Formation of *closo*-rhodacarboranes containing η^2,η^3-(CH_2=CHC_5H_6) ligand in the reaction of μ-dichloro-bis[(η^4-norbornadiene)rhodium] with *nido*-dicarbaundecaborates [K][*nido*-7-R^1-8-R^2-7,8-$C_2B_9H_{10}$]

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The reactions of a complex [(η^4-C_7H_8)RhCl]$_2$ (C_7H_8 is norbornadiene) with salts of substituted *nido*-dicarbaundecaborates, [K][*nido*-7-R^1-8-R^2-7,8-$C_2B_9H_{10}$] (R^1 = R^2 = H (**a**); R^1 = R^2 = Me (**b**); R^1, R^2 = 1′,2′-$(CH_2)_2C_6H_4$ (**c**); R^1 = Me, R^2 = Ph (**d**)), in CH_2Cl_2 afforded new *closo*-(η^2,η^3-(4-vinylcyclopenten-3-yl))rhodacarboranes. The structures of the compounds were studied by multinuclear NMR spectroscopy. A probable mechanism of the rearrangement of the norbornadiene ligand is discussed.

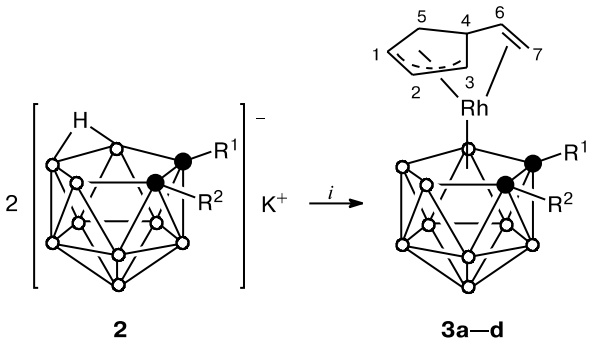
Key words: synthesis, *closo*-rhodacarboranes, η^2,η^3-(4-vinylcyclopenten-3-yl) ligand, norbornadiene rearrangement.

It is known[1—3] that the formation of π-complexes of transition metals is sometimes accompanied by the irreversible skeleton rearrangement of the starting hydrocarbon ligand due to the cleavage of its carbon—carbon bonds. The cleavage of the C—C bonds of the ligand is believed[4—6] to be preceded usually by C—H bond activation to form intermediate agostic (C—H...M) complexes, which can be identified in solution by IR and NMR spectroscopies. They can also be isolated in the solid state and characterized by X-ray diffraction analysis.[7] We have previously[8] studied the reaction of [(η^4-$C_{10}H_{12}$)IrCl]$_n$ (where $C_{10}H_{12}$ is dicyclopentadiene) with [K][*nido*-7,8-$(CH_3)_2$-7,8-$C_2B_9H_{10}$] and obtained a complex with the η^3-dimethylpentalenyl ligand containing the agostic C—H...Ir bond, *viz.*, *closo*-3-[$(CH_3)_2C_8H_9$]-1,2-$(CH_3)_2$-3,1,2-$IrC_2B_9H_9$, instead of the expected *closo*-(η-dicyclopentenyl)iridacarborane. In this work, we report the reaction leading, under mild conditions, to the transformation of the η^4-norbornadiene ligand (η^4-NBD) into η^2,η^3-vinylcyclopentenyl ligand during the formation of *closo*-rhodacarborane complexes.

The reaction of dimer [(η^4-C_7H_8)RhCl]$_2$ (**1**) (C_7H_8 is norbornadiene) with salts [K][*nido*-7-R^1-8-R^2-7,8-$C_2B_9H_{10}$] (**2**, R^1 = R^2 = H (**a**); R^1 = R^2 = Me (**b**); R^1 = R^2 = 1′,2′-$(CH_2)_2C_6H_4$ (**c**); R^1 = Me, R^2 = Ph (**d**)), in methylene chloride at 22 °C for the time from 2 to 24 h was found to afford *closo*-rhodacarboranes *closo*-3,3-[η^2,η^3-(CH_2=CHC_5H_6)]-1-R^1-2-R^2-3,1,2-$RhC_2B_9H_9$ (**3a—d**) (Scheme 1).

