Low-Temperature "1,2 → 1,7" Isomerization of Sterically Crowded Icosahedral *closo*-((2,3,8-η^3):(5,6-η^2)-Norbornadien-2-yl)rhodacarborane via the Formation of a Pseudocloso Intermediate. Molecular Structures of [3,3-((2,3,8-η^3):(5,6-η^2)-$C_7H_7CH_2$)-1,2-(4′-MeC_6H_4)$_2$-3,1,2-*pseudocloso*-$RhC_2B_9H_9$] and 1,2 → 1,7 Isomerized Products

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The metalation reaction of the K^+ salt of the carborane anion [7,8-(4′-MeC_6H_4)$_2$-7,8-*nido*-$C_2B_9H_{10}]^-$ (**1**) with [((2,3,5,6-η^4)-C_7H_7-2-CH_2OH)$RhCl]_2$ (**2**) in a solution of $CHCl_3$ or C_6H_6 at ambient temperature produced two diastereomeric closo complexes, [2,2-((2,3,8-η^3):(5,6-η^2)-$C_7H_7CH_2$)-1,8-(4′-MeC_6H_4)$_2$-2,1,8-*closo*-$RhC_2B_9H_9$] (**5** and **6**), the products of the low-temperature "1,2 → 1,7" carbon atom isomerization of a (nonisolable) [3,3-((2,3,8-η^3):(5,6-η^2)-$C_7H_7CH_2$)-1,2-(4′-MeC_6H_4)$_2$-3,1,2-*closo*-$RhC_2B_9H_9$]. The overall architecture and stereochemistry of diastereomers **5** and **6** have been determined crystallographically. It has been established that the isomerization reaction proceeds through the intermediate pseudocloso type complex [3,3-((2,3,8-η^3):(5,6-η^2)-$C_7H_7CH_2$)-1,2-(4′-MeC_6H_4)$_2$-3,1,2-*pseudocloso*-$RhC_2B_9H_9$] (**4**), which was isolated and characterized by microanalysis, multinuclear NMR spectroscopy, and a single-crystal X-ray diffraction study.

Introduction

Although it was known for nearly 30 years that steric overcrowding in *closo*-metallacarboranes caused by bulky cage substituents can dramatically reduce the temperature of their polyhedral rearrangement,[1,2] the importance of such low-temperature processes for the mechanistic study of isomerization of icosahedral heteroboranes has been widely recognized only recently. Interest in this area has been revived by Welch,[3] who has obtained the first experimental results on the mechanism of the low-temperature isomerization of the overcrowded (nonisolable) transition-metal metallacarboranes [1,2-R_2-3,1,2-*closo*-$MC_2B_9H_9$] (R is mostly Ph and, more rarely, other substituents) into complexes of {1,8-R_2-2,1,8-*closo*-MC_2B_9} or {1,2-R_2-4,1,2-*closo*-MC_2B_9} cluster structure, where M represents platinum-,[4] nickel-,[5] rhodium-,[6] and molybdenum-containing moieties.[7] In the reactions between [Mo(η^3-C_3H_5)$(CO)_2]^+$ and [7,8-Ph_2-*nido*-7,8-$C_2B_9H_8R']^{n-}$ (R′ = H, n = 1; R′ = 9-Me_2S, 10-Me_2S, n = 0),[7] resulting in isomeric complexes of {2,1,8-*closo*-MoC_2B_9R'} architecture, the preisomerized metallacarborane intermediates of the general formula $[Ph_2(CO)_2(\eta^3$-$C_3H_5)MoC_2B_9H_8R']^{n-}$ have been successfully isolated. Of particular interest is a nonicosahedral

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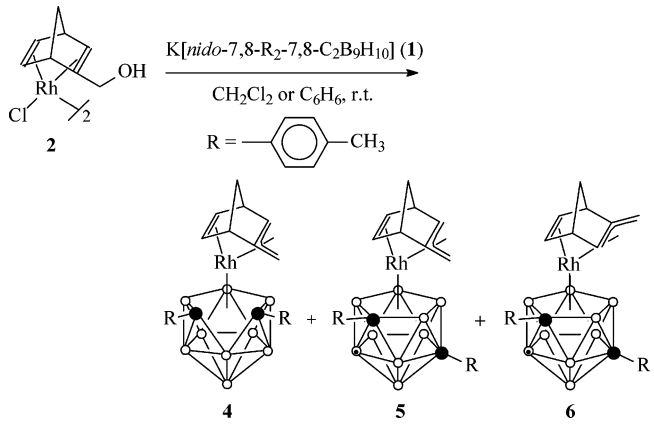
structure of these intermediate complexes, as determined in two cases by X-ray diffraction studies.[7a,b]

It should, however, be noted that products of the very first step of metalation reactions, which might be expected to retain a regular closo structure {1,2-R_2-3,1,2-*closo*-MC_2B_9} (where R is a bulky substituent), have never been isolated. This is evidently due to the spontaneous conversion of such overcrowded (presumed transient) complexes into complexes that adopt a structure with broken[8] (pseudocloso) and/or significantly strained[9] (semipseudocloso) C−C polyhedral connectivity or with heavily slipped distortions in a 3,1,2-*closo*-MC_2B_9 framework.[4c] In the course of isomerization reactions these species might, in principle, be further transformed either to nonicosahedral preisomerized complexes such as those discussed above[7a,b] or, in the case of "1,2 → 1,7" isomerization processes, directly into isomeric products of {1,8-R_2-2,1,8-*closo*-MC_2B_9} cluster structure via, for instance, the triangular face rotational mechanism. However, despite the success in the synthesis and structural characterization of a number of pseudocloso[8] and semipseudocloso[9] type metallacarboranes, none of these species, until very recently,[10a,b] have been reported to be reactive toward the low-temperature polyhedral rearrangement.

