Synthesis and stereochemistry of diastereomeric *closo*-(π,σ-dicyclopentenyl)rhodacarboranes with the agostic C—H...Rh bond

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A series of diastereomeric *closo*-($\eta^{1,2}$-dicyclopentenyl)rhodacarborane complexes with the agostic C—H...Rh bond were synthesized starting from mono-*C*-substituted anionic *nido*-carboranes [*nido*-7-R-7,8-$C_2B_9H_{11}]^-$. The resulting diastereomeric mixtures were separated into individual isomers by either crystallization or chromatography. The structures and the stereochemistry of the diastereomeric complexes were studied in detail by ^1H and ^{13}C NMR spectroscopy. The relative configurations of two key isomers were established by X-ray diffraction analysis. The mechanism of the stereospecific formation of diastereomeric complexes is discussed.

Key words: diastereomeric *closo*-rhodacarboranes, dicyclopentadiene, stereochemistry, agostic C—H...Rh interaction, NMR spectroscopy, X-ray diffraction analysis.

A well-known method for the preparation of cationic complexes with a two-electron three-center C—H...M interaction involves protonation of π-olefin or π-diene transition-metal complexes at the double bond of the hydrocarbon ligand.[1,2] This reaction was also investigated for a series of *closo*-metallacarboranes. Thus, protonation of the anionic complexes [*closo*-3,3-(η^4-diene)-1,2-R^1,R^2-3,1,2-$RhC_2B_9H_9]^-PPN^+$ (diene is cycloocta-1,5-diene (COD) or norborna-2,5-diene (NBN); R^1 and R^2 = H, Alk, or Ar; PPN^+ is bis(triphenylphosphoranylidene)ammonium) with TFA at −73 °C[3,4] afforded thermally unstable *closo*-(π,σ-cycloolefin)rhodacarboranes exhibiting an agostic C—H...Rh interaction. At high temperature, these intermediates were found to be converted into either complexes with the η^3-mode of coordination of the hydrocarbon ligand (in the case of COD) or complexes containing the π-hydrocarbon ligand with the fully transformed skeleton (in the case of NBN).

Previously,[5] we have prepared a series of quite stable *closo*-3,3-($\eta^{1,2}$-dicyclopentenyl)rhodacarboranes with the agostic C—H...Rh bond by the reactions of the anionic complexes [*closo*-3,3-(η^4-$C_{10}H_{12}$)-1,2-R_2-3,1,2-$RhC_2B_9H_9]^-PPN^+$ ($C_{10}H_{12}$ is *endo*-dicyclopentadiene (DCPD); 3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene; R = H or Me) with 70% HPF_6 in ether. More recently,[6] we have found that protonation of one of the anionic complexes (R = CH_2OH) at the double bond of the DCPD ligand can proceed even upon treatment by column chromatography on silica gel using CH_2Cl_2 as the eluent. In the present study, we prepared diastereomeric mono-*C*-substituted *closo*-($\eta^{1,2}$-dicyclopentenyl)rhodacarboranes with an agostic C—H...Rh interaction according to this modified procedure and separated the resulting diastereomeric mixtures of the complexes into individual isomers whose structures and stereochemistry were investigated in detail.

Results and Discussion

The initial anionic complexes [*closo*-3,3-(η^4-$C_{10}H_{12}$)-1-R^1-2-R^2-3,1,2-$RhC_2B_9H_9]^-PPN^+$ (**1a—d**) were synthesized by the ligand-exchange method[3,7] starting from the μ-halide dimer [(η^4-DCPD)$RhCl]_2$ and the corresponding dicarbaundecaborate salts [*nido*-7-R-7,8-$C_2B_9H_{11}]^-K^+$ in the presence of Pr^iONa in Pr^iOH. Taking into account that the compositions and structures of anionic *closo*-complexes **1e** and **1f** have been unambiguously confirmed earlier based on the analytical and spectroscopic data for these complexes,[5] the PPN salts of anionic complexes **1a—d** were used in subsequent reactions without additional purification and analysis. Besides, the structures of the latter complexes agree well with those of their protonation products, *viz.*, of neutral *closo*-(π,σ-dicyclopentenyl)rhodacarboranes.