Reaction products **3a—d** were isolated and purified by column chromatography on silica gel. The resulting compounds are stable in air, crystalline, yellow (**3a**) or orange (**3b—d**) substances, which are well soluble in organic solvents and almost insoluble in hydrocarbons. All compounds were characterized by the elemental analysis data, IR spectra, and ^{1}H and ^{11}B NMR spectra; for complexes **3a—c**, ^{13}C{^{1}H} NMR spectra were additionally obtained (Table 1).

Scheme 1



i. [(η^4-NBD)RhCl]$_2$ (**1**), CH_2Cl_2

3	R^1	R^2
a	H	H
b	Me	Me
c	*o*-$(CH_2)_2C_6H_4$	
d	Me	Ph

Using a similar method,[9] we have previously obtained a series of agostic (C—H...M) *closo*-metallacarboranes of rhodium[9] and iridium[8,10] with different π-ligands based on cyclic dienes. It could be assumed that complexes with

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Table 1. ^{1}H, $^{13}C\{^{1}H\}$, and ^{11}B NMR spectral data for complexes **3a—d** in $CDCl_3$

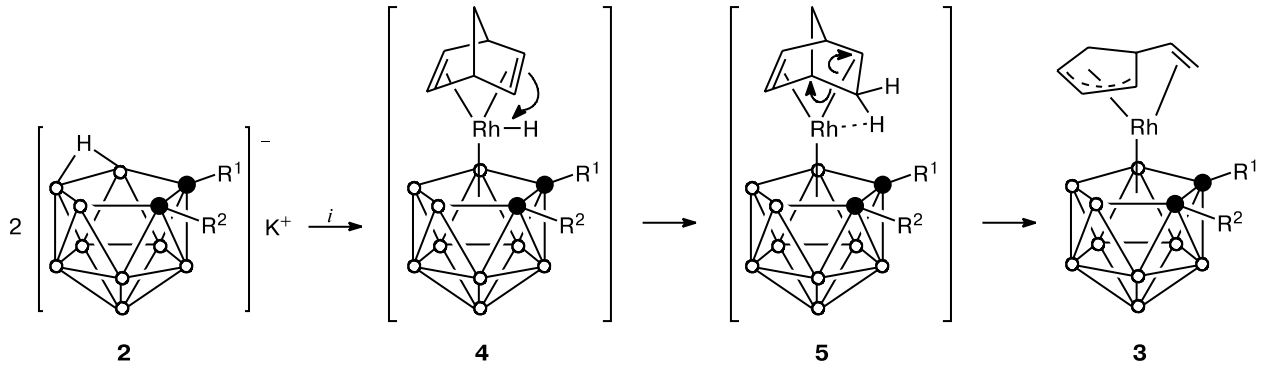
Compound	^{1}H NMR δ, $J_{H,H}$/Hz	$^{13}C\{^{1}H\}$ NMR δ, $J_{Rh,C}$/Hz	^{11}B NMR δ, $J_{B,H}$/Hz
3a[a]	5.14 (q*, 1 H, H(2), J = 2.8); 5.04 (m, 1 H, H(1)); 4.54 (q*, 1 H, H(3), J = 3.1); 3.83 (dd, 1 H, H_a, C(7)H_2, J_{gem} = 2.0, J_{cis} = 8.2); 3.75 (ddd, 1 H, H(6), ^{3}J = 2.8, J_{cis} = 8.2, J_{trans} = 13.4); 3.59 (dd+s, 2 H, H_b, C(7)H_2, H_{carb}, J_{gem} = 2.0, J_{trans} = 13.4); 3.51 (q*, 1 H, H(4), $J \approx 4$); 3.25 (s, 1 H, H_{carb}); 1.53 (dd, 1 H, H_a, C(5)H_2, $^{3}J \approx 4.6$, J_{AB} = 14.5); 1.45 (d, 1 H, H_b, C(5)H_2, J = 14.5)	88.90 (d, C(2), J = 6.9); 71.02 (d, C(1), J = 10.7); 66.45 (d, C(7), J = 8.0); 63.27 (d, C(6), J = 4.5); 58.40 (d, C(3), J = 4.2); 47.92 (C_{carb}), 45.56 (C_{carb}), 34.99 (C(4)), 27.63 (C(5))	5.19 (d, 1 B, J = 144); 2.20 (d, 1 B, J = 144); −5.73 (d, 1 B, J = 107); −6.32 (d, 2 B, J = 146); −8.16 (d, 1 B, J = 150); −17.55 (d, 1 B, J = 161); −18.05 (d, 1 B, J = 163); −21.86 (d, 1 B, J = 169)