In accord with our preliminary communication,[10a] we wish to report the metalation reaction of the K^+ salt of a new [7,8-(4′-MeC_6H_4)$_2$-*nido*-7,8-$C_2B_9H_{10}$]$^-$ anion (**1**) with the known metalation reagent [((2,3,5,6-η^4)-C_7H_7-2-CH_2OH)RhCl]$_2$ (**2**; C_7H_7 is 2,5-norbornadien-2-yl).[11] The *nido*-carborane salt **1** was synthesized by base (KOH) degradation of the neutral *closo*-carborane precursor [1,2-(4′-MeC_6H_4)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$] (**3**), which was prepared by direct reaction between (4-$CH_3C_6H_4$)$_2C_2$ and $B_{10}H_{14}$ in 71% yield. The metalation reaction of **1** has been found to proceed according to the low-temperature "1,2 → 1,7" carbon atom isomerization scheme through the intermediate *pseudocloso* species [3,3-((2,3,8-η^3):(5,6-η^2)-$C_7H_7CH_2$)-1,2-(4′-MeC_6H_4)$_2$-3,1,2-*pseudocloso*-$RhC_2B_9H_9$] (**4**), resulting finally in the two diastereomeric complexes [2,2-((2,3,8-η^3):(5,6-η^2)-C_7H_7-CH_2)-1,8-(4′-MeC_6H_4)$_2$-2,1,8-*closo*-$RhC_2B_9H_9$] (**5** and **6**).

Scheme 1



Results and Discussion

Synthesis and Characterization of the *pseudocloso*- and *closo*-Rhodacarborane Complexes 4−6. We have previously described a simple synthetic procedure for a series of 12-vertex hydrocarbon-containing complexes [(η-L)-*closo*-$MC_2B_9H_9R,R'$] (M = Rh, Ir; L = cyclodienyl, cycloenyl ligands), which is based on the room-temperature reaction of the K^+ salts of the isomeric *nido*-carborane monoanions [7,*n*-R,R′-*nido*-7,*n*-$C_2B_9H_{10}$]$^-$ (*n* = 8, 9; R, R′ = H, Alk) with the dimeric complexes [M(η^4-diene)Cl]$_2$.[12] In a similar reaction of **1** with **2** in a solution of benzene or chloroform for about 1 h, a mixture of metallacarborane species **4**−**6** in 63 and 56% yields (total content), respectively, was obtained (Scheme 1). As can be expected, the overcrowded icosahedral *closo*-rhodacarborane [3,3-((2,3,8-η^3):(5,6-η^2)-$C_7H_7CH_2$)-1,2-(4′-MeC_6H_4)$_2$-3,1,2-*closo*-$RhC_2B_9H_9$] was not detected among the reaction products.

It is important to note that the relative ratio of complexes **4**−**6** is influenced markedly by both the reaction time and the nature of solvent used in the reaction. When the reaction of **1** and **2** in benzene is terminated at an earlier stage, the ratio of **4** to mixture of **5** and **6** was higher, whereas a longer period of stirring of the reagents favored the formation of complexes **5** and **6** as predominant products. The same is true for the reaction of **1** with **2** in chloroform. These experimental results, coupled with the fact that the formation of complexes **5** and **6** was irreversible in these reactions, suggest that **4** is an apparent intermediate in this sequence. All products **4**−**6** have been individually isolated from the reaction mixture using preparative column chromatography on silica gel and fractional crystallization using a mixture of CH_2Cl_2/*n*-hexane. The multinuclear NMR spectra and analytical data are entirely consistent with the formulations of all three (vide infra).

Complex **4** has been characterized by ^1H, $^{13}C\{^1H\}$, and $^{11}B/^{11}B\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum

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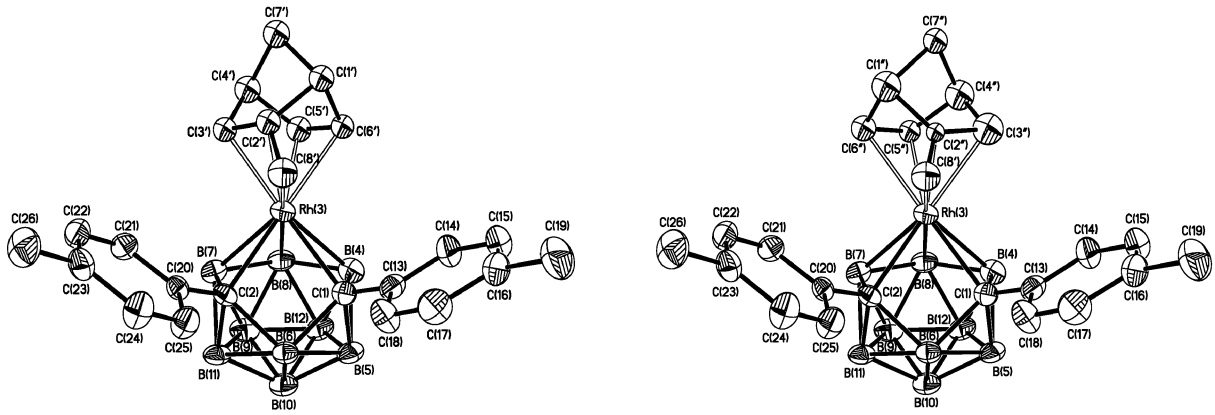

Figure 1. ORTEP representations of the molecular structures of the two enantiomeric species **A** (left) and **B** (right) for complex **4**, with thermal ellipsoids drawn at the 30% probability level. The hydrogen atoms are omitted for clarity.

