Organometallic Chemistry

Synthesis, structure and isomerism of "three-bridge" *exo-nido*-osmacarborane clusters

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The reaction of $OsCl_2(PPh_3)_3$ with $[nido\text{-}7\text{-}R^1\text{-}8\text{-}R^2\text{-}C_2B_9H_{10}]K^+$ produced a series of new *exo-nido*-osmacarborane complexes *exo-nido*-5,6,10-$[Cl(Ph_3P)_2Os]$-5,6,10-$(\mu\text{-}H)_3$-10-H-7-R^1-8-R^2-7,8-$C_2B_9H_6$ (**1**: $R^1 = R^2 = H$; **2**: $R^1 = R^2 = Me$; **3**: $R^1 = R^2 = PhCH_2$; **4**: $R^1 + R^2 = 1,2\text{-}C_6H_4(CH_2)_2$; **5**: $R^1 = H$, $R^2 = Me$) in which the osmium-containing group is linked to the *nido*-carborane ligand through three two-electron three-center bonds. Compounds **1**—**5** are formed as mixtures of symmetric (**a**) and asymmetric (**b**) isomers; pure symmetric isomers **2a** and **4a** were isolated by fractional crystallization, and the mixture of isomers **3a**,**b** was quantitatively separated into individual compounds **3a** and **3b** by column chromatography on silica gel. Detailed analysis of the $^{31}P\{^1H\}$, ^1H, ^{11}B NMR spectra of **1a**,**b**—**5a**,**b** and 2D $^1H\text{-}^1H\{^{11}B\}$ and $^{11}B\{^1H\}\text{-}^{11}B\{^1H\}$ NMR spectra of **3a** and **3b** was performed. The structures of isomers **2a** and **4a** were confirmed by an X-ray diffraction study. According to the NMR and X-ray diffraction data, the isomerism of *exo-nido*-complexes **1a**,**b**—**5a**,**b** is actually the *cis—trans*-isomerism of ligand arrangement in the octahedral coordination of the Os atom.

Key words: *exo-nido*-osmacarboranes, tris(triphenylphosphine)osmium dichloride, stereochemistry, *cis—trans*-isomerism.

Mononuclear *exo-nido*-metallacarboranes in which the metal atom occurs in the *exo*-position relative to the *nido*-carborane ligand and is linked to it by two two-electron three-center (2e,3c) B—H...M bonds are known for Ir,[1] Rh,[2—4] W,[5] Al,[6,7] and Sm.[8] There are also examples of modified *exo-nido*-ruthenacarboranes with one or two additional *exo*-polyhedral M—E bonds (E is phoshorus- or sulfur-containing substituents at the carbon atoms of *nido*-C_2B_9-carborane),[9—13] which retain one or two 2e,3c B—H...Ru bonds, depending on the number of hetero substituents coordinated to the metal atom. In a series of preliminary studies,[14—17] we reported synthesis of new *exo-nido*-ruthena- and *exo-nido*-osmacarborane complexes, *exo-nido*-5,6,10-$[Cl(Ph_3P)_2M]$-5,6,10-$(\mu\text{-}H)_3$-10-H-7-R^1-8-R^2-7,8-$C_2B_9H_6$ (M = Ru, Os; R^1, R^2 = H, Alk, ArAlk) in which the *nido*-carborane acts as a tridentate ligand linked to the metal center *via* three B—H...M 2e,3c bonds. Similar "three-bridge" ruthenium *exo-nido* complexes in which the *extra* H atom of *nido*-carborane has been replaced by HgR groups have been prepared recently.[18] It is noteworthy that participation of three B

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 677—686, April, 2001.

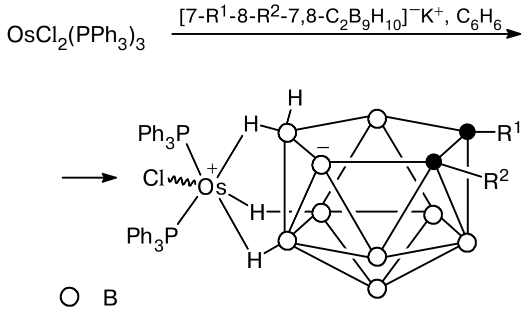
atoms in the formation of the B—H...M 2e,3c bond was found previously only for two manganoborane complexes, $(CO)_3Mn(B_8H_{13})$[19] and $(CO)_3Mn(B_3H_8)$.[20]

In this communication, we survey data on the synthesis of "three-bridge" *exo-nido*-osmacarboranes and the results of studies of the structures and isomerism of these compounds performed by homo- and heteronuclear NMR spectroscopy, including 2D correlation techniques, and X-ray diffraction analysis.

Results and Discussion

The osmium *exo-nido*-complexes *exo-nido*-5,6,10-$[Cl(Ph_3P)_2Os]$-5,6,10-μ-$(H)_3$-10-H-7-R^1-8-R^2-7,8-$C_2B_9H_6$ (**1**—**5**) were prepared by the reaction of the coordinatively unsaturated 16-electron complex $OsCl_2(PPh_3)_3$ with the K^+ salts of *nido*-dicarbaundecaborate anions derived from *ortho*-carborane in benzene at 20 °C (Scheme 1). The synthesis of complexes **1** and **2** was briefly described in our previous communication.[16]

Scheme 1



1—5

Compound	R^1	R^2
1	H	H
2	Me	Me
3	$PhCH_2$	$PhCH_2$
4	$1,2\text{-}C_6H_4(CH_2)_2$	$1,2\text{-}C_6H_4(CH_2)_2$
5	H	Me

A distinctive feature of ruthenium and osmium *exo-nido*-metallacarborane clusters with three B—H...M bonds is the presence of two isomeric forms.[14,16] According to ^1H and ^{11}B NMR spectra (detailed discussion is given below), the open pentagonal plane of the carborane ligand is retained in the isomeric complexes **1**—**5**, and the *extra* H atom is located above this plane. It is significant that, unlike the known "two-bridge" *exo-nido*-metallacarboranes, which usually exhibit equilibrium between *exo-nido*- and *closo*-tautomers in solutions,[2] *exo-nido*-osmacarboranes with mono- and disubstituted *nido*-carborane ligands exist in solutions for long periods as mixtures of only *exo-nido*-isomers. However, upon the synthesis of *exo-nido*-osmacarboranes, minor amounts of *closo*-complexes are formed apart from the major reaction products (a mixture of *exo-nido*-isomers); they result, apparently, from the irreversible *exo-nido*→*closo* rearrangement, which slowly occurs in benzene, and from other side reactions involving the ligand environment at the Os atom. For example, the reaction of $OsCl_2(PPh_3)_3$ with $[7,8\text{-}C_2B_9H_{12}]K^+$ gave, apart from compound **1**, the complexes *closo*-3,3-$(Ph_3P)_2$-3-H-3-Cl-3,1,2-$OsC_2B_9H_{11}$ (**6**) and its dihydride analog *closo*-3,3-$(Ph_3P)_2$-3,3-H_2-3,1,2-$OsC_2B_9H_{11}$ (**7**), which were isolated and identified by ^1H and ^{31}P NMR spectroscopy.

The ^1H NMR spectra of freshly prepared samples of *exo-nido*-osmacarboranes **1**—**5** exhibit a double set of signals similar in nature (see, for example, Fig. 1), indicating the presence of isomers. A typical feature of the spectra is the presence of quadruplet-like resonances due to the *extra* H atom of the *nido*-carborane ligands in the "near" hydride region (δ −0.7—−2.2) and high-field hydride signals with δ −4.5—−16.5, which correspond, as will be shown below, to the bridging hydrides of the B—H...Os bonds. A similar pattern, namely, a double set of signals was also detected in the $^{31}P\{^1H\}$ and $^{11}B/^{11}B\{^1H\}$ NMR spectra of complexes **1**—**5**. In all cases, one set of signals due to equivalent groups and nuclei (*e.g.*, H(5) and H(6), B(5) and B(6), PPh_3, *etc.*) should be assigned to isomers having an additional element of symmetry (we will designate them as *S* isomers), while the other set corresponds to isomers without this element of symmetry (heterinafter designated as *AS* isomers). For example, in the $^{31}P\{^1H\}$ NMR spectra of complexes **1**—**5**, the ^{31}P nuclei in the symmetric *S* isomers are responsible for one and those in asymmetric *AS* isomers are responsible for two broadened singlets. It should be noted that in the case of complex **5**, the asymmetrical *AS* isomer could be expected to form a diastereomeric mixture of complexes, due to the presence of asymmetric monomethyl-substituted *nido*-carborane ligand in the molecule. However, no differences in the chemical shift of signals of any diastereotopic groups were found in its ^1H and $^{31}P\{^1H\}$ NMR spectra.