3b	5.41 (m, 1 H, H(2)); 4.92 (m, 1 H, H(1)); 4.50 (dd, 1 H, H_a, C(7)H_2, J_{gem} = 1.4, J_{cis} = 7.3); 4.02 (m, 1 H, H(3)); 3.53 (dd, 1 H, H_b, C(7)H_2, J_{gem} = 1.4, J_{trans} = 13.5); 3.43 (ddd, 1 H, H(6), ^{3}J = 2.6, J_{cis} = 7.3, J_{trans} = 13.5); 3.38 (m, 1 H, H(4)); 2.23 (s, 3 H, Me); 2.14 (s, 3 H, Me); 1.32 (m, 2 H, C(5)H_2)	94.87 (d, C(2), J = 6.2); 70.67 (d, C(1), J = 11.1); 65.87 (d, C(7), J = 8.3); 65.20 (d, C(3), J = 2.8); 64.66 (d, C(6), J = 4.2); 34.61 (C(4)); 29.86 (Me); 28.78 (C(5)); 28.53 (Me)	5.87 (d, 1 B, J = 139); 1.80 (d, 1 B, J = 146); −1.33 (d, 1 B, J = 147); −1.94 (d, 1 B, J = 154); −5.57 (d, 1 B, J = 145); −7.84 (d, 1 B, J = 157); −9.28 (d, 1 B, J = 180); −11.20 (d, 1 B, J = 176); −12.04 (d, 1 B, J = 156)
3c	7.25 (m, 2 H, C_6H_4); 7.06 (m, 2 H, C_6H_4); 5.20 (m, 1 H, H(2)); 4.84 (m, 1 H, H(1)); 4.27 (dd, 1 H, H_a, C(7)H_2, J_{gem} = 1.2, J_{cis} = 7.5); 3.86 (d, 1 H, CH_2Ar); J_{AB} = 17.6); 3.74 (d, 1 H, CH_2Ar, J_{AB} = 18.4); 3.53 (d, 1 H, CH_2Ar, J_{AB} = 18.4); 3.37 (d, 2 H, CH_2Ar, H_b, C(7)H_2, J_{AB} = 17.6); 3.07 (m, 1 H, H(3)); 2.98 (m, 1 H, H(6)); 2.78 (m, 1 H, H(4)); 1.55 (m, 2 H, C(5)H_2)	129.98 (*ipso*-C_6H_4); 124.24, 123.19 (C_6H_4); 89.91 (C(2)); 70.24 (C_{carb}); 65.95 (d, C(1), J = 11.0); 64.96 (C(3)); 63.82 (C(6)); 61.36 (C_{carb}); 60.85 (C(7)); 39.40 (CH_2Ar); 37.66 (CH_2Ar); 30.50 (C(4)); 24.23 (C(5))	7.41 (d, 1 B, J = 139); 3.08 (d, 1 B, J = 144); −1.42 (d, 1 B, J = 162); −2.76 (d, 1 B, J = 161); −5.80 (d, 1 B, J = 143); −8.52 (d, 1 B, J = 131); −9.31 (d, 1 B, J = 124); −12.58 (d, 2 B, J = 158)
3d[b]	7.49** (m, 2 H, Ph); 7.45 (m, 2 H, Ph); 7.23 (m+m**, 3 H+3 H, Ph); 5.57** (m, 1 H, H(2)); 5.25 (m, 1 H, H(2)); 4.84 (m, 1 H, H(1)); 4.76** (m, 1 H, H(1)); 4.46 (d, 1 H, H_a, C(7)H_2, J_{cis} = 5.2); 3.92** (d, 1 H, H_a, C(7)H_2, J_{cis} = 9.6); 3.89 (m, 1 H, H(3)); 3.79** (m, 1 H, H(3)); 3.60 (d, 1 H, H_b, C(7)H_2, J_{trans} = 13.2); 3.32 (m, 1 H, H(4)); 3.27** (m, 1 H, H(4)); 3.21 (m+m**+m**, 1 H+1 H+1 H, H(6), H(6), H_b, C(7)H_2); 2.54** (s, 3 H, Me); 2.34 (s, 3 H, Me); 1.36** (m, 2 H, H_a, C(5)H_2); 1.30 (m, 2 H, H_b, C(5)H_2)		14.46** (d, 1 B, J = 129); 10.64 (d, 1 B, J = 148); 9.01** (d, 1 B, J = 168); 6.51 (d, 1 B, J = 156); 1.96** (d, 1 B, J = 132); 0.91 (d, 1 B, J = 140); −0.90** (d, 1 B, J = 139); −1.54 (d, 1 B**+2 B, J = 149); −3.31** (d, 2 B, J = 158); −4.24 (d, 1 B, J = 134); −5.35** (d, 1 B, J = 127); −7.47 (d, 2 B, J = 148); −14.06 (d, 1 B, J = 166); −15.97** (d, 1 B, J = 166)