of **4** in C_6D_6 revealed a set of eight signals characteristic of a η^3:η^2-norbornadienyl ligand and, in addition, the resonances of the cage arene substituent protons; all of these resonances are observed in the expected integral ratios. Two of the dienyl ligand resonances at δ 4.32 and 3.89 ppm were slightly broadened singlets and, therefore, were attributed to the syn and anti protons, respectively, at the exocyclic C(8) atom of the allylic moiety; it is known that resonances of such geminal protons appear in the ^{1}H NMR spectra with an extremely small ^2J(H,H) coupling constant.[13] The resonances originating from the nonequivalent methylene protons at the C(7) atom were observed as close AB doublets. It is noteworthy that in the $^{13}C\{^1H\}$ NMR spectrum of **4** the resonances arising from the carbocyclic ligand have different values of $J(^{103}Rh,C)$ coupling, which are strictly dependent on the position of the carbon atoms in the hydrocarbon framework. Specifically, those carbon resonances which are derived from the double or allylic bonds of the coordinated hydrocarbon ligand are mostly doublets, while others are, in fact, singlets. Taking into account these observations and using a 2D [$^1H-^{13}C$]-HETCOR correlation technique, we have assigned all resonances in the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **4**. In the $^{11}B/^{11}B\{^1H\}$ NMR spectra of **4** the resonances of the cage boron atoms are observed as partly overlapping doublets of 1:2:1:1:2:1:1 relative intensities between δ +25.5 and −19.5 ppm. Both the observed range of these resonances and the weighted-average ^{11}B chemical shift of $\langle\delta(^{11}B)\rangle = +5.45$ ppm are in good agreement with those values normally found in the $^{11}B/^{11}B\{^1H\}$ NMR spectra of typical pseudocloso complexes.[8] It was therefore of interest to confirm unequivocally the molecular structure of **4** in the solid state by a single-crystal diffraction study.

Diffraction-quality single crystals of **4** were grown from a CH_2Cl_2/*n*-hexane mixture. According to the results of the X-ray diffraction study (Figure 1), complex **4** adopts a full pseudocloso structure with a cage C(1)···C(2) separation of 2.539(7) Å. In the known nondeformed closo analogues [3,3-((2,3,8-η^3):(5,6-η^2)-$C_7H_7CH_2$)-1,2-R_2-3,1,2-*closo*-$RhC_2B_9H_9$] (R = H,[11b] Me[11a]) distances between the cage carbon atoms are 1.58 Å (an average value of three independent molecules) and 1.637 Å, respectively. The lengthening of the cage C(1)···C(2) distance in **4** results in generation of an essentially square C(1)Rh(3)C(2)B(6) open face with a contracted Rh(3)···B(6) interatomic distance of 2.971(6) Å. Both C(1)···C(2) and Rh(3)···B(6) distances found in **4** can be compared to those found in other known *pseudocloso*-metallacarboranes: for instance, in [3-(η^6-C_6H_6)-1,2-Ph_2-3,1,2-*pseudocloso*-$RuC_2B_9H_9$ (2.485 and 2.946 Å)[8b] and [3-(η^5-C_9Me_7)-1,2-Ph_2-3,1,2-*pseudocloso*-$RhC_2B_9H_9$ (2.485 Å)[8d] (2.491 and 2.960 Å). All these structural peculiarities established for **4** are thus typical for closo-to-pseudocloso deformation studied in detail by Welch et al.[3]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 4

Rh(3)-C(1)	2.194(5)	Rh(3)−C(3″)	2.259(18)
Rh(3)−C(2)	2.182(5)	Rh(3)−C(5″)	2.294(14)
Rh(3)−B(4)	2.252(7)	Rh(3)−C(6″)	2.347(15)
Rh(3)−B(7)	2.239(6)	C(1)···C(2)	2.539(7)
Rh(3)−B(8)	2.242(6)	C(1)−B(4)	1.633(7)
Rh(3)−C(2′)	2.197(10)	C(1)−B(6)	1.747(7)
Rh(3)−C(3′)	2.118(9)	C(2)−B(6)	1.748(7)
Rh(3)−C(5′)	2.223(10)	C(2)−B(7)	1.629(7)
Rh(3)−C(6′)	2.247(9)	B(4)−B(8)	1.836(9)
Rh(3)−C(8′)	2.327(4)	B(7)−B(8)	1.807(9)
Rh(3)−C(2″)	2.210(13)		
C(2)−Rh(3)−C(1)	70.92(18)	C(1)−B(4)−B(8)	112.8(5)
B(4)−C(1)−B(6)	111.3(4)	C(1)−B(6)−C(2)	93.2(4)
B(6)−C(1)−Rh(3)	97.2(3)	C(2)−B(7)−B(8)	112.8(4)
B(7)−C(2)−B(6)	112.5(4)	B(7)−B(8)−B(4)	115.3(4)
B(6)−C(2)−Rh(3)	97.6(3)		

The rhodium atom in **4** is attached to a norbornadienyl fragment via an η^2-olefin C(5′)−C(6′) bond and an η^3-allylic bond involving C(2′), C(3′), and C(8′) carbon atoms. Although **4** is a chiral molecule due to the asymmetry of the η^2:η^3-norbornadienyl ligand, the centrosymmetric crystal studied by X-ray diffraction is naturally racemic. It should, however, be noted that the carbocyclic ligand in the structure of **4** proved to be disordered over two mirror-related positions, forming two enantiomeric species **A** and **B** which share a common exocyclic C(8′) atom. In the X-ray diffraction experiment these components **A** and **B** have been successfully modeled with a ratio of 40:60, respectively. Figure 1 shows the perspective views of each of enantiomeric species **A** and **B**; selected bond lengths and angles for **4** are given in Table 1. The low accuracy of the determination of the norbornadienyl ligand carbon positions, due to the disorder, does not warrant any further discussion of geometrical details of this ligand in the structure of **4**.