In this study, pure *S* isomers **2a** and **4a** were isolated by fractional crystallization from a mixture of isomers **2** and **4** along with mixtures enriched in *AS* isomers **2b** and **4b** by ~87 and 95%, respectively. Meanwhile, the mixture of isomers **3** was found to be separated quantitatively into individual compounds **3a** and **3b** by column chromatography on silica gel.

X-Ray diffraction study of two symmetric isomers **2a** and **4a** proved conclusively that the complexes belong to the group of "three-bridge" *exo-nido*-metallacarboranes. The molecular structures of **2a** and **4a** are shown in Fig. 2, and selected bond lengths and angles are presented in Table 1. Since the Os atom in both complexes is linked to one acido ligand (Cl^-) and taking into account that the carborane cage retains the *nido*-geometry with the *extra*-H over the pentagonal face, these complexes should be rationalized as zwitterionic with the Os^{II} atom having a closed 18-electron configuration. Six

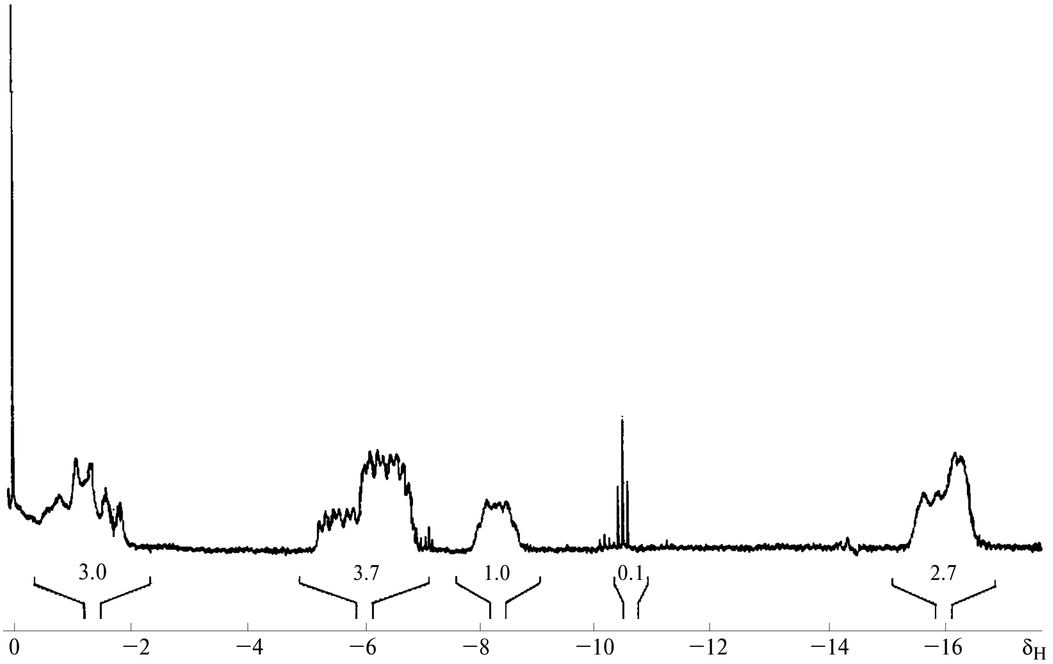


Fig. 1. ^{1}H NMR spectrum (hydride region) of a mixture of *exo*- and *nido*-isomers of complexes **2** (hereinafter, the triplet signals in the hydride region of the spectra correspond to the terminal hydride protons of side *closo*-hydridoosmacarboranes). The integral intensities of signals are indicated.

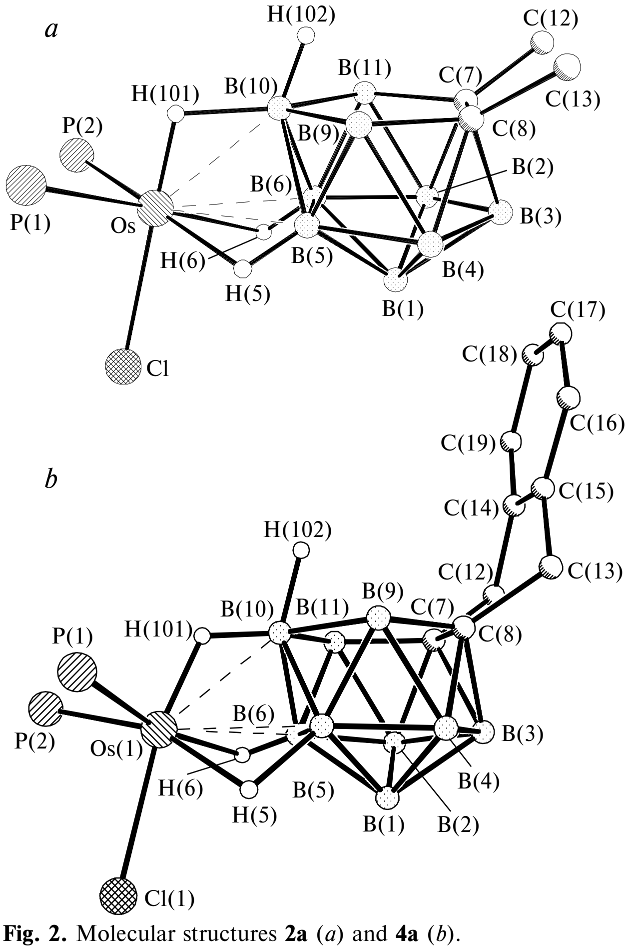


Fig. 2. Molecular structures **2a** (*a*) and **4a** (*b*).

ligands are involved in the octahedral coordination of the metal atom, of which four atoms (P(1), P(2) and H(5), H(6)) are located in the equatorial plane and the other two atoms (H(10) and Cl) occupy the axial positions (in the molecular structures of the complexes, the H(10) and H_{extra} atoms are denoted by H(101) and H(102)). Thus, the geometry of these molecules represents an octahedron, which is, however, slightly distorted. Thus the *trans*-H—Os—P or *trans*-Cl—Os—P angles as well as *cis*-P—Os—P or *cis*-H—Os—H angles (see Table 1) deviate from the standard value (90°) to either direction, which may be due to the rigid structure of the tridentate carborane ligand and to the large size of the PPh_3 group. An interesting feature of *exo*-*nido*-osmacarboranes studied here by X-ray diffraction analysis and the *exo*-*nido*-ruthenacarboranes with similar structures that we studied previously**[14]** is that the *extra* H atom is located exclusively at one boron atom, B(10) (the H_{extra}—B(10) interatomic distances are 1.07(5) and 1.25 Å in molecules **2a** and **4a**, respectively), *i.e.*, unlike the "two-bridge" *exo*-*nido*-metallacarboranes, in this case, the *extra* hydrogen occupies a terminal rather than a μ_2-bridging position over the two B—B bonds of the open face.**[4]**

According to NMR and X-ray diffraction data for complexes **2a** and **4a**, it seemed probable that in the solid state, these complexes have only the symmetric structure with three B—H...Os 2e,3c bonds, whereas in solutions they exist, as a result of intramolecular oxidative addition of Os^{II} at one of the three B—H...Os bonds, as an equilibrium mixture of symmetric and asymmetric isomers with two B—H...Os bonds and the additional B—Os^{IV}—H σ-bond (Fig. 3). At the first

Table 1. Selected bond lengths (*d*) and angles (ω) in complexes **2a** and **4a**