[a] The spectrum was obtained on an Avance-300 instrument (300.13 MHz), q* is a quadruplet-like multiplet signal.
[b] Ratio of diastereometers A : B = 1 : 0.6, signals of diastereomer B are marked by symbol "**."

the agostic C—H...Rh bond, *i.e.*, *closo*-3,3-(η^1,η^2-norbornen-2-yl)-1-R^1-2-R^2-3,1,2-rhodacarboranes, are formed in this reaction. In this connection we note that one of these agostic complexes, namely, *closo*-3,3-(η^1,η^2-C_7H_9)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$, was earlier[7] isolated upon the low-temperature protonation of an anionic complex [PPN][*closo*-(η^4-C_7H_8)-1,2-Me_2-3,1,2-$RhC_2B_9H_9$] (PPN is the bis(triphenylphosphoranylidene)ammonium cation) with CF_3COOH (CH_2Cl_2, −78 °C) and characterized in the solid state (X-ray diffraction analysis) and in solution (^{1}H NMR).

The ^{1}H NMR spectra of the most known agostic complexes,[11] including those mentioned above, usually contain upfield signals attributed to agostic hydrogen. However, in the case of **3a—d**, the ^{1}H NMR spectra do not contain these characteristic signals. The signals of the hydrocarbon ligand of the complexes appear in the ^{1}H NMR spectra at δ 6.0—1.0 and indicate, most likely,

Scheme 2



i. $[(\eta^4\text{-NBD})RhCl]_2$ (**1**), CH_2Cl_2

the deep transformation of the starting norbornadiene during π-coordination with the metal. The character and multiplicity of signals in a range of δ 3—4 indicate that each complex synthesized contains a vinyl group π-coordinated to the metal atom. In a lower field, the δ 4—5.5 interval contains three multiplet signals with 1H intensity of each signal. We assigned these resonances to the allylic moieties of the hydrocarbon ligand. The corresponding carbon signals of the vinyl and allyl groups were also observed in the $^{13}C\{^1H\}$ NMR spectra of complexes **3a—c** as doublets at δ 60—90 with the characteristic spin-spin coupling constants $^1J(Rh,C) \approx 3.5—11.0$ Hz (see Table 1). The aforementioned and other signals of the hydrocarbon and carborane ligands of the complexes (see Table 1) were assigned by correlation $[^1H—^1H]$ COSY and $[^1H—^{13}C\{^1H\}]$ HETCOR NMR spectroscopic methods, and those for complex **3d** were assigned by analogy.

Note that due to the asymmetry of the η^2,η^3-$(CH_2{=}CHC_5H_6)$ ligand signals from the boron atoms in the ^{11}B NMR spectra of the synthesized complexes are predominantly observed as eight or nine individual doublets, except for complex **3d**, whose both ^{11}B and ^1H NMR spectra exhibit a double set of the corresponding signals in a ratio of 1 : 0.6. Since complex **3d** was synthesized from the racemic salt of non-symmetrically substituted *nido*-C_2B_9-carborane **2d**, this result indicates the formation of a mixture of diastereomers that cannot be separated into individual isomers by column chromatography or TLC on silica gel.

The mechanism of rearrangement of the norbornadiene ligand is rather complicated and includes, most likely, several steps (Scheme 2). The oxidative addition of the $[(\eta^4\text{-}C_7H_8)Rh]^+$ moiety to the B—H—B bond of the *nido*-C_2B_9-carborane ligand followed by its coordination with the pentagonal plane of carborane should result in the formation of intermediate diene-hydride complexes **4** in the first step. The latter can irreversibly transform into agostic complexes **5** by the intramolecular insertion of one coordinated double bond of diene into the Rh—H bond. This transformation of complexes **4** into **5** is probably caused by a higher thermodynamic stability of agostic complexes.[7] Complexes **5** further undergo intramolecular rearrangement with the cleavage of one carbon—carbon bond in the head of the bridge to form 18-electron complexes **3** with a stronger η^2,η^3-coordination of the hydrocarbon ligand compared to η^1,η^2-complexes **5** in which the electron deficiency is eliminated only due to the agostic interaction C—H...Rh.