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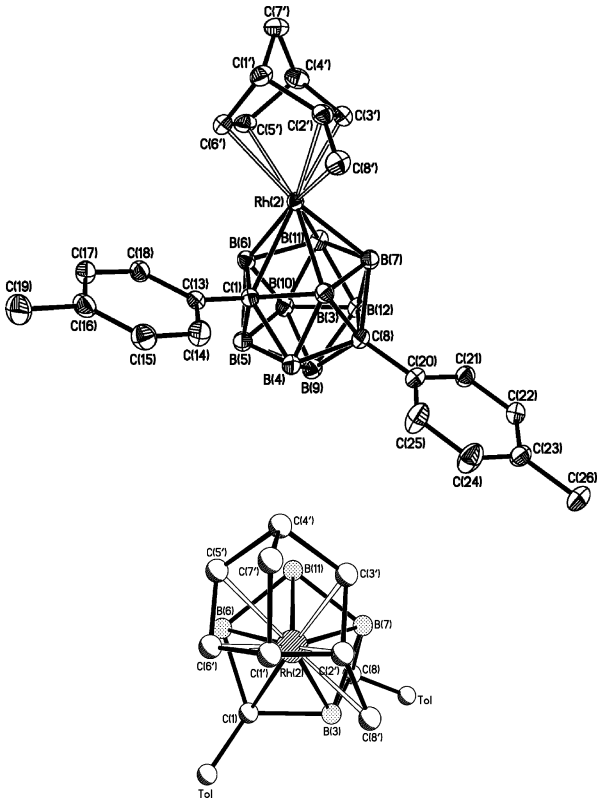


Figure 2. ORTEP representation of the molecular structure of complex **5** with thermal ellipsoids drawn at the 50% probability level (top) and projection on the CB_4 pentagonal face of the carborane ligand (bottom). The hydrogen atoms are omitted for clarity.

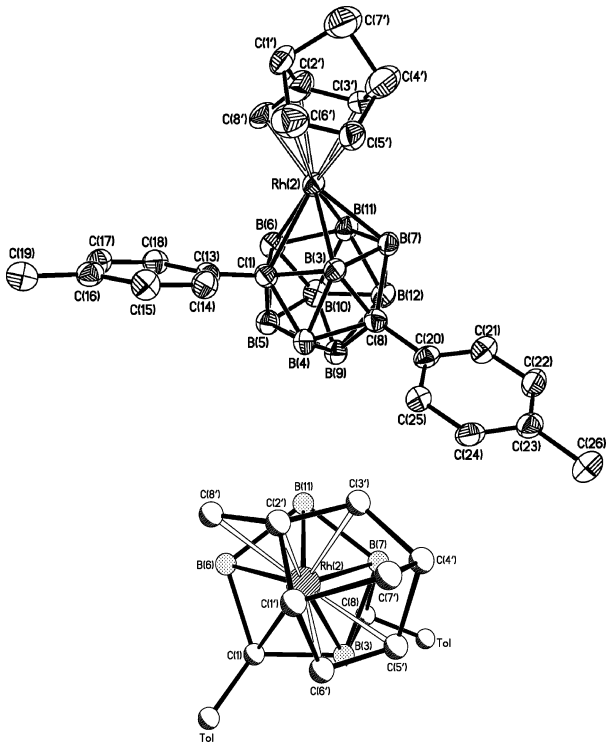


Figure 3. ORTEP representation of the molecular structure of complex **6** with thermal ellipsoids drawn at the 50% probability level (top) and projection on the CB_4 pentagonal face of the carborane ligand (bottom). The hydrogen atoms are omitted for clarity.

The ^1H NMR spectra of complexes **5** and **6** show many similarities with that of **4**, especially in the patterns associated with the η^3:η^2-norbornadienyl ligand. When this was taken into account, the assignment of proton resonances observed in the spectra of **5** and **6** was made by analogy with the spectrum of **4**. In the $^{11}B\{^1H\}$ NMR spectra of **5** and **6** the resonances were mostly separated peaks. These appeared in the range usually observed for the *closo*-metallacarborane complexes: i.e., at higher field than the resonances in the spectrum of **4**. Accordingly, the calculation for complexes **5** and **6** revealed $\langle\delta(^{11}B)\rangle$ values of -6.60 and -7.13 ppm, respectively, and these are also typical for complexes with regular closo structures. Considering all these spectroscopic data and taking into account the fact that both the carbocyclic and the carborane ligands in **5** and **6** do not possess molecular symmetry, it is reasonable to assume that these species are diastereomers.

To determine the overall architecture and stereochemistry of **5** and **6**, their X-ray diffraction studies have been undertaken. Well-formed single crystals of complexes **5** and **6** suitable for X-ray diffraction study were obtained by slow recrystallization from a mixture of CH_2Cl_2 and *n*-hexane. The molecular structures of **5** and **6** in two projections are shown in Figures 2 and 3, respectively, and selected bond lengths and angles are given in Table 2. Single-crystal X-ray diffraction studies of these complexes clearly established that their architecture is based on {2,1,8-*closo*-RhC_2B_9} cluster units, thus confirming the fact of polyhedral rearrangement of the initial *nido*-carborane **1** during the metalation reaction. The crystallographic data also confirmed that **5** and **6** are indeed diastereomers which, however, differ not only in the stereochemistry of the η^3:η^2-norbornadienyl ligands but also in their conformational disposition relative to the carborane cage. Thus, in the isomer **5** the carbocyclic ligand adopts a conformation where the allylic unit is projected onto the B(7)−B(3) bond and partly the arene substituent at the C(8) atom of the lower pentagonal belt (Figure 2). In the isomer **6** the allylic moiety is projected onto the B(6)−B(11) bond of the CB_4 open face; in this case, the exocyclic carbon atom C(8′) of the allylic group is positioned on the opposite side with regard to the lower belt arene substituent (Figure 3).

