Unexpected formation of clusters with a nortricyclene-containing carborane ligand, 1-(η^6-arene)-3-($C_7H_9CH_2O$)-*isonido*-1,2,4-$RuC_2B_8H_9$, in the reaction of 1,1,3-$(PPh_3)_3$-1-H-1,2,4-$RuC_2B_8H_9$ with 2-(hydroxymethyl)norbornadiene in arene solvents*

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Heating of 1,1,3-$(PPh_3)_3$-1-H-1,2,4-$RuC_2B_8H_9$ with 2-(hydroxymethyl)bicyclo[2.2.1]hepta-2,5-diene in arene solvents (benzene, toluene, or mesitylene) unexpectedly afforded the ruthenium arene complexes 1-(η^6-arene)-3-($C_7H_9CH_2O$)-*isonido*-1,2,4-$RuC_2B_8H_9$ containing the nortricyclene fragment in the carborane ligand.

Key words: *isonido*-ruthenacarboranes, π-arene complexes, norbornadiene, intramolecular cyclization, nortricyclene.

In our earlier studies,[1,2] we have prepared *closo*-($\eta^{3,2}$-norbornadienyl)rhodacarboranes, which are efficient catalysts of olefin hydrogenation,[3] using the thermal replacement of the phosphine ligands in the known hydride complexes *closo*-3,3-$(PPh_3)_2$-3-H-1-R-2-R´-3,1,2-$RhC_2B_9H_9$ (R, R´ = H, Alk)[4] by the carbocyclic diene ligands, *viz.*, 2-(α-hydroxyalkyl)bicyclo[2.2.1]hepta-2,5-dienes. Under the reaction conditions used (mild heating of the reagents in benzene), the latter readily underwent deoxygenation in the coordination sphere of the metal atom to form ligands of the $\eta^{3,2}$-allylolefinic type. As part of these studies, we examined the reaction of the known 11-vertex ruthenacarborane 1,1,3-$(PPh_3)_3$-1-H-1,2,4-$RuC_2B_8H_9$ (**1**)[5,6] with 2-(hydroxymethyl)bicyclo[2.2.1]hepta-2,5-diene (**2**).

Results and Discussion

Since complex **1** is, in fact, an isoelectronic analog of the above-mentioned *closo*-bis(triphenylphosphine)hydridorhodacarboranes and, moreover, has a similar ligand environment about the metal atom (two triphenylphosphine ligands and one hydride ligand), the analogous reaction starting from **1** was expected to afford new 11-vertex ($\eta^{3,2}$-norbornadienyl)-*isonido*-ruthenacarboranes. However, heating of a mixture of **1** and **2** in arene solvents unexpectedly gave rise to arene ruthenacarborane complexes. In this reaction, diene **2** proved to undergo partial cyclization to form a nortricyclene derivative, which was subsequently attached at position 3 of the carborane ligand formally replacing the PPh_3 group (Scheme 1). Thus, heating of a mixture of **1** and **2** in benzene, toluene, or mesitylene was found to yield the 1-(η^6-arene)-3-($C_7H_9CH_2O$)-*isonido*-1,2,4-$RuC_2B_8H_9$ complexes (**3a—c**) as the final products, which, however, exist as complex mixtures of stereoisomers and geometric isomers.

Reaction products **3a—c** were isolated from the reaction mixtures by column chromatography on silica gel as air-stable crystalline compounds in 43—47% yields (after recrystallization from a CH_2Cl_2—hexane mixture). In none of the cases, were the mixtures of isomeric complexes separated into individual compounds by crystallization and/or TLC on silica gel and, therefore, their structures were studied by a combination of IR and NMR spectroscopic methods confirmed by single-crystal X-ray diffraction of complex **3c**.

The ^1H NMR spectra of compounds **3a—c** appeared to be rather complicated and poorly informative. In the region of aliphatic protons (δ 1.0—2.4), the spectra have numerous overlapping multiplets characteristic of a complex mixture of saturated polycyclic systems, although

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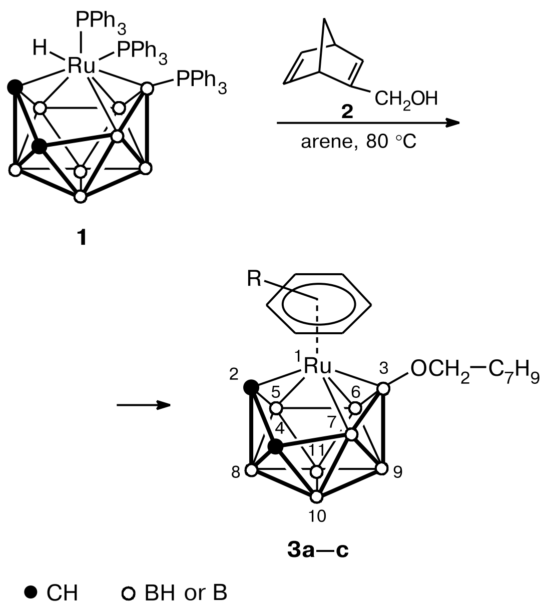
Scheme 1