Parameter	**2a**	**4a**
Bond	*d*/Å	
Os—P(2)	2.309(1)	2.312(3)
Os—P(1)	2.312(1)	2.321(3)
Os—Cl	2.406(1)	2.416(3)
Os—B(5)	2.376(5)	2.36(1)
Os—B(6)	2.379(5)	2.41(1)
Os—B(10)	2.275(5)	2.28(1)
Os—H(5)	1.90(6)	1.76
Os—H(6)	1.97(6)	1.86
Os—H(101)	1.79(5)	1.96
C(7)—C(8)	1.611(8)	1.60(1)
C(7)—C(12)	1.533(7)	1.54(1)
C(8)—C(13)	1.536(7)	1.53(1)
C(7)—B(11)	1.598(7)	1.56(2)
C(8)—B(9)	1.592(7)	1.58(2)
B(9)—B(10)	1.857(8)	1.84(2)
B(10)—B(11)	1.850(8)	1.87(2)
B(5)—H(5)	0.98(6)	1.61
B(6)—H(6)	1.10(6)	1.23
B(10)—H(101)	1.46(6)	1.62
B(10)—H(102)	1.07(5)	1.30
Angle	ω/deg	
P(2)—Os—P(1)	96.85(4)	98.8(1)
P(1)—Os—Cl	98.51(4)	96.4(1)
P(2)—Os—Cl	92.70(4)	92.4(1)
P(1)—Os—H(5)	90(2)	89
P(2)—Os—H(5)	173(2)	156
Cl—Os—H(5)	86(2)	64
P(1)—Os—H(6)	173(2)	168
P(2)—Os—H(6)	90(2)	79
Cl—Os—H(6)	82(2)	95
H(5)—Os—H(6)	83(2)	98
P(1)—Os—H(101)	80(2)	74
P(2)—Os—H(101)	87(2)	89
Cl—Os—H(101)	178(2)	170
H(5)—Os—H(101)	94(2)	115
H(6)—Os—H(101)	99(2)	95

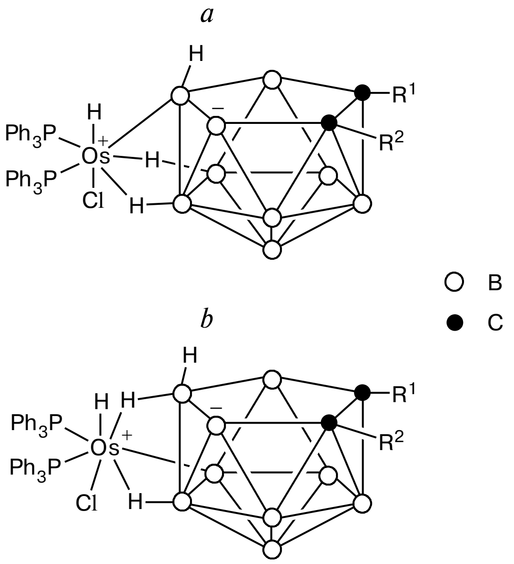


Fig. 3. Structure of symmetric (*a*) and asymmetric (*b*) (one enantiomer is shown) of isomers **1a**,**b**—**5a**,**b** in solutions with the assumption of intramolecular oxidative addition of Os^{II} at one B—H bond in the initial "three-bridge" clusters.

glance, this type of isomerism could stipulate the assignment of signals in the range from δ -15 to -16.5, typical of terminal Os—H hydrides,[21] to the σ-B—Os^{IV}—H fragment in complexes **1**—**5**. When discussing the structure of *exo-nido*-ruthenacarborane complexes,[14] we considered this assignment quite probable, especially taking into account the data on the mechanistic study of catalysis by *exo-nido*-rhodacarboranes,[22] in which the role of catalytically active species was attributed to *exo-nido*-clusters containing both terminal σ-B—Rh^{III}—H and bridging B—H...Rh bonds.

A second type of isomerism conceivable for *exo-nido*-osmacarboranes **1**—**5** is geometric *cis*—*trans*-isomerism of ligand arrangement at the central six-coordinate Os^{II} atom, which is often observed for phosphine- and hydride-substituted metal complexes with an octahedral metal configuration.[23,24] Since according to the X-ray diffraction study of complexes **2a** and **4a**, the Cl atom and one bridging hydride ligand H(10) in symmetric *S* isomers occupy *trans*-positions relative to each other, it might be suggested that in asymmetric *AS* isomers, one phosphine ligand is located in the *trans*-position to H(10), instead of the Cl atom. In terms of the notation accepted for six-coordinate complexes with tridentate ligands of the type [M(tridentate ligand)(monodentate ligand)$_3$],[25] both isomers should be identified as facial octahedral isomers with different types of symmetry, *i.e.*, *S* and *AS* isomers can be designated as *symm*-facial and *asymm*-facial isomers, respectively (Fig. 4).

Finally, one more variant of isomerism in these clusters could be related to migration of the metal atom over the carborane cage. In this case, asymmetric isomers could be described by a structure in which two bridging B—H...Os bonds are formed with participation of the B atoms of the open pentagonal plane, while the third one involves the B atoms from the B_5 bottom belt of the carborane cage (Fig. 5). For this type of asymmetric isomers, the presence of *cis*—*trans* forms also cannot be ruled out, by analogy with the octahedral *fac*-complexes. This type of metal—*nido*-carborane ligand bond is known for, at least, three "two-bridge" *exo-nido*-metallacarboranes: *exo-nido*-9,10-(μ-$AlMe_2$)-9,10-(μ-H)$_2$-7,8-$C_2B_9H_{10}$,[7] *exo-nido*-9,10-[W(CO)$_2$(η-C_5Me_5)]-9,10-(μ-H)$_2$-7,8-Me_2-7,8-$C_2B_9H_8$,[5] and *exo-nido*-10,11-[Cl(Ph_3P)$_2$OsH]-10,11-(μ-H)$_2$-7,9-$C_2B_9H_{10}$.[26] However, this description of "three-bridge" *AS*-isomers **1b**—**5b** appeared to be the least probable because the B(5), B(6), and B(10) atoms on the *nido*-C_2B_9-carborane ligands, most remote from the electropositive C atoms, should possess the highest negative charge and, therefore, they are prone, to a greater extent than other atoms, to transfer electrons from the B—H bond to the metal atom in the formation

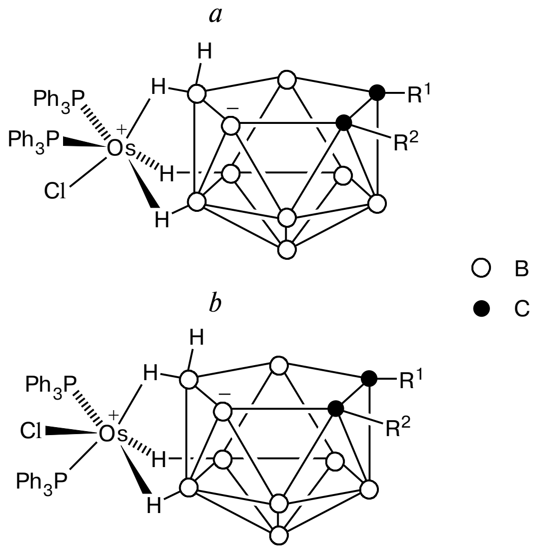


Fig. 4. Structure of symmetric (*S*) (*a*) and asymmetric (*AS*) *fac*-isomers **1a**,**b**—**5a**,**b** (*b*) with the assumption of *cis—trans*-isomerism of ligands at the Os^{II} atom.

of the B—H...M 2e,3c (agostic) bond. For example, in the zwitter-ionic (*closo*-$CB_{11}H_{12}$)$ZrMe_2$(η^5-C_5Me_5) complex,[27] in which the metal atom is also linked to the monocarbon *closo*-CB_{11}-carborane by three B—H...Zr 2e,3c bonds, this bond involves the B atoms from the triangular plane opposing the C atom.