On the basis of the X-ray structural data the *SS* and *RS* configurations should be assigned to the chiral C(1) and C(1′) centers of those enantiomers of **5** and **6**, which are depicted in Figures 2 and 3, respectively. The relative configurations of racemic crystals of **5** and **6** can thus be designated as *SS*/*RR* and *RS*/*SR*, respectively.[14]

In contrast to **4**, neither **5** nor **6** show any significant distortions of closo icosahedral geometry. Within the carborane ligands, which are η^5 coordinated by the rhodium atom in both **5** and **6**, the bond lengths and angles between carbon and boron atoms are as expected,

(14) As the cage C(1) atom in **5** (or C(1′) atom in **6**) is formally six-coordinated, the Cahn−Ingold−Prelog notation seems to be not applicable for the assignment of absolute configuration of these centers. Nevertheless, while naming the enantiomers of **5** and **6** (Figures 2 and 3), we used the extension of Cahn−Ingold−Prelog rules, which takes advantage of the fact that all of the B(4), B(5), or B(6) atoms are on the same side of the Ru(1), C(13), B(3) triangle, and any of the former boron atoms, if treated as the fourth position on the tetrahedron, should be considered as the lowest priority substituent at the chiral C(1) center.

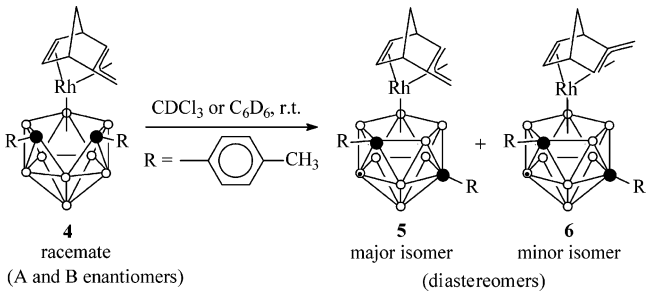
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 5 and 6

	5	6
Rh(2)−C(1)	2.285(2)	2.284(5)
Rh(2)−B(3)	2.166(3)	2.124(5)
Rh(2)−B(6)	2.161(3)	2.200(6)
Rh(2)−B(7)	2.184(3)	2.187(5)
Rh(2)−B(11)	2.203(3)	2.202(6)
Rh(2)−C(2′)	2.194(2)	2.231(7)
Rh(2)−C(3′)	2.130(3)	2.134(5)
Rh(2)−C(5′)	2.279(3)	2.293(5)
Rh(2)−C(6′)	2.289(3)	2.310(7)
Rh(2)−C(8′)	2.319(3)	2.292(5)
C(1′)-C(2′)	1.526(4)	1.543(9)
C(1′)-C(6′)	1.531(4)	1.545(8)
C(1′)−C(7′)	1.546(4)	1.571(9)
C(2′)−C(3′)	1.453(4)	1.449(8)
C(2′)−C(8′)	1.372(4)	1.318(9)
C(3′)−C(4′)	1.530(4)	1.501(9)
C(4′)−C(5′)	1.533(4)	1.567(9)
C(4′)−C(7′)	1.540(4)	1.557(8)
C(5′)−C(6′)	1.386(4)	1.366(8)
C(1)−B(3)	1.709(4)	1.726(7)
C(1)−B(6)	1.750(4)	1.737(7)
B(3)−B(7)	1.852(4)	1.837(8)
B(6)−B(11)	1.848(4)	1.859(8)
B(7)−B(11)	1.797(4)	1.793(8)
C(2′)−C(1′)−C(6′)	98.6(2)	100.3(5)
C(2′)−C(1′)−C(7′)	101.1(2)	100.9(5)
C(6′)−C(1′)−C(7′)	101.5(2)	100.3(5)
C(8′)−C(2′)−C(3′)	123.3(2)	123.5(6)
C(8′)−C(2′)−C(1′)	124.4(3)	122.7(6)
C(3′)−C(2′)−C(1′)	106.0(2)	104.8(5)
C(2′)−C(3′)−C(4′)	104.8(2)	105.9(5)
C(3′)−C(4′)−C(5′)	98.5(2)	100.1(5)
C(3′)−C(4′)−C(7′)	102.3(2)	103.6(5)
C(5′)−C(4′)−C(7′)	100.8(2)	101.5(5)
C(6′)−C(5′)−C(4′)	106.9(2)	104.3(5)
C(5′)−C(6′)−C(1′)	106.5(2)	109.0(5)
C(4′)−C(7′)−C(1′)	94.5(2)	92.4(5)
B(3)−C(1)−B(6)	108.1(2)	108.2(4)
C(1)−B(3)−B(7)	109.9(2)	110.7(4)
C(1)−B(6)−B(11)	109.9(2)	108.8(4)
B(11)−B(7)−B(3)	106.5(2)	105.2(4)
B(7)−B(11)−B(6)	105.0(2)	106.6(4)

with C−B = 1.69−1.75 Å and B−B = 1.73−1.86 Å. The coordination bonding mode of the rhodium atom with respect to the η^3:η^2-norbornadienyl ligands in **5** and **6** is quite similar to that found in a number of structurally related (η^3:η^2-norbornadien-2-yl)-*closo*-rhodacarboranes[11] as well as complex **4** reported in this work.