R = H (**3a**), Me (**3b**), 1,3,5-Me$_3$ (**3c**);
C_7H_9 is nortricyclenyl

rather simple signals are observed at lower field (δ 3.9—5.0). The latter signals resemble AB multiplets, which could be assigned to the exocyclic CH_2O or CH_2OH groups of ligand **2** that underwent transformation. The same region of the spectrum consists of broadened CH signals of the carborane ligand along with more intense signals characteristic of the π-coordinated arene ligands (in the spectra of complexes **3b,c**, signals of the methyl substituents in the arene ligands are observed in the region of aliphatic protons). It should be noted that, unexpectedly, the ^{1}H and ^{31}P{^{1}H} NMR spectra of compounds **3a—c** revealed no signals of the PPh$_3$ group, which was present at position 3 of the carborane ligand in the starting complex **1**. Moreover, although the ^{1}H NMR spectra of the complexes displayed several sets of signals similar in positions, multiplicities, and intensities, which indicate that each of these compounds consists of a mixture of isomeric species in approximately the same ratio, the ^{11}B/^{11}B{^{1}H} NMR spectra of complexes **3a—c** could not confirm this fact. The signals of the C_2B_8 carborane ligand in the ^{11}B NMR spectra of all complexes are observed as seven sharp doublets at δ from –45 to +4.6 and one singlet at δ 70—72, which is indicative of the presence of the substituent at the coordinatively unsaturated boron atom.[7] The assignments of the signals in the ^{11}B/^{11}B{^{1}H} NMR spectra were made by analogy with structurally similar 11-vertex 1-(η^6-arene)-*isonido*-ruthenacarboranes.[6]

The IR spectra of complexes **3a—c** show strong bands at 2502—2522 cm^{-1} (ν(BH)) and 1202—1207 cm^{-1} (ν(C—O)). The medium-intensity bands observed at 1446—1461 cm^{-1} were assigned to the ν(C=C) vibrations of the η^6-coordinated arene ligands by analogy with the published data.[8,9]

The conventional ^{13}C NMR spectra and the ^{13}C{^{1}H} NMR spectra recorded using both the standard and DEPT (for **3a** and **3c**) techniques proved to be excep-

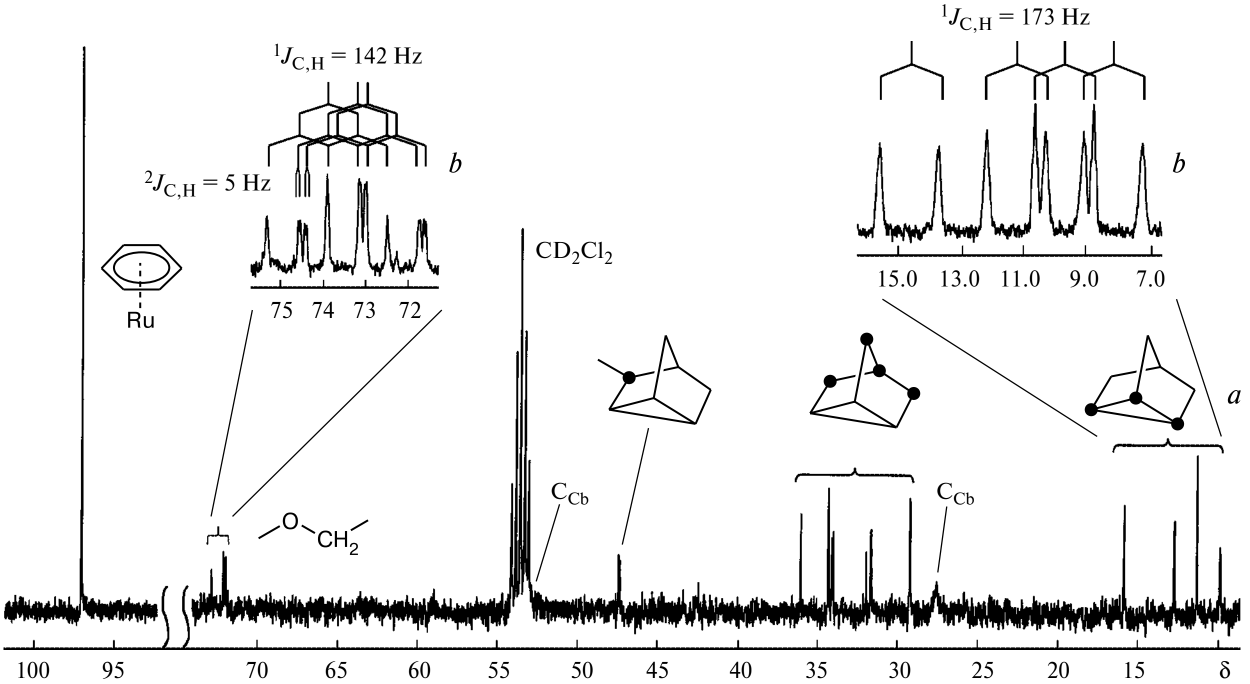


Fig. 1. ^{13}C{^{1}H} NMR spectrum (*a*) and fragments of the ^{13}C NMR spectrum (*b*) of complex **3a**; C_{Cb} is the C atom of the carborane cage.

tionally informative for establishing the structures and isomerism of the complexes obtained. The $^{13}C\{^1H\}$ NMR spectrum and fragments of the ^{13}C NMR spectrum of complex **3a** are shown in Fig. 1. Since the $^{13}C\{^1H\}$ and ^{13}C NMR spectra of compound **3a** differ only slightly from those of **3c** due to the similar nature of the arene ligands, the spectroscopic data for complex **3a** only will be discussed in detail below.