Chromatography of anionic complexes **1a—c** on a silica gel column (CH_2Cl_2 as the eluent) afforded neutral products of monoprotonation at one of the double bonds of the coordinated DCPD ligand, *viz.*, the complexes *closo*-3,3,3-($\eta^{1,2}$-$C_{10}H_{13}$)-1-R^1-2-R^2-3,1,2-$RhC_2B_9H_9$ (**2—4**), in 65—85% yields. These complexes contain the σ-bond between the metal atom and the hydrocarbon ligand, and the agostic C—H...Rh bond. This procedure was used for the preparation not only of the above-mentioned complexes, but also of *closo*-rhodacarboranes of this type (**5**,[6] **6**, and **7** [5]) described by us previously.

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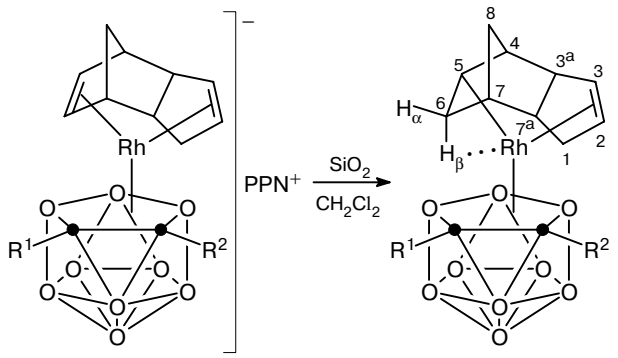

	1a, 2	1b, 3	1c, 4	1d, 5	1e, 6	1f, 7
R^1	H	H	H	H	H	Me
R^2	Me	$CH{=}CH_2$	$CMe{=}CH_2$	CH_2OH	H	Me

Generally, the direction of the attack of the proton is determined by the basicity of the corresponding protonation centers in π-complexes. Previously,[5] we have established that protonation of anionic complexes **1e**,**f** with HPF_6 in ether led exclusively to the *endo*-addition of the proton at one of the double bonds of the η^4-coordinated DCPD ligand. It is reasonable to expect that the direction of the attack of the proton and, as a consequence, the structures of the reaction products can be changed by introducing π- or *n*-basic substituents into the carborane ligand of the anionic complexes. Actually, the stable zwitterionic Rh^I complexes, *viz.*, *closo*-3,3-(η^4-COD)-1-(C^+RMe)-3,1,2-$RhC_2B^-{}_9H_{10}$, along with the products of protonation at the double bond of the COD ligand, *viz.*, the Rh^{III} complexes *closo*-3-(η^3-C_8H_{13})-1-($CR{=}CH_2$)-3,1,2-$RhC_2B_9H_{10}$ (C_8H_{13} is the cyclooctenyl ligand), have been isolated[8] upon treatment of [*closo*-3,3-(η^4-COD)-1-($CR{=}CH_2$)-3,1,2-$RhC_2B_9H_{10}$]$^-PPN^+$ (R = H or Me) with 70% HPF_6 in ether. The former complexes were obtained as a result of competitive protonation of the double bond in the alkenyl substituents. The structurally similar zwitterionic complexes *closo*-3,3-(η^4-diene)-1-(C^+H_2)-3,1,2-$RhC_2B^-{}_9H_{10}$ (diene is COD or NBN) were also prepared by protonation of anionic *closo*-(η^4-diene)rhodacarboranes containing the CH_2OH group in the dicarbollyl ligand.[9] However, no zwitterionic compounds were detected upon chromatography (on a silica gel column using CH_2Cl_2 as the eluent) of the related anionic complexes **1b**,**c** or **1d** containing the DCPD ligand. In the latter case, neutral Rh^{III} complexes **3**—**5** were obtained as the only reaction products. Protonation of complexes **1b**,**c** under more severe conditions with the use of 70% HPF_6 in ether gave analogous results with the only difference that compounds **3** and **4** were obtained in lower yields due to their partial decomposition in the presence of the strong acid. Therefore, protonation of anionic *closo*-rhodacarborane complexes containing the DCPD ligand always proceeds regiospecifically and results in the addition of the proton exclusively at one of the cyclic double bonds of the hydrocarbon ligand.