Although the pseudocloso complex **4** is quite stable in the solid state, in solution it undergoes irreversible transformation to form the diastereomeric complexes **5** and **6** (Scheme 2), which has been proven by in situ

Scheme 2



NMR studies. In particular, the ^{1}H NMR monitoring of the isomerization reaction of **4** in solution of C_6D_6 (Figure 4) revealed the formation of the diastereomeric

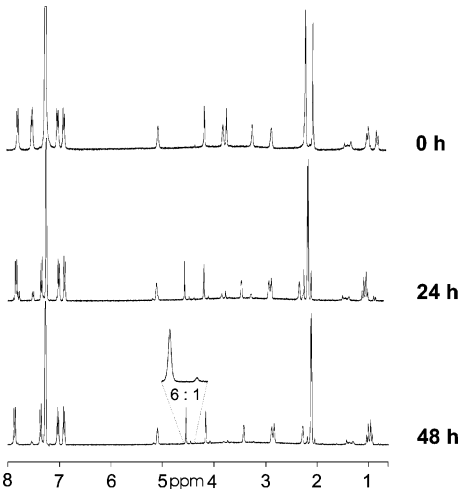


Figure 4. Monitoring of the 400.13 MHz (C_6D_6) ^{1}H NMR spectrum of **4** in the 8.0−0.7 ppm region.

species **5** and **6** in a ratio of 6:1. This is in good agreement with the comparative chemical experiments. Thus, stirring of **1** and **2** in solution of benzene for 1 week at room temperature followed by column chromatography on silica gel resulted in the formation of a mixture of compounds **5** and **6** in 30% yield and in a ratio of 5:1, close to that observed in the ^{1}H NMR monitoring experiment.

Concluding Remarks

We have synthesized the new *nido*-carborane anion [7,8-(4′-MeC_6H_4)$_2$-*nido*-7,8-$C_2B_9H_{10}$]$^-$ (**1**) and examined its room-temperature metalation reaction with the dimeric rhodium complex [((2,3,5,6-η^4)-$C_7H_7CH_2OH$)-RhCl]$_2$ (**2**; C_7H_7 is 2,5-norbornadien-2-yl). The reaction has been found to proceed according to the low-temperature "1,2 → 1,7" carbon atom isomerization scheme, producing the two η^3:η^2-allylolefinic type diastereomeric complexes **5** and **6** of {2,1,8-*closo*-RhC_2B_9} cluster structure as final products. During metalation of *nido*-carborane **1** the pseudocloso complex [3,3-((2,3,8-η^3):(5,6-η^2)-$C_7H_7CH_2$)-1,2-(4′-MeC_6H_4)$_2$-3,1,2-*pseudocloso*-$RhC_2B_9H_9$] (**4**) is formed, which was individually isolated and structurally characterized. Since this species was shown to isomerize at room temperature in solution to give complexes **5** and **6**, it should be regarded as an apparent isomerization intermediate.

Experimental Section

General Considerations. All reactions and manipulations except for column chromatography were carried out under an atmosphere of dry argon using standard Schlenk techniques. All solvents, including those used for column chromatography, as eluents were dried under appropriate drying agents and distilled under argon prior to use. Chromatographic columns (ca. 25 cm in length and 2 cm in diameter) packed with silica gel (Merck, 230−400 mesh) were used for purification of the complexes. The starting bis(*p*-tolyl)acetylene used for the preparation of carborane **3** was synthesized by a four-step procedure fully analogous to that described for Ph_2C_2.[15] The dimeric rhodium complex **2** was prepared according to the

(15) Tietze, L.-F.; Eicher, T. *Reactions and Syntheses in the Organic Chemistry Laboratory;* University Science Books: Mill Valley, CA, 1989.

Table 3. Crystal Data, Data Collection, and Structure Refinement Parameters for Complexes 4−6

	4	5	6
formula	$C_{24}H_{32}B_9Rh$	$C_{24}H_{32}B_9Rh$	$C_{24}H_{32}B_9Rh$
mol wt	520.70	520.70	520.70
cryst color, habit	orange plate	yellow plate	yellow prism
temp, K	293(2)	115(1)	110(1)
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/c$	$P2_1/n$
a, Å	16.191(3)	11.495(2)	12.764(1)
b, Å	15.763(3)	15.988(3)	12.327(1)
c, Å	19.781(4)	13.396(3)	15.863(2)
β, deg		100.015(4)	100.063(2)
V, Å^3	5049(2)	2424.4(8)	2457.6(4)
Z	8	4	4
d(calcd), g cm^{-3}	1.370	1.427	1.407
diffractometer	Enraf-Nonius CAD4	SMART 1000 CCD	
scan mode	$\theta-5/3\theta$	ω and φ	
θ_{max}, deg	25.0	30.0	28.1
μ(MoKα), cm^{-1} (λ = 0.710 73 Å)	6.89	7.17	7.07
no. of unique rflns (R_{int})	4447 (0.0000)	7048 (0.0333)	5967 (0.0891)
no. of obsd rflns ($I > 2\sigma(I)$)	2164	5886	3301
R1 (on *F* for obsd rflns)[a]	0.0419	0.0459	0.0587
wR2 (on F^2 for all rflns)[b]	0.1090	0.1107	0.1455

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

published method.[11a] The ^{1}H, ^{11}B/^{11}B{^{1}H}, and ^{13}C/^{13}C{^{1}H} as well as 2D correlation NMR spectra were recorded on Bruker AMX-400 (^{1}H at 400.13 MHz, ^{13}C at 100.61 MHz, and ^{11}B at 128.33 MHz) and Avance-300 instruments (^{1}H at 300.13 MHz). IR spectra were obtained on a Carl-Zeiss M-82 spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS.

Preparation of K[7,8-(4′-$CH_3C_6H_4$)$_2$-*nido*-7,8-$C_2B_9H_{10}$] (1). To a solution of KOH (0.52 g, 9.202 mmol) in 50 mL of absolute ethanol was added solid *closo*-carborane **3** (1 g, 3.067 mmol), and the resulting mixture was refluxed with stirring for 72 h. After the reaction mixture was cooled to room temperature, CO_2 was bubbled through it until precipitation of K_2CO_3 was completed. The solution was filtered and evaporated to dryness, affording oily material. To this oil was added 30 mL of dry benzene, and the mixture was refluxed with a Dean−Stark trap until the liberation of water was completed. The resulting mixture was evaporated to dryness, affording **1** (1.06 g, 98%) as a white powder. IR (hexachlorobutadiene, cm^{-1}): 2528 (ν_{B-H}). ^{1}H NMR (acetone-d_6, 400.13 MHz, *J*(H,H), Hz): δ 7.01 (d, 4H, *J* = 8.0, C_6H_4), 6.65 (d, 4H, *J* = 8.0, C_6H_4), 2.05 (s, 6H, CH_3), −1.74 (br m, 1H, B−*H*−B). ^{11}B NMR (acetone-d_6, 128.33 MHz, *J*(B,H), Hz): δ −7.45 (d, 2B, *J* = 135), −13.75 (d, 1B, *J* = 155), −15.9 (d, 2B, *J* = 135), −18.3 (d, 2B, *J* = 150), −32.6 (dd, 1B, $J_{B-H_{term}}$ = 170, J_{B-H-B} = 46), −34.9 (d, 1B, *J* = 140).

