definitely seen as non-overlapping from other two isomers **8b,c**.

2.3. Single-crystal X-ray diffraction studies of *exo-nido* complex **8a** and paramagnetic *closo* complex **9**

Suitable single crystals of the major isomer **8a** grown by slow evaporation of solution of **8** in a mixture of CHCl₃/*n*-hexane as well as crystals of the *closo* complex **9** were the subjects for the X-ray diffraction studies. The molecular structures of complexes **8a** and **9** are shown in Figs. 4 and 5, and selected geometrical parameters (bond distances and angles) are listed in Table 1.

An X-ray diffraction study of **8a** showed that this species is indeed “three-bridge” *exo-nido*-ruthenacarborane wherein the *exo*-{Ru(bdpp)Cl}⁺ fragment is attached to the formally anionic [*nido*-7,8-Me₂-7,8-C₂B₉H₁₀][–] carborane unit by three B–H···Ru bonds. Complex **8a** can thus be rationalized as zwitterionic species with the Ru^{II} atom having a closed 18-electron configuration. Of the three B–H···Ru bonds participating in the interaction with the metal atom, one, B(10)–H(10A) bond, is from the upper

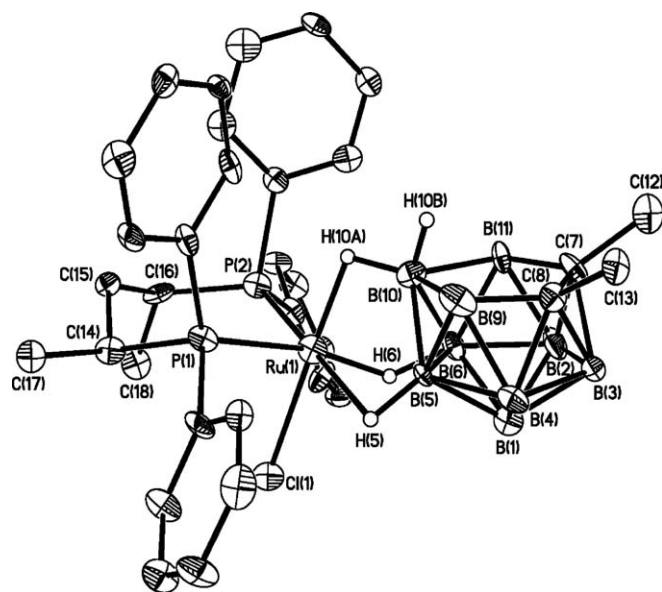


Fig. 4. An ORTEP representation of the molecular structure of **8a** with thermal ellipsoid drawn at 30% probability level. The hydrogen atoms are omitted for clarity.

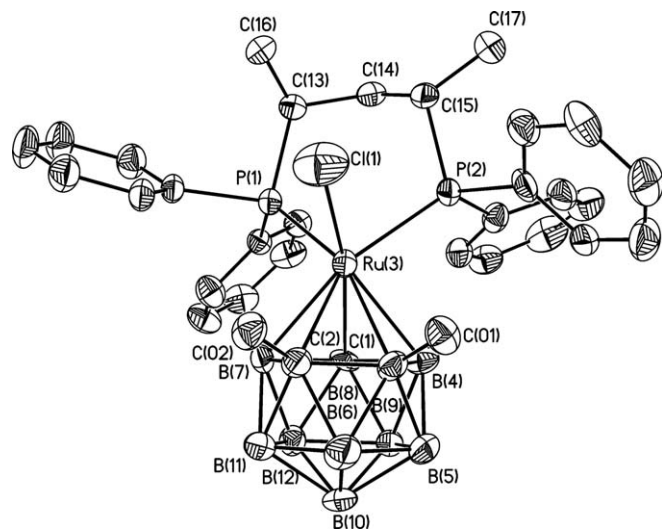


Fig. 5. An ORTEP representation of the molecular structure of **9** with thermal ellipsoid drawn at 30% probability level. The hydrogen atoms are omitted for clarity.