It appeared that the problem of existence of, at least, isomers with σ-B—Os—H bonds could be readily solved based on the analysis of the ^{11}B and $^{11}B\{^1H\}$ NMR spectra of individual isomeric complexes **3a** and **3b**. Thus, in the ^{11}B NMR spectrum of symmetric *S* isomer **3a**, the signal of B(10) shows itself as a broadened doublet ($J_{B,H}$ ≈ 127 Hz), and that for the asymmetric *AS* isomer **3b** is a triplet ($J_{B,H}$ = 89 Hz); in the $^{11}B\{^1H\}$ NMR spectra, these signals were observed as broadened singlets. At the first glance, this could point to the absence of the BH_2 group in symmetric *S* isomers and to the presence of this group in asymmetric isomers, as implied by the first type of isomerism considered above (see Fig. 3). From the ^{11}B NMR spectra of isomeric mixtures **1a**,**b**, **2a**,**b**, **4a**,**b**, or **5a**,**b**, the presence or absence of singlet resonances attributable to the B atoms that might be involved in σ-bonding interaction with the Os atom could not be readily identified, since most of the resonances present were partly overlapped. Meanwhile, the ^{11}B NMR spectrum of the *AS* isomer **3b** recorded under standard conditions contained, among a set of doublets, one separate, somewhat broadened singlet at δ +19.9. However, in an experiment using the line narrowing technique, this unique resonance proved actually to be a doublet with relatively small spin-spin coupling constant ($J_{B,H}$ ≈ 72 Hz), which, in accord with the published data,[28] was finally assigned to the B atom involved in the relatively strong B—H...M bond. In the ^1H NMR spectra of complexes **1**—**5**, attention was attracted by the multiplet pattern of the signals with δ −15 to −16.5, supposed to be due to "terminal" metal hydride groups (see Fig. 1). whereas in the ^1H NMR spectrum of the known metallacarborane complex [RhIrH(μ-σ:η^5-$C_2B_9H_{10}$)$(CO)_3(PPh_3)_2$] with a B—Ir—H bond, whose structure was confirmed by X-ray diffraction analysis, the terminal hydride (δ −11.0) was responsible for a narrow doublet with only a long-range spin-spin coupling constant, $^2J_{H,P}$ = 14 Hz.[28] Unfortunately, although pure asymmetric *AS* isomer **3b** was synthesized, our numerous attempts to grow single crystals for X-ray diffraction study failed. Therefore, to establish the structure of individual isomers **3a** and **3b**, we used special $^1H\{^{11}B\}$ NMR techniques with selective and broad-band boron decoupling and 2D homo- and heteronuclear correlation $^1H\{^{11}B\}$—$^{11}B\{^1H\}$ and $^{11}B\{^1H\}$—$^{11}B\{^1H\}$ NMR spectroscopy.

Analysis of the resulting NMR spectra of isomers **3a** and **3b** allowed the following statements: the $^1H\{^{11}B\}$—$^{11}B\{^1H\}$ NMR spectra (Fig. 6) contain clear-cut cross-peaks between hydride signals (including those in the region of δ −15 to −16.5) and the corresponding signals of the B atoms in the triangular plane of the carborane cage, indicating that they are indeed linked by a B—H bond and that the hydride signals (except for H_{extra}) belong to the bridging hydrogen atoms of B—H...Os groups. The attachment of B(10) to both the *extra* H atom and one of the bridging hydride atoms was also clearly confirmed for both symmetric (**3a**) and asymmetric (**3b**) isomers (see the corresponding cross-peaks in Figs. 6, *a*, *b*); this implies that both complexes contain the BH_2 group. In accord with the published data,[29—31] in the $^{11}B\{^1H\}$ NMR spectra of complexes **3a** and **3b**, the signals of the B atoms involved in the B—H...Os interaction are represented by much narrower lines than others, and in the ^{11}B NMR spectra, these have the smallest

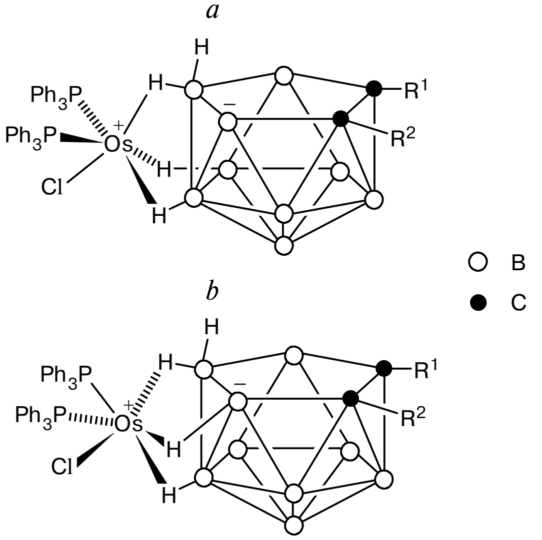


Fig. 5. Structure of symmetric (*a*) and asymmetric (*b*) (one enantiomer is shown) of isomers **1a**,**b**—**5a**,**b** with the assumption of metal migration over the carborane cage.

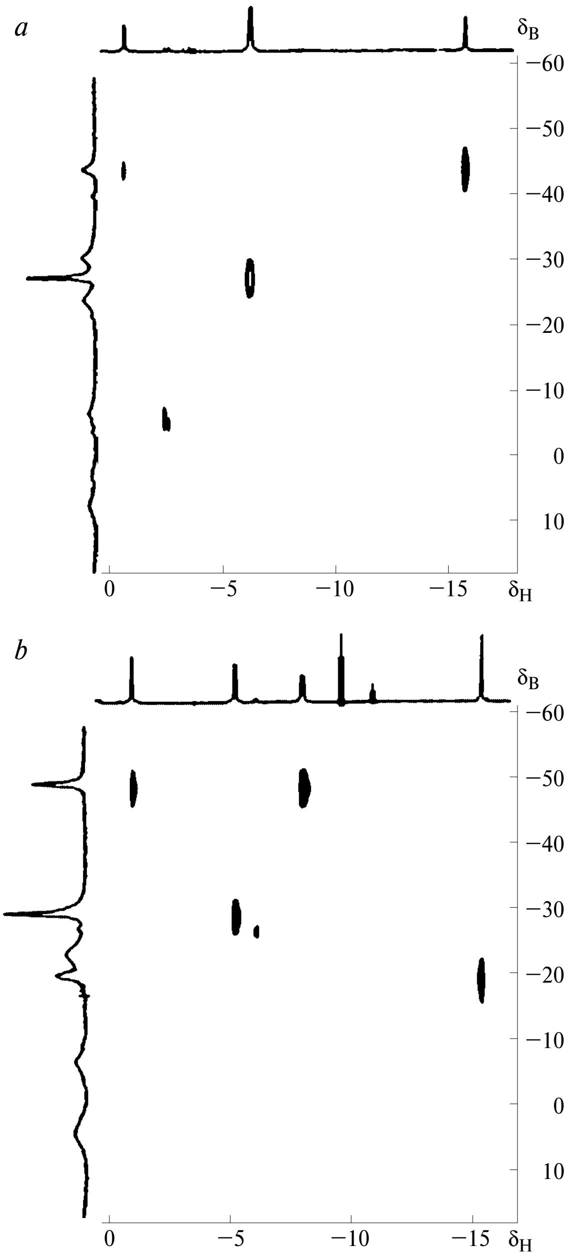


Fig. 6. $^1H\{^{11}B\}$—$^{11}B\{^1H\}$ NMR spectra of isomers **3a** (*a*) and **3b** (*b*).

spin-spin coupling constants ($J_{B,H} \le 100$—105 Hz). The $^{11}B\{^1H\}$—$^{11}B\{^1H\}$ NMR spectrum of the *AS* isomer **3b** has the corresponding cross-peaks exactly for these signals, which confirms that they are due to the B atoms of one triangular plane (Fig. 7).

In view of the foregoing, we excluded from consideration the first of the above-discussed types of isomerism related to the existence of stable complexes with the B—Os^{IV}—H bonds in solutions. It also became obvious that, at least, for the symmetric *S* isomer **3a**, the pronounced shielding of the bridging H(10) atom in the ^1H NMR spectrum and the fact that the ^{11}B NMR signal for B(10) is a broadened doublet with $J_{B,H}$ = 127 Hz

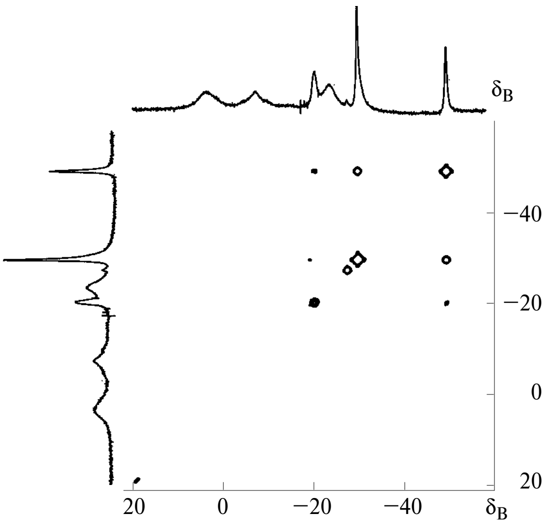


Fig. 7. $^{11}B\{^1H\}$—$^{11}B\{^1H\}$ NMR spectra of isomer **3b**.