In the $^{13}C\{^1H\}$ NMR spectrum of compound **3a**, a group of eight partially overlapped CH signals at δ 9.8—15.9 is particularly noteworthy. These signals in the ^{13}C NMR spectrum are observed as clear doublets with $^1J_{C,H}$ = 173 Hz (see Fig. 1). The high-field CH signals with such large coupling constants are indicative of the presence of the cyclopropane-containing fragments.[10] This fact coupled with the observation of both resonances of the cyclic CH_2 and CH groups at δ 29—36 with characteristic $^1J_{C,H}$ = 128—152 Hz in the $^{13}C\{^1H\}$ NMR spectrum of **3a** indicates that norbornadiene ligand **2** was, evidently, transformed into a nortricyclene derivative in the course of the reaction. Based on the total number of signals belonging to the cyclopropane-containing fragments and the cyclic CH_2 and CH groups, it was concluded that complex **3a** (and, correspondingly, complexes **3b,c**) exists in solutions as three isomers **A**, **B**, and **C** (Fig. 2).

Other $^{13}C\{^1H\}$ NMR spectroscopic data for complexes **3a** and **3c** are also in good agreement with the above conclusion. Thus, three separate signals of the exocyclic CH_2O fragments of isomers **A—C** are observed at δ 72—73. There are also signals of the endocyclic C atoms directly bound to these fragments at δ 25.8 (1 C, **A**), 47.4, and 47.5 (2 CH, **B** and **C**). The assignment of these signals as well as of the signals of the nonequivalent C atoms of the carborane ligand whose positions are identical in the spectra of all three isomers of complexes **3a** and **3c** (**A**, **B**, and **C**) (see the Experimental section) was made based on the $^{13}C\{^1H\}$—^1H correlation 2D NMR spectra and a comparative analysis of the $^{13}C\{^1H\}$ NMR spectra measured with the use of the DEPT technique and the conventional ^{13}C NMR spectra.

It is known[11] that the *nido*-$C_2B_8H_{12}$ carborane molecule is chiral and can exist in the optically active form. Recently, a series of 11-vertex 1-(η^6-C_6Me_6)-*isonido*-1,2,4-ruthenacarboranes containing the *B*-substituted *nido*-$C_2B_8H_9R$ ligands (R = 5-Br and 7-Br) have been separated into enantiomers using preparative HPLC on chiral columns.[12] Since the starting complex **1** was synthesized using *nido*-$C_2B_8H_{12}$ carborane in the racemic form,[7] products **3a—c** were also racemic. However, it should be noted that the nortricyclene substituents in complexes **3a—c** have different stereochemistry. For example, the nortricyclene substituent in isomers of type **A** is achiral and, hence, these isomers exist as racemic mixtures of enantiomers. By contrast, this substituent in isomers of types **B** and **C** is chiral and, hence, isomers of this types are racemic diastereomers. In this connection, the results of single-crystal X-ray diffraction analysis of complex **3c** (Fig. 3), whose crystals were grown by slow crystallization from a dilute solution in MeCN, are of considerable importance.

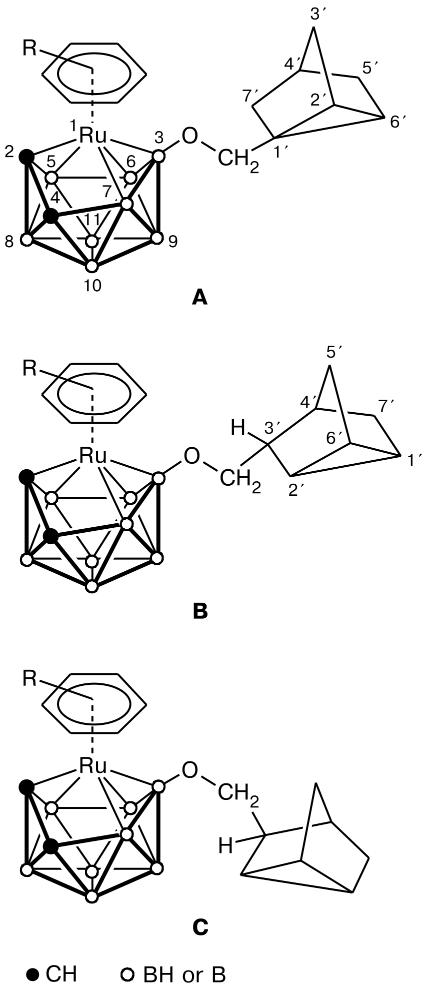


Fig. 2. Structures of isomers **A—C** of complexes **3a—c**.