C₂B₃-belt and two other, B(5)–H and B(6)–H, belong to the lower B₅-belt of the cage ligand. In all crystallographically studied “three-bridge” *exo-nido*-metallacarboranes of ruthenium [1,12] and osmium [3], the maximum lengthening of the three B–H bonds involving in the B–H···M interaction exhibits that one having *trans* orientation to the Cl ligand. In this respect, complex **8a** displays the same trend, *i.e.* the B(10)–H(10A) bond length of 1.24 Å is noticeably longer than those of B(5)–H, 1.12 Å, and B(6)–H, 1.14 Å. Based on the ^1H NMR data, the *endo*-hydrogen atom H(10B) in complex **8a** can be regarded as terminal rather than bridging hydrogen located between any of the two

Table 1
Selected bond distances and angles of **8a** and **9**

8a		9	
Ru(1)–Cl(1)	2.400(3)	Ru(3)–Cl(1)	2.278(2)
Ru(1)–P(1)	2.250(3)	Ru(3)–P(1)	2.366(2)
Ru(1)–P(2)	2.272(3)	Ru(3)–P(2)	2.391(2)
Ru(1)–B(5)	2.353(11)	Ru(3)–C(1)	2.342(6)
Ru(1)–B(6)	2.436(11)	Ru(3)–C(2)	2.327(5)
Ru(1)–B(10)	2.254(12)	Ru(3)–B(4)	2.241(6)
Ru(1)–H(5)	2.10	Ru(3)–B(7)	2.257(6)
Ru(1)–H(6)	2.12	Ru(3)–B(8)	2.239(5)
Ru(1)–H(10A)	1.68		
P(1)–C(14)	1.856(9)	P(1)–C(13)	1.872(6)
P(2)–C(16)	1.802(10)	P(2)–C(15)	1.854(6)
C(7)–C(8)	1.604(13)	C(1)–C(2)	1.627(7)
C(14)–C(15)	1.506(11)	C(13)–C(14)	1.532(8)
C(14)–C(17)	1.517(11)	C(13)–C(16)	1.519(8)
C(15)–C(16)	1.558(12)	C(14)–C(15)	1.524(8)
C(16)–C(18)	1.541(12)	C(15)–C(17)	1.535(9)
P(1)–Ru(1)–P(2)	92.8(1)	P(1)–Ru(3)–P(2)	90.56(6)
P(1)–Ru(1)–Cl(1)	89.4(1)	P(1)–Ru(3)–Cl(1)	87.70(8)
P(2)–Ru(1)–Cl(1)	93.6(1)	P(2)–Ru(3)–Cl(1)	85.95(8)
P(2)–Ru(1)–H(5)	177.9		
P(1)–Ru(1)–H(6)	160.4		
Cl(1)–Ru(1)–H(10A)	173.9		
H(10A)–B(10)–H(10B)	106.9		

adjacent boron atoms on the open C_2B_3 face of the cage ligand. Accordingly, the distance between H(10B) and B(10) of 1.18 Å is much shorter than those observed between H(10B) and B(9), 1.64 Å, or H(10B) and B(11), 2.17 Å. The original (2*S*,4*S*) absolute configuration of the chiral *bdpp* ligand is remained unchanged on coordination with the ruthenium atom, and therefore in **8a** no molecule symmetry plane exists. The diphosphine ligand in **8a** seems to be stronger coordinated by the ruthenium atom than PPh_3 ligands in the known “three-bridge” *exo-nido*-metallacarborane complexes [1,3,12]. Thus, the Ru–P(1,2) distances of 2.250(3) and 2.272(3) in **8a** are shorter than those found, for example, in the [*exo-nido*–{Cl(Ph₃P)₂Ru}–(μ-H)₃–10-H-7,8-C₂B₉H₈] (**12**, Ru–P(1), 2.304; Ru–P(2), 2.301 Å [1]) and [*exo-nido*–{Br(Ph₃P)₂Os}–(μ-H)₃–10-H-7,8-C₂B₉H₈] (**13**, Ru–P(1), 2.306; Ru–P(2), 2.310 Å [12b]). At the same time, the Ru–Cl bond length of 2.400(3) Å in **8a** and in all these *exo-nido* complexes (2.393–2.406 Å) are quite similar.

The X-ray diffraction data obtained for complex **9** fully confirmed its 17-electron *closo* structure. The ruthenium atom in **9** is quite symmetrically η^5 -coordinated by the open C_2B_3 face of the dianionic *nido*–{7,8-Me₂-7,8-C₂B₉H₉} cage ligand, and, in addition, ligated by one chlorine ligand and one *bdpp* ligand which in sum occupying three additional facial coordination sites around the metal atom. Thus, the Ru atom in this complex has a coordination number of six being formally three-valent 17-electron metal centre. The chelate diphosphine ligand orientation in **9** is similar to that observed in the other known example of paramagnetic complex **5** [6], where the central methylene unit of diphosphine ligand lies in the position *anti* with respect to the Cl ligand on the metal atom. The Ru–P bond

lengths (2.3655(15), 2.3906(15) Å) as well as all the ruthenium-to-cage-atom distances in **9** (Table 1) are close to those found in a number of anionic [2,13] or neutral/zwitterionic [7,14] *closo*-ruthenacarboranes having monophosphine ligands at the metal vertex. On the contrary, the Ru–Cl distance in **9** (2.274(2) Å) is typically [6] shorter than were found in 18-electron Cl-containing *closo*-ruthenacarboranes [7,15]. The geometry of the dicarbollyl ligand is unexceptional [16].