(rather than the expected triplet) are caused by the *trans*-influence exerted by the chloro ligand attached to the Os atom. This conclusion is in good agreement with the X-ray diffraction data for complex **2a** and its unsubstituted ruthenium analog *exo-nido*-5,6,10-[Cl(Ph$_3$P)$_2$Ru]-5,6,10-(μ-H)$_3$-10-H-7,8-C$_2$B$_9$H$_8$ (**8**),[14] in which the B(10)—H(101) bond is markedly longer (**2a**, 1.46(6) Å; **8**, 1.43(5) Å) than the B(5)—H(5) bond (**2a**, 1.19(5) Å; **8**, 1.19(5) Å) or B(6)—H(6) bond (**2a**, 1.18(4) Å; **8**, 1.18(4) Å), respectively. (We were unable to perform a similar analysis of the variation of the B—H...Os bond lengths in the structure of complex **4a** because of the lower accuracy of the X-ray diffraction experiment.)

Qualitative analysis of signal distribution in the $^{11}B\{^1H\}$ NMR spectra of complexes **3a** and **3b**, in which the signal intensities are related as 2 : 1 : 2 : 2 : 1 : 1 and 2 : 1 : 1 : 2 : 2 : 1, respectively, indicated that the isomers are still rather similar in symmetry. The most pronounced difference in shielding is observed for the B atoms of the bottom belt of the *nido*-carborane cage, which is due to the nonequivalence of B(5) and B(6) in isomer **3b** ($\delta_{B(5)(B(6))}$ −27.2, $\delta_{B(6)(B(5))}$ −19.9); however, in the spectrum of **3a**, in which these B atoms are equivalent, they account for one signal with double intensity with δ −27.2. It should be noted here that the $^{11}B\{^1H\}$ NMR spectrum of the above-mentioned "two-bridge" *exo-nido*-9,10-[W(CO)$_2$(η-C$_5$Me$_5$)]-9,10-(μ-H)$_2$-7,8-Me$_2$-7,8-C$_2$B$_9$H$_8$, in which the metal atom is coordinated to the *nido*-carborane through two B—H...W bridges involving B atoms of the open face, consists of nine equally intense single resonances, pointing to the complete distortion of the *nido*-carborane symmetry in this complex. In terms of the third type of *exo-nido*-osmacarborane isomerism (see Fig. 5), which also implies the formation of three B—H...Os bonds in asymmetric *AS* isomers with participation of two B atoms of the pentagonal plane, B(10) and B(9) (or B(11)) and one B atom of the bottom belt, B(5) (or B(6)), the $^{11}B/^{11}B\{^1H\}$ NMR spectrum of **3b** should be closely similar to that of *exo-nido*-tungstenacarborane, irrespective of whether this isomer exists in the *trans*- or *cis*-form; however, this is not the case in reality. Thus, this type of isomerism, caused by the possible migration of the metal atom over the carborane cage, was also ruled out from consideration, and the attention was focused on the geometric *cis—trans*-isomerism of ligands in the octahedral coordination of the Os atom.

The most convincing proof of the last-mentioned version was derived from the broad-band boron decoupling $^1H\{^{11}B\}$ NMR studies of isomers **3a** and **3b** with broad-band boron decoupling. First of all, these data made it possible to analyze in detail the long-range $^2J_{H,P}$ constants, which played the crucial role in determining the ligand arrangement at the metal atom with respect to each other in isomeric complexes. It can be seen from the $^1H\{^{11}B\}$ NMR spectra of complexes **3b** and **3a** (Fig. 8 and 9, respectively) that with boron decoupling all the signals in the hydride region of the spectra are converted into multiplets, which can be interpreted rather easily. In the spectra of both isomers, the signals of the *extra* H atoms are doublets with J_{gem} = 12—12.5 Hz, which can be regarded as additional evidence for the absence of the Os—B(10) σ-bond in the symmetric isomer **3a**. In the spectrum of asymmetric isomer **3b** (see Fig. 8), the bridging bottom belt H(5) proton (δ −5.40), located in the equatorial plane in the *trans*-position to the PPh$_3$ group also shows itself as a doublet but with $^2J_{H(5),P(2)}$ = 40.0 Hz. The signal of the second bridging proton H(6) (which occupies the *trans*-position to the chloro ligand), shifted upfield (δ −15.6), is, in the first approximation, a broadened triplet due to the close values of the *cis* spin-spin coupling constants, $^2J_{H(6),P(2)} \approx {}^2J_{H(6),P(1)}$ = 10.5 Hz. The most intricate signal is that corresponding to the axial bridging H(10) atom with δ −8.2, which is a doublet of triplets whose *trans* and *cis* spin-spin coupling constants ($^2J_{H(10),P(1)}$ = 44.2 Hz and $^2J_{H(10),P(2)}$ = 10.0 Hz) are rather close to those observed for the H(5) and H(6) signals, respectively; the additional (triplet) splitting of the H(10) signal is due to the coupling of this proton with the *extra* H atom (J_{gem} = 12.5 Hz).

The NMR data obtained for the isomer **3b** were successfully used to analyze the $^1H\{^{11}B\}$ NMR spectrum of the symmetric isomer **3a** (see Fig. 9). In this case, too, the signal of the axial bridging H atom located in the *trans*-position to the Cl atom is shifted upfield (δ −15.9) and, as the first approximation, it is a broadened quadruplet. The multiplicity of the signal observed is due to coupling of this bridging hydrogen to two equivalent *cis*-PPh$_3$ groups ($^2J_{H(10),P(1)} \approx {}^2J_{H(10),P(2)}$ = 11.5 Hz) and the *extra* H atom with a similar spin-spin coupling