Preparation of [1,2-(4′-$CH_3C_6H_4$)$_2$-1,2-*closo*-$C_2B_{10}H_{10}$] (3). To a solution of freshly sublimed decaborane (1 g, 8.060 mmol) in 100 mL of degassed toluene was added 1.03 mL (8.060 mmol) of *N*,*N*-dimethylaniline via syringe. After 5 min of stirring, solid bis(*p*-tolyl)acetylene (1.66 g, 8.060 mmol) was added to the solution, and the mixture was stirred at room temperature additionally for 1 h. The solution was then kept at 112−114 °C for 7.5 h and after cooling was decanted from the solid residue and evaporated to dryness. To the yellow oil thus obtained was added 100 mL of ice-cold ethanol, and white crystals were collected by filtration, washed with ice-cold ethanol (3 × 5 mL), and dried under vacuum to give 1.86 g (71%) of analytically pure compound **3** as colorless crystals. Anal. Calcd for $C_{16}H_{24}B_{10}$: C, 59.26; H, 7.41; B, 33.33. Found: C, 59.43; H, 7.74; B, 33.42. IR (hexachlorobutadiene, cm^{-1}): 2573 (ν_{B-H}). ^{1}H NMR (acetone-d_6, 400.13 MHz, *J*(H,H), Hz): δ 7.46 (d, 4H, *J* = 8.4, C_6H_4), 7.05 (d, 4H, *J* = 8.4, C_6H_4), 2.21 (s, 6H, CH_3). ^{11}B NMR (acetone-d_6, 128.33 MHz, *J*(B,H), Hz): δ −2.25 (d, 2B, *J* = 150), −8.35 (d, 4B, *J* = 230), −10.1 (d, 3B, *J* = 220), −10.7 (d, 1B, *J* = 175).

Preparation of [3,3-((2,3,8-η^3):(5,6-η^2)-$C_7H_7CH_2$)-1,2-(4′-MeC_6H_4)$_2$-3,1,2-*pseudocloso*-$RhC_2B_9H_9$] (4) and Diastereomers [3,3-((2,3,8-η^3):(5,6-η^2)-$C_7H_7CH_2$)-1,8-(4′-MeC_6H_4)$_2$-2,1,8-*closo*-$RhC_2B_9H_9$] (5 and 6). To a mixture of **1** (0.136 g, 0.384 mmol) and **2** (0.1 g, 0.192 mmol) was added via syringe 10 mL of degassed chloroform. The resulting mixture was stirred at room temperature for 0.5 h, while the suspension became orange. The mixture of products formed was then treated by column chromatography on silica gel. The first yellow band was eluted with a 1:2 $CHCl_3$/*n*-hexane mixture to afford, after evaporation, 0.031 g (16%) of a yellow oil, consisting of a crude mixture of **5** and **6** in the ratio of 1:2, as estimated by ^{1}H NMR spectroscopy. The mixture of **5** and **6** was repeatedly recrystallized from CH_2Cl_2/*n*-hexane solution at 0 °C, finally affording 0.012 g (6.1%) of pure compound **6**. Anal. Calcd for $C_{24}H_{32}B_9Rh$: C, 55.37; H, 6.15; B, 18.68. Found: C, 55.44; H, 6.35; B, 18.59. IR (KBr, cm^{-1}): 2570 (ν_{B-H}). ^{1}H NMR ($CDCl_3$, 400.13 MHz, *J*(H,H), Hz): δ 7.50 (d, 2H, *J* = 8.0, C_6H_4), 7.08 (d, 4H, *J* = 7.7, C_6H_4), 6.90 (d, 2H, *J* = 8.0, C_6H_4), 5.59 (m, 1H, H_5), 4.84 (br s, 1H, H_{8-syn}), 4.22 (br s, 1H, H_{8-anti}), 3.77 (m, 1H, H_3), 3.57 (m, 1H, H_4), 3.33 (m, 1H, H_1), 3.07 (m, 1H, H_6), 2.33 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.78 (d, 1H, J_{AB} = 9.5, $H_{7\alpha}$ ($H_{7\beta}$)), 1.74 (d, 1H, J_{AB} = 9.5, $H_{7\beta}$ ($H_{7\alpha}$)). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz, *J*(Rh,C), Hz): δ 141.26, 137.93, 136.88, 135.18, 128.50, 128.01, 125.01 (s, C_6H_4), 100.87 (d, *J* = 1.9, C_2), 84.67 (d, *J* = 1.9, C_8), 76.85 (d, *J* = 2.9, C_5), 73.55 (d, *J* = 2.8, C_6), 55.42 (s, C_7), 45.90 (s, C_4), 43.68 (s, C_1), 36.65 (d, *J* = 9.5, C_3), 20.84, 20.74 (s, CH_3). ^{11}B NMR ($CDCl_3$, 128.33 MHz, *J*(B,H), Hz): δ 0.95 (d, 2B, *J* = 165), −1.0 (d, 1B, *J* = 155), −4.6 (d, 2B, *J* = 140), −6.5 (d, 1B, *J* = 180), −14.6 (d, 2B, *J* = 160), −17.2 (d, 1B, *J* = 145). The orange band which was eluted next using the same mixture of solvents gave, after evaporation, 0.08 g (40%) of complex **4**, isolated as an orange microcrystalline solid. Anal. Calcd for $C_{24}H_{32}B_9Rh$: C, 55.37; H, 6.15; B, 18.68. Found: C, 55.18; H, 6.19; B, 18.79. IR (KBr, cm^{-1}): 2536 (ν_{B-H}). ^{1}H NMR (C_6D_6, 300.13 MHz; *J*(H,H), Hz): δ 7.93 (d, 2H, *J* = 7.8, C_6H_4), 7.66 (d, 2H, *J* = 8.0, C_6H_4), 7.16 (d, 2H, *J* = 8.0, C_6H_4), 7.04 (d, 2H, *J* = 7.8, C_6H_4), 5.22 (m, 1H, $H_{5(6)}$), 4.32 (br s, 1H, H_{8-syn}), 3.96 (m, 1H, $H_{6(5)}$), 3.89 (br s, 1H, H_{8-anti}), 3.39 (m, 1H, H_3), 3.02 (m, 1H, $H_{1(4)}$), 2.36 (br s, 4H, CH_3, $H_{4(1)}$), 2.21 (s, 3H, CH_3), 1.16 (d, 1H, J_{AB} = 9.7, $H_{7\alpha}$ ($H_{7\beta}$)), 0.97 (d, 1H, J_{AB} = 9.7, $H_{7\beta}$ ($H_{7\alpha}$)). ^{13}C{^{1}H} NMR (C_6D_6, 100.61 MHz, *J*(Rh,C), Hz): δ 149.62, 144.87, 136.71, 134.95 (C_6H_4), 105.26 (s br, C_2), 104.47 (s.br, C_8), 68.05 (d, *J* = 4.2, C_5), 66.03 (d, *J* = 4.8, C_6), 55.19 (s, C_7), 45.01 (s, C_4), 43.19 (s, C_1), 36.53 (d, *J* = 7.6, C_3), 20.76 (s, CH_3).