Analysis of difference Fourier syntheses revealed that the tricyclene substituent is disordered and can be described as a superposition of two fragments, which differ in the position of the three-membered ring with respect to the exocyclic CH_2O group. We succeeded in refining the positions of all atoms of the tricyclene substituents of these fragments, which allowed us to establish that the centrosymmetrical single crystal of the complex consists of two different molecules in a ratio of 1 : 1, *viz.*, the **A**-type isomer and the **C**-type diastereomer with the *RS* configuration relative to the asymmetrical C(O3′) and C(2) atoms, respectively (see Fig. 3, *b*). The configuration of the C(2) atom in the carborane fragment of molecule **3c** was determined using a procedure, which has been developed earlier for the configuration assignments

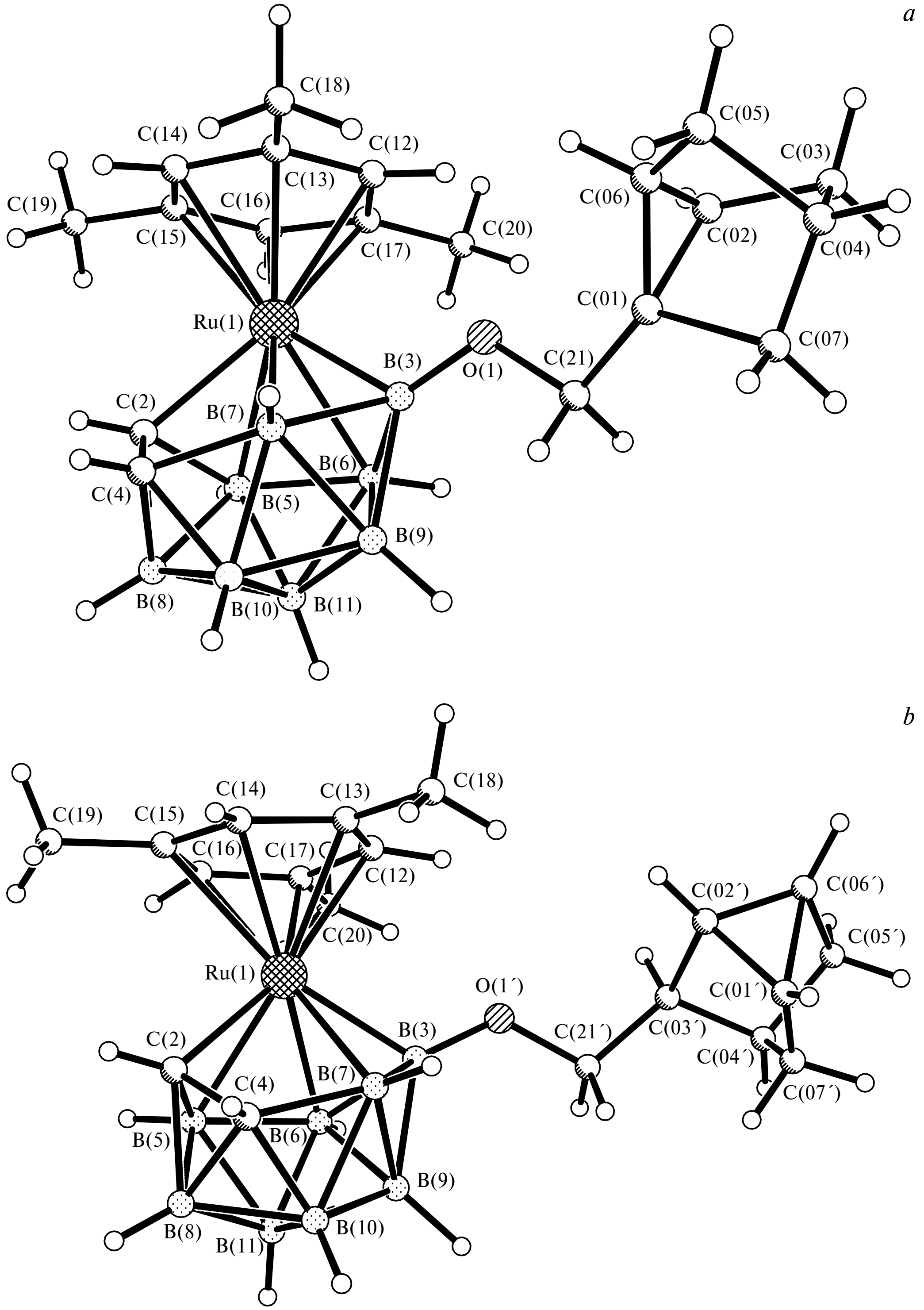


Fig. 3. Molecular structures of isomer **A** (*a*) and one of the enantiomers of isomer **C** (*b*).

in metallacarboranes with an asymmetrical carborane ligand.[13] Since attempts to reveal the positions of the atoms for the second diastereomer failed, it can be assumed that crystallization of complex **3c** was accompanied by spontaneous separation of diastereomers **B** and **C**, one of which cocrystallized together with the **A**-type isomer. The selected bond lengths and bond angles for isomers **A** and **C** of complex **3c** are given in Table 1 (due to disorder of the tricyclene substituent in molecule **3c**, the accuracy of the determination of the C-atom positions is