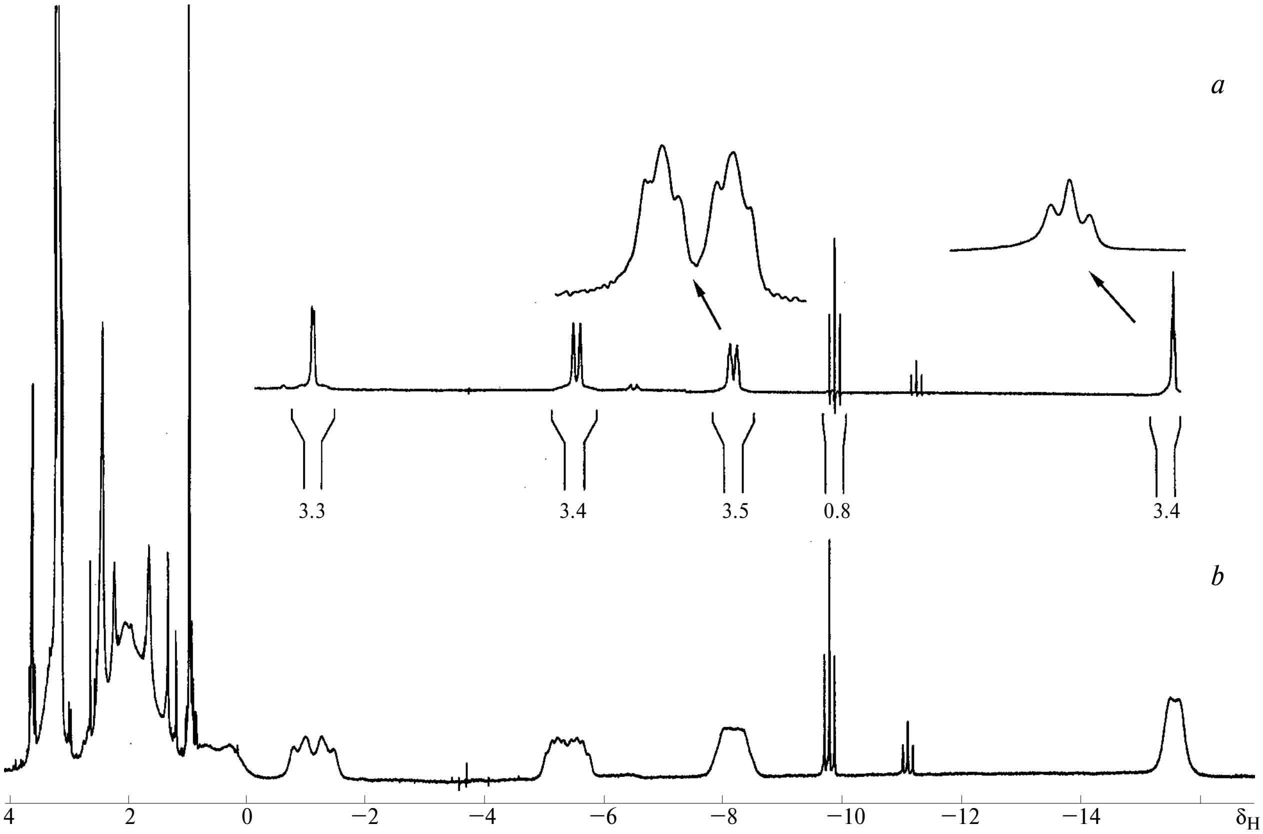


Fig. 8. $^1H\{^{11}B\}$ (*a*) and ^1H (*b*) NMR spectra of isomers **3b** (for the $^1H\{^{11}B\}$ NMR spectrum, only the hydride region is shown). The integral intensities of signals are indicated.

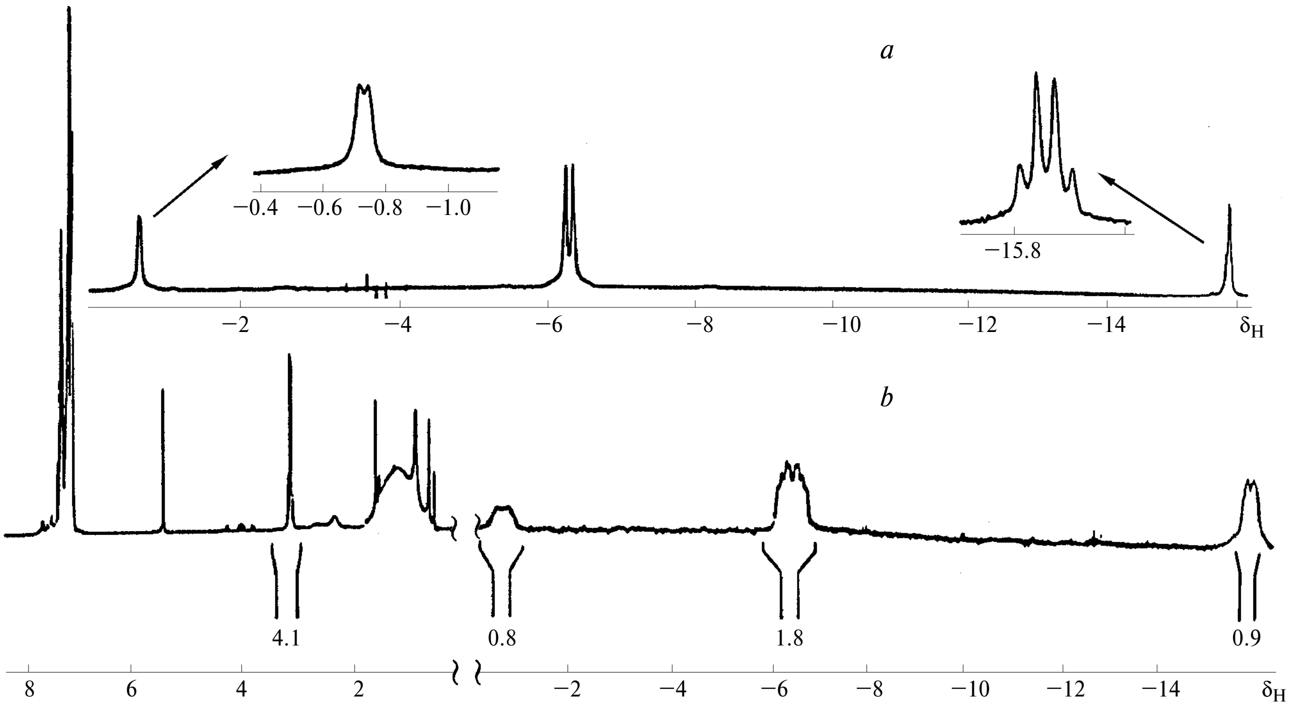


Fig. 9. $^1H\{^{11}B\}$ (*a*) and ^1H (*b*) NMR spectra of isomers **3a** (for the $^1H\{^{11}B\}$ NMR spectrum, only the hydride region is shown). The integral intensities of signals are indicated.

constant, J_{gem} = 12.0 Hz. The signal for the equatorial bridging H atoms of the bottom belt, H(5) and H(6), which are equivalent in this isomer, is a broadened doublet with double intensity and with a *trans* spin-spin coupling constant $^2J_{H(5),P(1)} = {}^2J_{H(6),P(2)}$ = 35.0 Hz.

Thus, the whole set of spectroscopic NMR data obtained for individual *exo*-*nido*-osmacarborane isomers **3a** and **3b** and other complexes of this series with similar structures is consistent with the geometric *cis*—*trans*-isomerism of the ligands in the octahedral coordination sphere of the Os atom.

Experimental

The reaction products were synthesized, isolated, and purified under argon using anhydrous solvents prepared by standard procedures. Chromatography was carried out using Merck silica gel 230—400 mesh (Aldrich). The K^+ salts of dicarbo-undecaborates were prepared by a known method;[32] the starting complex $OsCl_2(PPh_3)_3$ was synthesized as described elsewhere.[33,34] Conventional and correlation (2D) NMR spectra were recorded on a Bruker AMX-400 spectrometer (^1H, 400.13 MHz; ^{31}P, 161.98 MHz; ^{11}B, 128.3 MHz). The integral intensities in the NMR spectra correspond to the expected values. The elemental analysis for the new complexes was carried out at the laboratory of microanalysis of the Institute of Organoelement Compounds of the RAS.

Preparation of *exo*-*nido*-osmacarboranes (general procedure). Anhydrous benzene (10—15 mL) was added to a mixture of $OsCl_2(PPh_3)_3$ (150—200 mg) and the corresponding complex $[7,8\text{-}R^1R^2\text{-}7,8\text{-}C_2B_9H_{10}]^-K^+$ taken with a 10% molar excess, and the reaction mixture was stirred for 2—4 h at ~20 °C. During this period, the color of the mixture changed from dark-green to yellow-brown. The solvent was removed *in vacuo*, and the residue was chromatographed on a column with silica gel, the resulting isomer mixture being eluted with benzene or a CH_2Cl_2—*n*-hexane mixture. The product was recrystallized from a CH_2Cl_2—*n*-hexane or benzene—*n*-hexane mixture. The purity of the products was checked by ^1H and ^{31}P NMR spectroscopy. *exo*-*nido*-Osmacarboranes are colored yellow-orange and are relatively stable in air in the solid state.