^{11}B NMR ($CDCl_3$, 128.33 MHz, J(B,H), Hz): δ 25.5 (d, 1B, J = 135), 14.8 (d, 2B, J = 140), 10.7 (d, 1B, J = 155), 5.2 (d, 1B, J = 140), 3.2 (d, 1B, J = 140), 2.5 (d, 1B, J = 115), −1.75 (d, 1B, J = 140), −19.5 (d, 1B, J = 155).

A similar reaction of **1** (0.136 g, 0.384 mmol) with **2** (0.1 g, 0.192 mmol) was carried out in 10 mL of degassed benzene for 1 h. This, after exactly the same workup procedure as described above, resulted in complexes **4** (0.080 g, 40%) and a mixture of **5** and **6** (0.046 g, 23%) in a ratio of 2:1. Repeated redissolution of a crude mixture of isomers **5** and **6** in CH_2Cl_2 with subsequent addition of a few drops of *n*-hexane afforded 0.009 g (4.5%) of pure isomer **5**. Anal. Calcd for $C_{24}H_{32}B_9Rh$: C, 55.44; H, 6.35; B, 18.59. Found: C, 55.37; H, 6.15; B, 18.68. IR (KBr, cm^{-1}): 2570 (ν_{B-H}). ^{1}H NMR ($CDCl_3$, 400.13 MHz, J(H,H), Hz): δ 7.43 (d, 2H, J = 8.1, C_6H_4), 7.08 (d, 2H, J = 7.9, C_6H_4), 7.01 (d, 2H, J = 8.1, C_6H_4), 6.88 (d, 2H, J = 7.9, C_6H_4), 5.31 (m, 1H, H_5), 4.92 (br s, 1H, H_{8-syn}), 4.46 (br s, 1H, H_{8-anti}), 3.73 (m, 1H, H_3), 3.53 (m, 1H, H_4), 3.30 (m, 1H, H_1), 3.05 (m, 1H, H_6), 2.28 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 1.76 (dd, 2H, J_{AB} = 10.0, $H_{7\alpha}$ ($H_{7\beta}$)), 1.72 (dd, 2H, J_{AB} = 10.0, $H_{7\beta}$ ($H_{7\alpha}$)). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz, J(Rh,C), Hz): δ 141.77, 137.94, 136.97, 135.12, 130.48, 128.92, 128.50, 125.11 (s, C_6H_4), 101.21 (d, J = 2.9, C_2), 85.35 (s.br, C_8), 77.23 (d, J = 4.2, C_5), 72.49 (d, J = 2.9, C_6), 59.78 (s, C_7), 45.71 (s, C_4), 43.59 (s, C_1), 36.49 (d, J = 9.5, C_3), 20.84, 20.74 (s, CH_3). ^{11}B{^{1}H} NMR ($CDCl_3$, 128.33 MHz; J(B,H), Hz): δ 2.0 (1B), 0.9 (1B), −2.0 (1B), −2.9 (1B), −6.35 (1B), −8.35 (1B), −14.25 (1B), −15.1 (1B), −17.5 (1B).

X-ray Data Collection and Structure Refinement Parameters for Complexes 4−6. Details of crystal data, data collection, and structure refinement parameters are given in Table 3. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic temperature factors for all non-hydrogen atoms except for carbon atoms of the disordered organic ligand in **4**, which were refined isotropically. Hydrogen atoms at the carborane ligand in **4** and all hydrogen atoms in **5** and **6** were located from the Fourier synthesis; hydrogen atoms of the disordered organic ligand in **4** were placed geometrically. All hydrogen atoms in **4**−**6** were included in the structure factor calculations in the riding motion approximation. SHELXTL-97[16] was used throughout the calculations.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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