The moving force of the whole reaction can be a factor of decreasing the "rigidity" of the hydrocarbon skeleton in 2,5-norbornadiene coordinated with rhodium.

Experimental

All reactions were carried out in dry argon. Reaction products were isolated and purified in air by column chromatography on silica gel (Merck, 230—400 mesh). The starting rhodium complex $[(\eta^4\text{-}C_7H_8)RhCl]_2$ was synthesized according to a previously published procedure.[12] The substituted *closo*-carboranes 1,2-Me_2-1,2-$C_2B_{10}H_{10}$,[13] 1,2-μ-(*o*-$(CH_2)_2C_6H_4$)-1,2-$C_2B_{10}H_{10}$,[14] and 1-Me-2-Ph-1,2-$C_2B_{10}H_{10}$[15] were synthesized by known methods and transformed into the corresponding *nido*-dicarbaundecaborates.[16] The $^{13}C\{^1H\}$, 2D $[^1H—^1H]$ COSY and 2D $[^1H—^{13}C]$ HETCOR NMR spectra were obtained on an Avance-300 instrument (^1H, 300.13 MHz; ^{13}C, 75.46 MHz). ^1H and $^{11}B/^{11}B\{^1H\}$ NMR spectra were recorded on a Bruker AMX-400 instrument (^1H, 400.13 MHz; ^{11}B, 128.33 MHz). IR spectra were recorded on an Specord M-82 instrument. Elemental analyses were performed at the Laboratory of Microanalysis of the Institute of Organoelement Compounds of the Russian Academy of Sciences.

Synthesis complexes 3a—d (general procedure). Dry complex **1** (0.1 mmol) was mixed under argon with salt **2** (0.24 mmol), after which anhydrous CH_2Cl_2 (5 mL) was added *via* syringe. The reaction mixture was stirred at room temperature until the starting complex **1** disappeared (TLC monitoring) and then chromatographed on a column with silica gel using a CH_2Cl_2—*n*-hexane (1 : 1) mixture as eluent. After the solvent

was removed, the product was recrystallized from the same mixture to obtain colored crystals.

***closo*-3,3-[η²,η³-(4-Vinylcyclopenten-3-yl)]-3,1,2-dicarbollylrhodium (3a)** was synthesized by the general procedure from compounds **1** and **2a** for 4.5 h as yellow crystals in 29% yield. Found (%): C, 33.15; H, 5.76; B, 29.58. $C_9H_{20}B_9Rh$. Calculated (%): C, 32.92; H, 6.09; B, 29.62. IR (KBr), ν/cm^{-1}: 2564 (B—H).

***closo*-3,3-[η²,η³-(4-Vinylcyclopenten-3-yl)]-1,2-dimethyl-3,1,2-dicarbollylrhodium (3b)** was synthesized by the general procedure from compounds **1** and **2b** for 3 h as orange crystals in 71% yield. Found (%): C, 37.13; H, 6.48; B, 26.96. $C_{11}H_{24}B_9Rh$. Calculated (%): C, 37.06; H, 6.73; B, 27.29. IR (KBr), ν/cm^{-1}: 2541 (B—H).

***closo*-3,3-[η²,η³-(4-Vinylcyclopenten-3-yl)]-1,2-μ-(*o*-xylene)-3,1,2-dicarbollylrhodium (3c)** was synthesized by the general procedure from compounds **1** and **2c** for 1.75 h as orange crystals in 80% yield. Found (%): C, 47.45; H, 5.86; B, 22.57. $C_{17}H_{26}B_9Rh$. Calculated (%): C, 47.43; H, 6.04; B, 22.59. IR (KBr), ν/cm^{-1}: 2561 (B—H).

***closo*-3,3-[η²,η³-(4-Vinylcyclopenten-3-yl)]-1-methyl-2-phenyl-3,1,2-dicarbollylrhodium (3d, mixture of diastereomers)** was synthesized by the general procedure from compounds **1** and **2d** for 24 h as orange crystals in 66% yield. Found (%): C, 45.77; H, 5.95; B, 23.08. $C_{16}H_{26}B_9Rh$. Calculated (%): C, 45.92; H, 6.21; B, 23.24. IR (KBr), ν/cm^{-1}: 2556 (B—H).

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