Chlorobis(triphenylphosphine)-*exo*-*nido*-[10-hydroorthocarborane-5,6,10-tris(hydrido)]osmium (1a,b). The complex was prepared from $OsCl_2(PPh_3)_3$ (0.2 g, 0.19 mmol) and [*nido*-7,8-$C_2B_9H_{12}]^-K^+$ (0.04 g, 0.23 mmol). The reaction product was chromatographed on a column with silica gel using first an *n*-hexane—benzene (1 : 1) mixture as the eluent; this gave successively a light-yellow fraction containing *closo*-3,1,2-$[(PPh_3)_2OsHCl]$-1,2-$C_2B_9H_{11}$ (**6**) (0.02 g, 12%) and a colorless fraction containing *closo*-3,1,2-$[(PPh_3)_2OsH_2]$-1,2-$C_2B_9H_{11}$ (**7**) (traces) (the NMR data for complexes **6** and **7** fully correspond to those for the samples prepared previously[15]). Then benzene was used to elute the major product, a mixture of isomers **1a**,**b** (~1 : 1) (0.13 g, 78%). Found (%): C, 48.49; H, 4.71; B, 10.09; Cl, 11.35; Os, 19.86; P, 6.43. $C_{38}H_{42}B_9ClOsP_2 \cdot CH_2Cl_2$. Calculated (%): C, 48.36; H, 4.59; B, 10.04; Cl, 11.00; Os, 19.64; P, 6.39. ^1H NMR (CD_2Cl_2 23 °C), δ: 6.00—6.25 (m, Ph, **1a**,**b**); 2.34 (s, CH_{carb}, **1b**); 2.27 (s, 2×CH_{carb}, **1a**); 2.20 (s, CH_{carb}, **1b**); −0.10—−1.60 (q,*,* $H(10)_{extra}$, **1a**,**b**); −4.40—−4.95 (m, H(5) or H(6), **1b**); −5.40—−5.60 (m, H(5), H(6), **1a**); −7.60—−7.78 (m, H(10), **1b**); −14.58—−14.72 (m, H(6) or H(5), **1b**); −15.25—−15.40 (m, H(10), **1a**). ^{31}P NMR (CD_2Cl_2, 23 °C), δ: 0.23 (br.s, P(1), **1b**); −0.21 (s, P(1), P(2), **1a**); −2.38 (br.s, P(2), **1b**).

Chlorobis(triphenylphosphine)-*exo*-*nido*-[7,8-dimethyl-10-hydroorthocarborane-5,6,10-tris(hydrido)]osmium (2a,b). A

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* Hereinafter q* are quadruplet-like multiplets.

mixture of isomers **2a**,**b** (2 : 1) was prepared in a similar way from $OsCl_2(PPh_3)_3$ (0.2 g, 0.19 mmol) and [*nido*-7,8-Me_2-7,8-$C_2B_9H_{10}]^-K^+$ (0.045 g, 0.22 mmol) in a yield of 0.15 g (85%). Found (%): C, 52.89; H, 5.16; B, 10.44; Cl, 3.76; Os, 20.53; P, 6.62. $C_{40}H_{46}B_9ClOsP_2$. Calculated (%): C, 52.69; H, 5.05; B, 10.67; Cl, 3.89; Os, 20.86; P, 6.80. ^1H NMR (CD_2Cl_2, 23 °C), δ: 7.24—6.93 (m, Ph, **2a**,**b**); 1.44 (br.s, Me, **2b**); 1.40 (s, Me, **2b**); 1.39 (br.s, 2×Me, **2a**); −0.10—−1.70 (q*, $H(10)_{extra}$, **2a**,**b**); −5.38—−5.44 (m, H(5) or H(6), **2b**); −6.10—−6.70 (br.dq, H(5), H(6), **2a**, $J_{H—B} \approx 100$ Hz, $J_{H—P} \approx 40$ Hz); −8.20—−8.80 (m, H(10), **2b**); −15.60—−15.80 (m, H(6) or H(5), **2b**); −16.10—−16.30 (m, H(10), **2a**). ^{31}P NMR (CD_2Cl_2, 23 °C), δ: 0.42 (br.s, P(1), **2b**); −0.19 (s, P(1), P(2), **2a**); −2.80 (br.s, P(2), **2b**). Three recrystallizations of 0.12 g of the isomer mixture from a CH_2Cl_2—*n*-hexane mixture gave 0.04 g of pure symmetric isomer **2a**. ^{11}B NMR (CD_2Cl_2), δ: 8.0 (br.d, B(2), B(4) (B(3), B(4) or B(2), B(3)), $J \approx 130$ Hz); −5.5 (br.d, B(3) (B(2) or B(4)), $J \approx 160$ Hz); −23.4 (d, B(9), B(11), $J \approx 168$ Hz); −28.4 (d, B(5), B(6), $J = 103$ Hz); −30.4 (d, B(1), $J = 150$ Hz); −44.5 (br.d, B(10), $J = 150$ Hz).

Chlorobis(triphenylphosphine)-*exo-nido*-[7,8-dibenzyl-10-hydroorthocarborane-5,6,10-tris(hydrido)]osmium (3a,b). A mixture of isomers **3a**,**b** (1.0 : 1.5) was prepared in a similar way from $OsCl_2(PPh_3)_3$ (0.2 g, 0.19 mmol) and [*nido*-7,8-$(C_6H_5CH_2)_2$-7,8-$C_2B_9H_{10}]^-K^+$ (0.075 g, 0.21 mmol) in a yield of 0.14 g (70%). Found (%): C, 58.30; H, 5.49; B, 8.79; Cl, 3.27; Os, 18.05; P, 5.60. $C_{52}H_{54}B_9ClOsP_2$. Calculated (%): C, 58.70; H, 5.08; B, 9.14; Cl, 3.34; Os, 17.87; P, 5.83. The second chromatography of the reaction product on silica gel Silpearl (Czechia) using a CH_2Cl_2—petroleum ether (2 : 1) mixture as the eluent gave 0.065 g (32%) of a pure symmetric isomer **3a** (R_f 0.25) and 0.045 g (22%) of asymmetric isomeric **3b** (R_f 0.35). Found (%) for **3a**: C, 58.51; H, 4.86; Cl, 3.48; Os, 17.65; P, 5.93. ^1H NMR isomer **3a** (CD_2Cl_2, 23 °C), hereinafter, the multiplicity and the spin-spin coupling constants given additionally in parentheses were determined from the $^1H\{^{11}B\}$ NMR spectrum, δ: 7.60—7.00 (m, 40 H, $\underline{Ph}CH_2$+Ph); 3.25—3.35 (d, 1 H, $PhC\underline{H}_AH_B$, $J_{AB} = 15.3$ Hz); 3.05—3.10 (d, 1 H, $PhCH_A\underline{H}_B$, $J_{AB} = 15.3$ Hz); −0.42—−1.70 (q*, 1 H (d, $J_{H,Hgem} = 12.0$ Hz), $H(10)_{extra}$); −6.15—−6.43 (m, 2 H, (d, $J_{H,Ptrans} = 12.0$ Hz), H(5), H(6)); −15.50—−16.00 (m, 1 H, (dt, $J_{H,Hgem} = 12.0$ Hz, $J_{H,Pcis} \approx 11.5\pm0.5$ Hz), H(10)). ^{11}B NMR (CD_2Cl_2), δ: 7.80 (br.s, 2 B, B(2), B(4) (B(3), B(4) or B(2), B(3))); −6.60 (br.s, 1 B, B(3) (B(2) or B(4))); −24.05—−25.00 (d, 2 B, B(9), B(11), $J \approx 172$ Hz); −27.00—−27.90 (d, 2 B, B(5), B(6), $J = 106$ Hz); −30.00—−30.50 (d, 1 B, B(1), $J = 140$ Hz); −43.00—−44.70 (br.d, 1 B, B(10), $J = 127$ Hz). ^{31}P NMR (CD_2Cl_2, 23 °C), δ: 0.70 (s, P(1), P(2)). $^1H\{^{11}B\}$ NMR for isomer **3b** (CD_2Cl_2, 23 °C), δ: 6.80−6.60 (m, 40 H, $\underline{Ph}CH_2$+Ph); 3.00−3.20 (m, 2 H, $PhC\underline{H}_2$); −0.15—−1.95 (q*, 1 H (d, $J_{H,Hgem} = 12.5$ Hz), $H(10)_{extra}$); −5.30—−5.60 (m, 1 H (d, $J_{H,Ptrans} = 40.0$ Hz), H(5) or (6)); −8.10—−8.40 (m, 1 H (dt, $J_{H,Pcis} \approx 10.0$ Hz, $J_{H,Ptrans} = 44.2$ Hz), H(10)); −15.30—−16.00 (m, 1 H (br.t, $J_{H,Hgem} = 12.0$ Hz, $J_{H,Pcis} \approx 10.5$ Hz), H(6) or H(5)). ^{11}B NMR (CD_2Cl_2), δ: 4.18 (br.s, 2 B, B(2), B(4) (B(3), B(4) or B(2), B(3))); −6.50 (br.s, 1 B, B(3) (B(2) or B(4))); −19.50—−21.10 (d, 1 B, B(6) or B(5)), $J = 72$ Hz); −23.2 (br.s, 2 B, B(9), B(11)); −26.2—−28.2 (d, 2 B, B(5) or B(6) + B(1), $J = 106$ Hz); −48.10—−49.90 (br.d, 1 B, B(10), $J = 89$ Hz). ^{31}P NMR (CD_2Cl_2, 23 °C), δ: −0.22 (s, P(1)); −1.36 (s, P(2)).