3. Experimental

3.1. General comments

All reactions were carried out under an argon atmosphere using Schlenk techniques. All solvents were distilled from appropriate drying agents prior to use. Complexes **1** and **2** were successfully prepared starting from the (Ph₃P)₃RuCl₂ [17] and the K⁺-salts of the corresponding *nido*-carborane anions by slightly modifying the published procedure [1] where benzene was used as a solvent instead of Et₂O–THF mixture. Short chromatography columns packed with silica gel (Merck, 230–400 mesh) were applied for separation and purification of the reaction products, and these were carried out on air. The ¹H, ¹H{¹¹B}, ³¹P{¹H} and ¹¹B/¹¹B{¹H} NMR spectra were recorded on Bruker AMX-400 (¹H at 400.13 MHz; ³¹P at 161.98 MHz; ¹¹B at 128.33 MHz) using TMS as an internal reference, and 85% H₃PO₄ and BF₃·Et₂O as the external references, respectively. IR spectra were obtained on a Carl-Zeiss M-82 spectrometer. CD and EPR spectra of paramagnetic complex **9** were recorded on Jasco J-500A spectrometer and Varian E-12A radiospectrometer, respectively. Elemental analyses for all new compounds were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS.

3.2. Preparation of [*exo-nido*–{Cl(*S,S*-*bdpp*)Ru}–(μ-H)₃–10-H-7,8-C₂B₉H₈] (**7**) and [*closo*-3,3-(*S,S*-*bdpp*)-3-Cl-3-H-3,1,2-RuC₂B₉H₉] (**4**)

To a solution of **3** (30 mg, 0.07 mmol) in 8 ml of benzene was added *exo-nido* complex **1** (40 mg, 0.05 mmol) in the solid state, and the resulting mixture was stirred at room temperature for 16 h. Solvent was evaporated under reduced pressure, and the residue was treated by column chromatography on silica gel. The first yellow band eluted from the column using a benzene/*n*-hexane (1:1) mixture was found to contain complex **4** (10 mg, 28% yield). The second yellow band contains complex **7** (16 mg, 44% yield) as the principal product along with traces of **4** which has presumably appeared in the solution of **7** during either evaporation or chromatographic treatment of the crude product. NMR data for the mixture of isomers **7a–c** (1.25:1:0.3) and **4** (traces) are as follows: ¹H NMR (C₆D₆, 22 °C): δ +8.15 to +6.85 (m, Ph, **4**; **7a–c**), +4.98, +2.53 (br s, 1H, CH-carb, **4**), +3.88 (7-line m, 1H, 2-

CHCH₃, **4**), +3.64, +3.32, +2.87, +2.72, +2.20, 2.08, +1.94, +1.52 (all m, CHCH₂CH, **7a–c**), +3.52, +2.82 (br s, CH-carb, **7a**), +2.96, +2.32, (m + q-like, 1H, 4- and 3-CHCH₃, **4**), +1.95, +1.50 (m, 1H, CHCH₂CH, **4**), +1.45, +1.32, +1.17, +1.0 to +0.82 (overlapped m, 1- and 5-CH₃, **4**, **7**), –0.55 to –4.75 (overlapped br m, H(5,6)-**7a**; H(6,10)-**7b**; H(5,10)-**7c**; H(10-endo)-**7a–c**), –8.30 (7-line m, 1H, RuH, **4**), –15.33 (br m, H(5,6)-**7b,c**), –16.80 (br m, H(10)-**7a**); ³¹P{¹H} NMR (C₆D₆, 22 °C; **7a–c** - 1.25:1:0.3): δ +65.7 (br d, ²J(P,P) = 48.2 Hz, 1P, **7a**), +61.7 (br d, ²J(P,P) = 51.0 Hz, 1P, **7c**), +54.4 (br d, ²J(P,P) = 51.0 Hz, 1P, **7c**), +51.6 (br d, ²J(P,P) = 48.2 Hz, 1P, **7a**), +51.0 (d, ²J(P,P) = 9.5 Hz, 1P, **4**), +38.1 (d, ²J(P,P) = 69.8 Hz, 1P, **7b**), +34.4 (d, ²J(P,P) = 69.8 Hz, 1P, **7b**), +29.2 (d, ²J(P,P) = 9.5 Hz, 1P, **4**).