Table 1. Selected bond lengths (*d*) and bond angles (ω) in complex **3c**

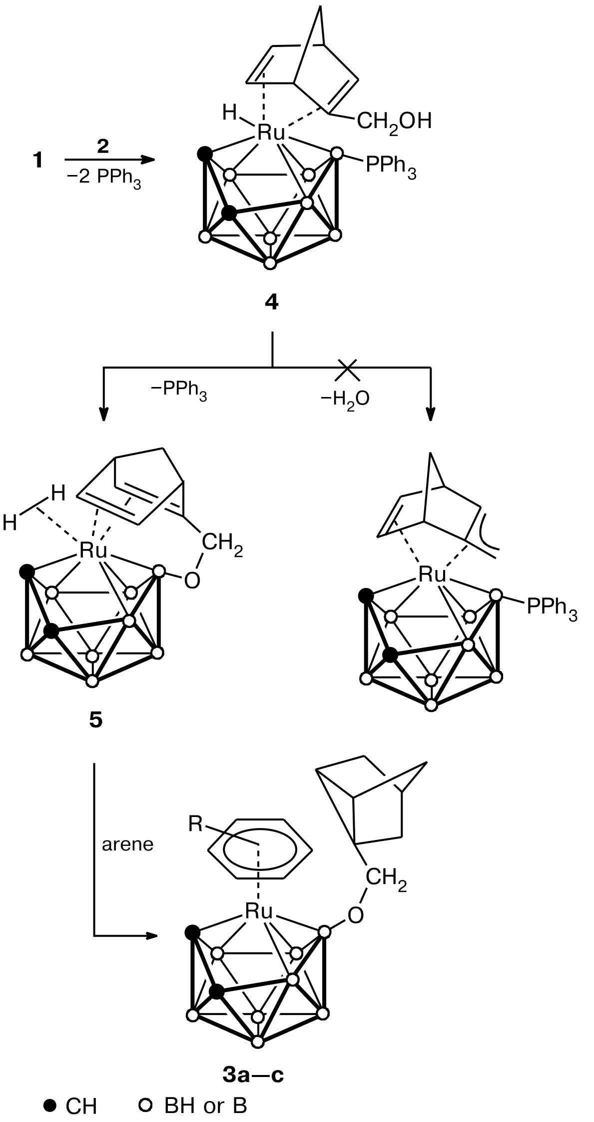
Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg
Ru(1)—C(2)	2.096(4)	Ru(1)—C(15)	2.330(4)	C(4)—C(2)—B(5)	112.3(4)
Ru(1)...C(4)	2.723(4)	Ru(1)—C(16)	2.273(4)	B(6)—B(3)—B(7)	98.1(3)
Ru(1)—B(3)	2.065(5)	Ru(1)—C(17)	2.204(4)	C(2)—C(4)—B(7)	106.2(4)
Ru(1)—B(5)	2.308(5)	C(2)—C(4)	1.498(7)	C(2)—B(5)—B(6)	116.1(3)
Ru(1)—B(6)	2.293(4)	B(3)—O(1)	1.368(8)	B(3)—B(6)—B(5)	118.1(3)
Ru(1)—B(7)	2.332(5)	B(3)—O(1´)	1.401(8)	C(4)—B(7)—B(3)	130.2(4)
Ru(1)—C(12)	2.210(4)	O(1)—C(21)	1.458(12)	B(3)—O(1)—C(21)	121.4(6)
Ru(1)—C(13)	2.242(4)	O(1´)—C(21´)	1.393(12)	C(21´)—O(1´)—B(3)	125.2(7)
Ru(1)—C(14)	2.255(4)				

low and, correspondingly, the C—C bond lengths are distorted; therefore, it is unreasonable to discuss the structural features of this fragment in isomers **A** and **C** and, hence, its geometric parameters are not presented in Table 1). To summarize, it should be noted that complex **3c** studied by X-ray diffraction belongs to a rare group of 11-vertex *isonido*-metallahetaroborane clusters,[6,12,14—19] which are characterized by the four-membered open plane and the presence of three vertices in the carborane cage that have cluster connectivities of 4. In both isomers of complex **3c** (see Fig. 3), the C(2), C(4), and B(3) atoms and the Ru(1)C(2)C(4)B(7) plane serve as such vertices and the plane, respectively.

Based on the possible pathway leading to the synthesis of complexes **3a—c** (Scheme 2), it may be assumed that heating of compound **1** resulted in the complete replacement of the phosphine ligand at the metal atom by diene ligand **2**, apparently, already in the first step of the reaction to form an intermediate complex (**4**).

It should be emphasized that the reaction of isoelectronic *closo*-$(PPh_3)_2HRhC_2B_9H_{12}$ with diene **2** involves the analogous coordination of the diene to the Rh center followed, apparently, by intramolecular protonation at the hydroxy group with elimination of the water molecule to form, finally, the allylolefin complex *closo*-($\eta^{3,2}$-$C_7H_7CH_2$)$RhC_2B_9H_{11}$.[1,20] The transformation of complex **4** proceeds differently, and the expected allylolefinic analog *isonido*-($\eta^{3,2}$-$C_7H_7CH_2$)$RuC_2B_8H_{10}$ is not produced, which is, most likely, associated with the difference in the nature of the hydride ligands, *i.e.*, with the difference in the acidic-basic properties in the starting isoelectronic ruthenium and rhodium complexes. For example, it is known that under specific conditions, the terminal hydride ligand in *closo*-bis(phosphine)hydridorhodacarboranes exhibits the pronounced acidic properties.[21] Evidences in favor of the analogous properties of the hydride ligand in complex **1** are lacking in the literature. Taking into account that coordination of diene **2** to transition metals should lead to a substantial increase in the nucleophilicity of the O atom of the hydroxymethyl group,[22] we believe that the next step of the reaction involves the nucleophilic displacement of the PPh_3 group of the carborane ligand by the alkoxy group of ligand **2** accompanied by the transfer of the proton from the OH group to terminal metal hydride giving rise to a non-