Chlorobis(triphenylphosphine)-*exo-nido*-[7,8-(1′,2′-xylyl)-10-hydroorthocarborane-5,6,10-tris(hydrido)]osmium (4a,b). A mixture of isomers **4a**,**b** (1 : 1) was prepared in a similar way from $OsCl_2(PPh_3)_3$ (0.15 g, 0.14 mmol) and [*nido*-7,8-(1′,2′-$CH_2C_6H_4CH_2$)-7,8-$C_2B_9H_{10}]^-K^+$ (0.045 g, 0.16 mmol) in a yield of 0.09 g (68%). Found (%): C, 53.10; H, 4.59; B, 8.91; Cl, 9.75; Os, 17.42; P, 5.49. $C_{46}H_{48}B_9ClOsP_2 \cdot CH_2Cl_2$. Calculated (%): C, 52.71; H, 4.72; B, 9.08; Cl, 9.94; Os, 17.76; P, 5.78. ^1H NMR (CD_2Cl_2, 23 °C), δ: 7.70—6.80 (m, $CH_2—C_6\underline{H}_4—CH_2$+Ph, **4a**,**b**); 3.05—3.25 (d, $C\underline{H}_AH_B—C_6H_4—CH_AH_B$, **4b**, $J_{AB} = 15.3$ Hz); 3.05—3.25 (d, $C\underline{H}_AH_B—C_6H_4—C\underline{H}_AH_B$, **4a**, $J_{AB} = 15.3$ Hz); 3.12—3.40 (d, $CH_A\underline{H}_B—C_6H_4—CH_AH_B$, **4b**, $J_{AB} = 15.3$ Hz); 2.90—3.11 (br.d, $CH_A\underline{H}_B—C_6H_4—CH_A\underline{H}_B$, **4a**, $CH_AH_B—C_6H_4—C\underline{H}_A\underline{H}_B$, **4b**, $J_{AB} = 15.3$ Hz); −0.15—−1.90 (m, $H(10)_{extra}$, **4a**,**b**); −5.00—−6.00 (dq, H(5) or H(6), **4b**, $J_{B,H} \approx 100$ Hz, $J_{H,P} \approx 40$ Hz); −5.60—−6.70 (dq, H(5), H(6), **4a**, $J_{B,H} \approx 100$ Hz, $J_{H,P} \approx 42$ Hz); −8.20—−8.70 (m, H(10), **4b**); −15.20—−15.40 (m, H(6) or H(5), **4b**); −15.60—−15.90 (m, H(10), **4a**). ^{31}P NMR (CD_2Cl_2, 23 °C), δ: 0.38 (s, P(1), P(2), **4a**); −0.66 (s, P(1), **4b**); −2.59 (s, P(2), **4b**). Two recrystallizations of the isomer mixture (0.10 g) from a benzene—*n*-hexane mixture gave 0.03 g of pure crystalline symmetric isomer **4a**, whose structure was confirmed by X-ray diffraction analysis.

Chlorobis(triphenylphosphine)-*exo-nido*-[7-methyl-10-hydroorthocarborane-5,6,10-tris(hydrido)]osmium (5a,b). A mixture of isomers **5a**,**b** (1.0 : 1.5) was prepared in a similar way from $OsCl_2(PPh_3)_3$ (0.11 g, 0.01 mmol) and [*nido*-7-Me-7,8-$C_2B_9H_{10}]^-K^+$ (0.021 g, 0.011 mmol) in a yield of 0.085 g (90%). Found (%): C, 51.83; H, 4.87; B, 10.83; Os, 20.67. $C_{39}H_{44}B_9ClOsP_2$. Calculated (%): C, 52.17; H, 4.95; B, 10.84;

Table 2. Crystallographic data, X-ray diffraction experiment details, and refinement parameters for compounds **2a** and **4a**

Parameter	**2a**	**4a**
Formula	$C_{40}H_{46}B_9ClOsP_2$	$C_{46}H_{48}B_9ClOsP_2 \cdot$ $\cdot 2.5C_6H_6$
Molecular mass	911.65	1180.99
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.576(2)	12.817(4)
b/Å	12.9972)	13.136(4)
c/Å	15.376(3)	18.188(7)
α/deg	81.72(1)	93.98(3)
β/deg	75.64(1)	94.21(3)
γ/deg	83.84(1)	110.73(2)
V/Å^3	2020.7(6)	2841(2)
Z	2	2
d_{calc}/g cm^{-3}	1.498	1.380
μ/cm^{-1}	33.30	23.86
Absorption corrections	DIFABS [35]	DIFABS [35]
T_{min}/T_{max}	0.887/1.152	0.839/1.098
$2\theta_{max}$/град	60	46
The number of independent reflections	11831	7819
R_1 (over F for reflections with $I > 2\sigma(I)$)	0.0453	0.0624
The number of reflections	8819	4999
wR_2 (over F^2 for all reflections)	0.1080	0.1471
The number of refined parameters	509	707
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (\alpha P)^2 + \beta P$, where $P = 1/3(F_0^2 + 2F_0^2)$	
α	0.0623	0.0614
β	0.0000	0.0000

Os, 21.19. ^{1}H NMR ($CDCl_3$, 23 °C), δ: 7.28—6.97 (m, Ph, **5a**,**b**); 2.39 (s, CH_{carb}, **5b**); 2.27 (s, CH_{carb}, **5a**); 1.33 (s, Me, **5b**); 1.30 (s, Me, **5a**); −0.30—−1.90 (q*, $H(10)_{extra}$, **5a**,**b**); −5.20—−5.80 (m, H(5) or H(6), **5b**); −6.60—−6.90 (m, H(5), H(6), **5a**); −8.20—−8.50 (m, H(10), **5b**); −15.50—−15.90 (m, H(6) or H(5), **5b**); −16.00—−16.50 (m, H(10), **5a**). ^{31}P NMR ($CDCl_3$, 23 °C), δ: 0.42 (br.s, P(1), P(2), **5a**); −0.04 (br.s, P(1), **5b**); −2.50 (br.s, P(2), **5b**).

X-ray diffraction study of complexes 2a and 4a. A single-crystalline sample of complex **2a** for X-ray diffraction analysis was prepared by crystallization from a CH_2Cl_2—*n*-hexane mixture, and a sample of complex **4a** was obtained by crystallization from a C_6H_6—*n*-hexane mixture. X-Ray diffraction experiments were performed on a Syntex $P2_1$ four-circle automated diffractometer equipped with a low-temperature attachment (graphite monochromator, Mo-Kα-radiation, $\lambda = 0.71073$ Å, $T = 193$ K, θ/2θ scan mode). The crystallographic data and the main refinement parameters for compounds **2a** and **4a** are listed in Table 2. Both structures were solved by the direct method. The positions and thermal parameters for nonhydrogen atoms were refined in the isotropic and then in the anisotropic approximation by the full-matrix least-squares method. The H atoms at boron of the carborane ligands in complexes **2a** and **4a** were identified objectively from the Fourier difference synthesis and included in the refinement in the isotropic approximation (**2a**) and with fixed coordinates (**4a**). The rest H atoms in structures **2a** and **4a** were placed in the geometrically calculated positions and included in the refinement in the "riding" model. The atom coordinates are deposited with the Cambridge Structural Database. In structure **4a**, 2.5 solvation benzene molecules were revealed (two molecules in general positions and one molecule in a special position near the inversion center). All the calculations were performed on a PC using the SHELXTL PLUS 5 program package.[35]

The authors are grateful to S. V. Meshkov for recording 2D correlation NMR spectra for complexes **3a** and **3b**.

This work was supported for the Russian Foundation for Basic Research (Projects Nos. 00-03-32824 and 00-03-32807).

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Received December 8, 2000