3.3. Synthesis of [exo-nido-{Cl(S,S-bdpp)Ru}-(μ-H)₃-10-H-7,8-(CH₃)₂-7,8-C₂B₉H₆] (**8**) and [closo-3,3-(S,S-bdpp)-3-Cl-1,2-Me₂-3,1,2-RuC₂B₉H₉] (**9**)

To a stirred solution of **3** (50 mg, 0.11 mmol) in 15 ml of benzene was added *exo-nido* complex **2** (80 mg, 0.10 mmol) and the resulting mixture was additionally stirred at room temperature for 1 h, then gently refluxed for 45 h until starting complex **1** was disappeared from the reaction mixture. After cooling, solvent was removed under reduced pressure, and the residue was treated by column chromatography on silica gel eluting with benzene. The narrow dark-red band was eluted first affording, after evaporation of the solvent and recrystallization of the crude material from CH₂Cl₂/*n*-hexane, 20 mg (27%) of analytically pure paramagnetic *closo* compound **9**. Anal. Calc. for C₃₃H₄₅B₉ClP₂Ru: C, 53.73; H, 6.11; B, 13.19. Found: C, 53.24; H, 5.65; B, 13.33%. IR (KBr, cm⁻¹): 2557(ν_{B–H}), 325(ν_{Ru–Cl}); [α]_D²⁰ = –852° (c 0.65, CH₂Cl₂); EPR (CH₂Cl₂, 77 K): g₁ = 2.40, g₂ = 2.06, g₃ = 1.97. The band eluted next gave after evaporation 35 mg (48%) of **8** as orange crystalline solid; this crude material was found to contain mixture of isomers **8a–c** in the approximate ratio 10:1:0.3, respectively. Anal. Calc. for C₃₃H₄₆B₉ClP₂Ru: C, 53.68; H, 6.24; B, 13.19. Found: C, 53.79; H, 6.59; B, 12.83; IR (KBr, cm⁻¹): 2545 (ν_{B–H}), 2164, 2135 (ν_{B–H...Ru}); [α]_D²⁰ = +222° (c 0.74, CH₂Cl₂); ¹H{¹¹B} NMR (CD₂Cl₂, 22 °C), δ +7.78 to +6.82 (m, Ph, **8a–c**), +3.48 (7-line m, 1H, 2-CHCH₃, **8a**), +3.15 (m, 1H, 4-CHCH₃, **8a**), +3.03 (br s, 1H, BH, **8a**) +2.88 (br m, BH, **8b(c)**), 2.75 (br m, BH, **8c(b)**), 2.39 (br s, 1H, BH, **8a**), 2.15 (qw-like, 1H, 3-CHH, **8a**) 1.97 (m, 1H, 3-CHH, **8a**), 1.80 (br s, 1H, BH, **8a**), 1.62 (br s, 1H, BH, **8a**), 1.52 (br s, 1H, BH, **8a**), +1.44 (br s, 3H, CH₃-carb, **8a,b**), +1.37 (br s, CH₃-carb, **8b**), 1.34 (br s, 3H, CH₃-carb, **8a**), 1.24 (dd, ³J(H,P) = 15 Hz, ³J(H,H) = 7 Hz, 3H, 5-CH₃, **8a**), 1.06 (overlapped dd, ³J(H,H) = 3 Hz, 5-CH₃, **8b(c)**), 1.02 (dd, ³J(H,P) = 15 Hz, ³J(H,H) = 7 Hz, 3H, 1-CH₃, **8a**), +0.87 (br s, 1H, BH, **8a**), –1.14 (d, ²J(H,H) = 13 Hz, 1H, H-endo, **8b**), –1.49 (d, ²J(H,H) = 11.3 Hz, 1H, H-endo, **8a**), –1.83 (d, ²J(H,H) = 10.5 Hz, 1H, H-endo, **8c**), –2.21 (d,