Scheme 2



classical complex with molecular hydrogen (**5**). Numerous examples of complexes with molecular hydrogen were published in the literature.[23,24] Although $[L_nM(H_2)(L')/(L'')_2]^+$ (L′ is diene and L″ is olefin) are considered as kinetically unstable compounds, because the proton is readily transferred from the coordinated H_2 ligand to the diene/olefin double bonds, some of these compounds involving Group VI (Cr, Mo, W)[25,26] or VIII (Ru)[27] metals were detected by low-temperature IR and NMR spectroscopy. Moreover, the reaction of the cationic complex $[Cp^*Ru(H_2O)(\eta^4\text{-NBD})]^+BF_4^-$ (NBD is norbornadiene) with H_2 in benzene studied recently gave nortricyclene and the ruthenium arene cationic complex $[Cp^*Ru(\eta^6\text{-}C_6H_6)]^+BF_4^-$ as the final products.[28] The authors of the cited study believed that this reaction proceeded through the intermediate formation of a structurally similar complex with molecular hydrogen, *viz.*, $[Cp^*Ru(H_2)(\eta^4\text{-NBD})]^+$. Based on the results of the study,[28] we assumed that the analogous intramolecular transfer of hydrogen may proceed in complex **5** giving rise to the nortricyclene fragment. While being eliminated from the coordination sphere of the metal atom, the latter is nevertheless bound to the carborane ligand through the CH_2O bridge. The coordination site that becomes free is occupied by the η^6-coordinating arene ligand with the result that the metal atom in products **3a—c** retains a 18-electron shell. The addition of coordinated H_2 at the double bonds of the diene ligand in complex **5** on the *endo* side, the occurrence of which can be assumed taking into account the results of the earlier study,[25] does not contradict the formation of three isomers **A—C**, because the starting complex **1** and carbinol **2** were used in the reaction as racemates.

In conclusion, it should be noted that the 12-vertex binuclear *closo*-cluster $RhW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)_2\{\eta^5\text{-}C_2B_9H_8(C_7H_9)Me_2\}$[29] has been the only known example of metallacarboranes containing the nortricyclene substituent in the C_2B_9 carborane ligand, whose structure was established by X-ray diffraction analysis. However, the tricyclene structure in the latter complex was formed *via* the addition of the norbornadiene ligand (from the molecule of the starting $[Rh(PPh_3)_2(C_7H_8)][PF_6]$ complex) at the B—H bond of the carborane ligand, which was accompanied by partial cyclization of the diene.

Experimental

The reactions were carried out under argon using anhydrous solvents, which were prepared according to standard procedures. The reactions products were isolated by column chromatography and purified by crystallization in air. Chromatography was performed on silica gel (Merck, 230—400 μm). The starting complex **1** [6] and carbinol **2** [30] were synthesized according to methods described in the literature. The NMR spectra were recorded on a Bruker AMX-400 spectrometer (^{1}H, 400.13 MHz; ^{31}P, 161.98 MHz; ^{11}B, 128.33 MHz; ^{13}C, 100.51 MHz). The IR spectra were measured on a Specord M-82 instrument in KBr pellets. Elemental analysis of the compounds synthesized was carried out at the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

Synthesis of complexes 3a—c (general procedure). Diene **2** (0.18 g, 1.5 mmol) was added to a solution of complex **1** (0.5 g, 0.5 mmol) in anhydrous arene solvent (25 mL). The solution was heated at 80 °C for 3 h with stirring using a magnetic stirrer. The color of the reaction mixture gradually changed from dark-red to orange. The solvent was distilled off *in vacuo* and the residue was chromatographed on a column with silica gel by eluting a mixture of isomeric reaction products (orange band) with benzene. After removal of the solvent, the residue was twice recrystallized from a CH_2Cl_2—*n*-hexane mixture.

1-(η^6-Benzene)-3-(tricyclo[2.2.1.0^{2,6}]hept-1(3)-ylmethoxy)-*isonido*-1,2,4-ruthenadicarbaundecaborane (3a) was prepared according to the general procedure from compounds **1** (0.2 g) and **2** (0.07 g) as orange crystals in a yield of 0.04 g (47%). Found (%): C, 45.12; H, 6.25; B, 20.57. $C_{16}H_{26}B_8ORu$. Calculated (%): C, 45.55; H, 6.21; B, 20.50. IR, ν/cm^{-1}: 3054 (C—H$_{Ar}$); 2507 (B—H); 1446 (C=C$_{Ar}$); 1207 (C—O). ^{1}H NMR (CD_2Cl_2), δ; hereinafter, the spectra are given for a mixture of isomers **A—C**, C_{Cb} is the C atom of the carborane cage): 5.84 (br.s, 18 H, C_6H_6, **A—C**); 4.68 (br.s, 3 H, CH_{Cb}, **A—C**); 4.44 (d, 1 H, $C\underline{H}_AH_BO$, $J_{A,B}$ = 11 Hz, **A**); 4.41 (d, 1 H, $CH_A\underline{H}_BO$, $J_{A,B}$ = 11 Hz, **A**); 4.15 (dd, 1 H, $C\underline{H}_AH_BO$, ^3J = 3 Hz, $J_{A,B}$ = 7 Hz, **B**); 4.12 (dd, 1 H, $CH_A\underline{H}_BO$, ^3J = 3 Hz, $J_{A,B}$ = 7 Hz, **B**); 4.03 (d, 1 H, $C\underline{H}_AH_BO$, $J_{A,B}$ = 8 Hz, **C**); 3.98 (d, 1 H, $CH_A\underline{H}_BO$, $J_{A,B}$ = 8 Hz, **C**); 3.91 (br.s, 3 H, $C_{Cb}H$, **A—C**); 2.10—1.00 (m, 27 H, $C_7\underline{H}_9$, **A—C**). ^{11}B NMR (C_6D_6), δ: 71.6 (s, 1 B, B(3)); 4.6 (d, 1 B, B(9), $^1J_{B,H}$ = 137 Hz); –1.8 (d, 1 B, B(6), $^1J_{B,H}$ = 168 Hz); –2.7 (d, 1 B, B(5), $^1J_{B,H}$ = 168 Hz); –11.6 (d, 1 B, B(10), $^1J_{B,H}$ = 153 Hz); –26.1 (d, 1 B, B(8), $^1J_{B,H}$ = 168 Hz); –29.6 (d, 1 B, B(11), $^1J_{B,H}$ = 148 Hz); –45.6 (d, 1 B, B(7), $^1J_{B,H}$ = 148 Hz). ^{13}C NMR (CD_2Cl_2), δ: 94.9 (d, C_6H_6, $^1J_{C,H}$ = 177 Hz, **A—C**); 72.9 (t, CH_2O, $^1J_{C,H}$ = 142 Hz, **A**); 72.2 and 72.0 (both td, CH_2O, $^1J_{C,H}$ = 142 Hz, ^2J = 5 Hz, **B**, **C**); ~53 (br.d, C_{Cb}, $^1J_{C,H} \approx$ 170 Hz); 47.5 and 47.4 (both d, C(3), $^1J_{C,H}$ = 128 Hz, **B**, **C**); 36.1 (t, C(7), $^1J_{C,H}$ = 130 Hz, **A**); 34.35 and 34.33 (both t, C(5) or C(7), $^1J_{C,H}$ = 131 Hz, **B**, **C**); 34.14 and 34.05 (both t, C(7) or C(5), $^1J_{C,H}$ = 134 Hz, **B**, **C**); 31.9 (d, C(4), J = 152 Hz, **A**); 31.67 and 31.62 (both d, C(4), J = 148 Hz, **B**, **C**); 29.22 and 29.17 (both t, C(3), C(5), $^1J_{C,H}$ = 128 Hz, **A**); 27.6 (br.d, C_{Cb}, $^1J_{C,H}$ = 177 Hz); 25.8 (s, C(1), **A**); 15.9 (d, C(2), C(6), $^1J_{C,H}$ = 175 Hz, **A**); 12.8, 12.7, 11.3, 9.9, and 9.8 (all d, C(1), C(2), C(6), $^1J_{C,H}$ = 173 Hz, **B**, **C**; the signal at δ 11.3 has a double intensity).

1-(η^6-Toluene)-3-(tricyclo[2.2.1.0^{2,6}]hept-1(3)-ylmethoxy)-*isonido*-1,2,4-ruthenadicarbaundecaborane (3b) was prepared according to the general procedure from compounds **1** (0.2 g) and **2** (0.07 g) as orange crystals in a yield of 0.04 g (46%). Found (%): C, 46.52; H, 6.16; B, 19.86. $C_{17}H_{28}B_8ORu$. Calculated (%): C, 46.84; H, 6.47; B, 19.84. IR, ν/cm^{-1}: 3064 (CH$_{Ar}$); 2502 (B—H); 1461 (C=C$_{Ar}$); 1202 (C—O). ^{1}H NMR (C_6D_6), δ: 5.40—4.80 (m, 15 H, H$_{Ar}$, **A—C**); 4.85 (m, 2 H, CH_2O, **A**); 4.60 (m, 2 H, CH_2O, **B**); 4.46 (m, 2 H, CH_2O, **C**); 4.09 (br.s, 3 H, $C_{Cb}H$); 3.90 (br.s, 3 H, $C_{Cb}H$); 2.40—1.10 (series of m, 27 H, C_7H_9, **A—C**); 1.69, 1.65, and 1.64 (all s, 9 H, Me, **A—C**).

^{11}B NMR (C_6D_6), δ: 71.3 (s, 1 B, B(3)); 4.3 (d, 1 B, B(9), $^1J_{B,H}$ = 138 Hz); –1.7 (d, 1 B, B(6), $^1J_{B,H}$ = 136 Hz); –2.1 (d, 1 B, B(5), $^1J_{B,H}$ = 140 Hz); –11.6 (d, 1 B, B(10), $^1J_{B,H}$ = 162 Hz); –26.1 (d, 1 B, B(8), $^1J_{B,H}$ = 162 Hz); –29.8 (d, 1 B, B(11), $^1J_{B,H}$ = 148 Hz); –45.3 (d, 1 B, B(7), $^1J_{B,H}$ = 142 Hz).