²J(H,P) = 30.5 Hz, 1H, H(5), **8c**), –3.00 (d, ²J(H,P) = 35.4 Hz, 1H, H5(6), **8a**), –3.65 (d, ²J(H,P) = 38.4 Hz, 1H, H(6), **8b**), –4.20 (d, ²J(H,P) = 41.4 Hz, 1H, H6(5), **8a**), –5.05 (dd, ²J(H,P) = 35.5 Hz, ²J(H,H-endo) = 13 Hz, 1H, H(10), **8b**), –5.82 (dd, ²J(H,P) = 43.5 Hz, ²J(H,H) = 10.5 Hz, 1H, H(10), **8c**), –16.28 (t-like, ²J(H,P) = 6.5 Hz, 1H, H(5), **8b**), –16.38 (t-like, ²J(H,P) = 7.5 Hz, 1H, H(6), **8c**), –17.60 (dt, ²J(H,P) = 9.5 Hz, ²J(H,H) = 10.5 Hz, 1H, H(10), **8a**); ³¹P{¹H} NMR (CD₂Cl₂, 22 °C; **8a–c** - 10:1:0.3): δ 68.9 (d, ²J(P,P) = 45 Hz, 1P, **8c**), 64.7 (d, ²J(P,P) = 41 Hz, 1P, **8a**), 60.1 (d, ²J(P,P) = 50 Hz, 1P, **8b**), 54.7 (d, ²J(P,P) = 50 Hz, 1P, **8b**), 51.1 (d, ²J(P,P) = 41 Hz, 1P, **8a**), 48.0 (d, ²J(P,P) = 45 Hz, 1P, **8c**). ¹¹B{¹H} NMR (CD₂Cl₂, 22 °C): δ +2.4 (1B, **8a**), –9.5 (1B, **8a**), –12.5 (**8b(c)**), –16.6 (**8b(c)**), –22.8 (2B, **8a**), –26.9 (1B, **8a**), –28.0 (1B, **8a**), –32.3 (**8b(c)**), –35.2 (1B, **8a**), –44.7 (1B, **8a**), –46.9 (**8b(c)**).

3.4. Alternative synthesis of [closo-3,3-(S,S-bdpp)-3-Cl-1,2-Me₂-3,1,2-RuC₂B₉H₉] (**9**)

A stirred solution of *exo-nido*-complex **8** (10 mg, 0.0133 mmol) in 10 ml of toluene was refluxed for 3.5 h and then evaporated to dryness under reduced pressure. The residue was purified via column chromatography on silica gel as for **9** in the above procedure to give after evaporation and subsequent recrystallization of the residue from CH₂Cl₂/*n*-hexane 6 mg (61%) of the dark-red crystalline product, which from analysis of EPR spectrum is deduced to be paramagnetic complex **9**.

Table 2
Crystallographic and experimental parameters of **8a** and **9**

	8a	9
Molecular formula	C ₃₃ H ₄₆ B ₉ ClP ₂ Ru	C ₃₃ H ₄₅ B ₉ ClP ₂ Ru
Formula weight	738.45	737.44
Dimension, mm	0.4 × 0.3 × 0.05	0.1 × 0.08 × 0.03
Crystal system	Monoclinic	Orthorhombic
Space group	P2 ₁	P2 ₁ 2 ₁ 2 ₁
a, Å	11.030(6)	10.612(3)
b, Å	15.887(9)	11.788(3)
c, Å	11.173(6)	29.100(7)
β, °	112.78(1)	–
V, Å ³	1805(2)	3640(2)
Z	2	4
ρ _{calc} , g cm ⁻³	1.359	1.346
Temperature, °K	110	120
2θ _{max} , deg.°	48.0	54.0
Linear absorption (μ), cm ⁻¹	6.21	6.16
T _{min} /T _{max}	0.789/0.970	0.931/0.958
Total reflections	10,609	21,136
Number of independent reflections (R _{int})	5536 (0.0869)	7875 (0.0648)
Number of observed reflections with I > 2(σ)	2837	4556
Parameters	415	415
wR ₂ (all independent reflections)	0.1059	0.0998
R ₁ (I > 2(σ))	0.0554	0.0506
Flack parameter	0.01(5)	0.01(4)
ρ _{max} /ρ _{min} , e Å ⁻³	0.67/–0.49	1.11/–0.73

3.5. X-ray studies of **8a** and **9**

Single-crystal X-ray diffraction experiment was carried out with a Bruker SMART 1000 CCD diffractometer. Collected frames were integrated by SAINT software [18] and corrected for absorption using SADABS program [19]. The structure of **8a** and **9** were solved by direct method and refined by full-matrix technique against F^2 in anisotropic approximation using SHELXTL 5.1 program package [20]. The positions of hydrogen atoms were calculated geometrically and included in refinement in rigid body approximation. The exception is H atoms of carborane cage in **9**, which are located from difference Fourier maps and refined in rigid body approximation. The absolute configurations of **8a** and **9** were determined by use of the Flack parameter [21]. The principal experimental and crystallographic parameters are presented in the Table 2.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 603040 and 603041 for complexes **9** and **8a**, respectively. Copies of these information may be obtained free of charge at www.ccdc.acm.ac.uk/retrieving.html or from the Cambridge Crystallographic Data Centre 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](http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.05.051](https://doi.org/10.1016/j.jorganchem.2006.05.051).

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