1-(η^6-1,3,5-Trimethylbenzene)-3-(tricyclo[2.2.1.0^{2,6}]hept-1(3)-ylmethoxy)-*isonido*-1,2,4-ruthenadicarbaundecaborane (3c) was prepared according to the general procedure from compounds **1** (0.2 g) and **2** (0.07 g) as orange crystals in a yield of 0.04 g (43%). Found (%): C, 48.73; H, 6.94; B, 18.84. $C_{19}H_{32}B_8ORu$. Calculated (%): C, 49.18; H, 6.95; B, 18.64. IR, ν/cm^{-1}: 3054 ($C—H_{Ar}$); 2522 (B—H); 1451 ($C=C_{Ar}$); 1197 (C—O). ^{1}H NMR (CD_2Cl_2), δ: 5.38 (m, 9 H, H_{Ar}); 4.40 (s, 2 H, CH_2O, **A**); 4.15 (d, 1 H, $C\underline{H}_AH_B$, $J_{A,B}$ = 9 Hz, **B**); 4.12 (d, 1 H, $CH_A\underline{H}_B$, $J_{A,B}$ = 9 Hz, **B**); 4.04 (d, 1 H, $C\underline{H}_AH_B$, $J_{A,B}$ = 9 Hz, **C**); 3.98 (d, 1 H, $CH_A\underline{H}_B$, $J_{A,B}$ = 9 Hz, **B**); 3.93 (br.s, 6 H, $C_{Cb}H$, **A—C**); 2.16 (s, 9 H, Me, **A—C**); 2.10—1.10 (m, 21 H, C_7H_9, **A—C**). ^{11}B NMR (C_6D_6), δ: 70.6 (s, 1 B, B(3)); 3.4 (d, 1 B, B(9), $^1J_{B,H}$ = 137 Hz); –0.7 (d, 1 B, B(6), $^1J_{B,H}$ = 152 Hz); –2.0 (d, 1 B, B(5), $^1J_{B,H}$ = 165 Hz); –11.4 (d, 1 B, B(10), $^1J_{B,H}$ = 155 Hz); –26.0 (d, 1 B, B(8), $^1J_{B,H}$ = 153 Hz); –30.0 (d, 1 B, B(11), $^1J_{B,H}$ = 144 Hz); –44.6 (d, 1 B, B(7), $^1J_{B,H}$ = 148 Hz). ^{13}C NMR (CD_2Cl_2), δ: 110.3 (s, $C_{Ar_{ipso}}$, **A—C**); 94.9, 94.8, and 94.7 (all d, CH_{Ar}, $^1J_{C,H}$ = 172 Hz, **A—C**); 72.7 (t, CH_2O, $^1J_{C,H}$ = 142 Hz, **A**); 72.0 (t, CH_2O, $^1J_{C,H}$ = 142 Hz, **B**, **C**); 52.3 (br.d, C_{Cb}, $^1J_{C,H} \approx$ 170 Hz); 47.5 and 47.4 (both d, C(3), $^1J_{C,H}$ = 131 Hz, **B**, **C**); 36.1 (t, C(7), $^1J_{C,H} \approx$ 130 Hz, **A**); 34.37 and 34.31 (both t, C(5) or C(7), $^1J_{C,H} \approx$ 130 Hz, **B**, **C**); 34.07 and 34.02 (both t, C(7) or C(5), $^1J_{C,H} \approx$ 130 Hz, **B**, **C**); 32.08 (br.d, C_{Cb}, $^1J_{C,H}$ = 168 Hz); 31.98 (d, C(4), $^1J_{C,H} \approx$ 130 Hz, **A**); 31.8 and 31.7 (both d, C(4), $^1J_{C,H} \approx$ 130 Hz, **B**, **C**); 29.2 and 29.1 (both t, C(3), C(5), $^1J_{C,H}$ = 132 Hz, **A**); 25.8 (s, C(1), **A**); 15.9 (d, C(2), C(6), $^1J_{C,H}$ = 175 Hz, **A**); 19.2 (q, Me, $^1J_{C,H}$ = 129 Hz, **A**); 19.0 (q, Me, $^1J_{C,H}$ = 129 Hz, **B**, **C**); 12.9, 12.7, 11.3, 11.2, 9.9, and 9.8 (all d, C(1), C(2), C(6), $^1J_{C,H}$ = 174 Hz, **B**, **C**).

X-ray diffraction study of complex 5. Crystals of $C_{19}H_{32}B_8ORu$ (M = 464.00) are monoclinic, space group $P2_1/c$, at 110 K a = 9.449(2) Å, b = 9.182(2) Å, c = 24.744(5) Å, β = 94.142(6)°, V = 2141.2(8) Å^3, Z = 4, d_{calc} = 1.439 g cm^{-3}, μ(Mo-Kα) = 7.40 cm^{-1}. The intensities of 6245 independent reflections (R_{int} = 0.0443) were measured on an automated Bruker SMART 1000 CCD diffractometer (graphite monochormator, Mo-Kα radiation, λ = 0.71073 Å, T = 110 K, ω scan technique, the scan step was 0.3°, frames were exposed for 10 s, $2\theta \leq 60°$). The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for all ordered nonhydrogen atoms and isotropic thermal parameters for the disordered atoms of the molecule. The H atoms of the carborane cage were revealed from the difference electron density synthesis and refined isotropically. The remaining H atoms were placed in geometrically calculated positions and refined using the riding model. The final reliability factors were as follows: R_1 = 0.0570 (calculated based on F_{hkl} for 3741 observed reflections with $I > 2\sigma(I)$), wR_2 = 0.1422 (calculated based on F^2_{hkl} for all independent reflections). The atomic coordinates were deposited with the Cambridge Structural Database. All calculations were carried out using the SHELXTL program package.[31]

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