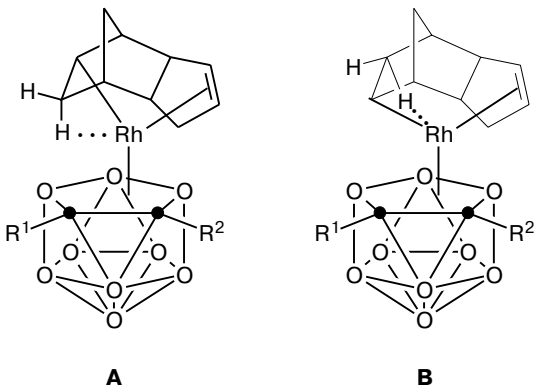

Fig. 1. Possible geometric isomers of the products of protonation of anionic complexes **1a**—**d** at the C(5)=C(6) double bond of the DCPD ligand.

It is known[10—13] that the C(5)=C(6) double bond of the norbornene fragment both in the free and η^4-coordinated DCPD ligands is much more reactive than the C(2)=C(3) double bond. Of four carbon atoms belonging to the double bonds of the coordinated DCPD ligand, which could be involved in the agostic C—H...Rh bond in complexes **2**—**7**, only the C(5) and C(6) atoms would be expected to participate in these bonding interactions. In this connection, the possibility of existence of the geometrical isomers of two types **A** and **B** was considered (Fig. 1). It is significant that in the case of complexes **6** and **7** containing the symmetrical dicarbollyl ligands, these isomers should, in principle, be racemic, whereas in the case of complexes **2**—**5** with the mono-*C*-substituted dicarbollyl ligands, the geometrical isomers both of the **A** and **B** types should exist as mixtures of diastereomeric complexes.

Previously,[5] we have observed only one protonated form in the ^1H and ^{13}C NMR spectra of complexes **6** and **7**. The results of selective decoupling ^1H-{^1H} NMR experiment performed for complex **7** provide unambiguous evidence that only the **A**-type geometrical isomerism is realized in this case. The ^1H NMR spectra of complexes **2**—**5** have two sets of signals with approximately equal intensities. The positions and the multiplicities of these signals are similar to those observed in the spectra of complexes **6** and **7**. These facts indicate that mixtures of diastereomers **2a**,**b**—**5a**,**b** were formed.

In the ^1H NMR spectra of the diastereomeric complexes, the high-field slightly broadened doublet signals for the protons of the agostic C(6)—H(6β)...Rh bond with the spin-spin coupling constants $J_{gem} \approx 18$—19 Hz at $\delta \approx -3$ and the signals for the H(6α) protons, which generally consist of 16 lines (doublets of doublets of doublets of doublets), at $\delta \approx 0.2$—0.9 are most characteristic, which confirms the $\eta^{1,2}$-mode of coordination of the dicyclopentenyl ligand. Since most of the signals of this ligand in the spectra of the diastereomeric mixtures are partially or completely overlapped, they can be unambiguously assigned only in studies of their individual isomers.

For this purpose and with the aim of studying the stereochemistry and the geometrical isomerism of the resulting diastereomeric complexes, we found the conditions for the preparative separation and separated the diastereomeric mixtures of **2a**,**b**—**5a**,**b** into individual isomers. The mixtures of diastereomers **2a**,**b** and **4a**,**b** were quantitatively separated by chromatography on silica gel, whereas the mixture of **3a**,**b** was separated by preparative HPLC. One of the diastereomeric complexes, *viz.*, **5a**, was isolated in the stereochemically pure form by threefold recrystallization of a mixture of **5a**,**b** from $CHCl_3$. In this case, the second diastereomer (**5b**) was obtained in the enriched form as a mixture with **5a** (~1.6 : 1) and was characterized by ^1H NMR spectroscopy. The structures of all diastereomeric complexes were confirmed by the ^1H NMR spectroscopic data (see the Experimental section). The structures of isomers **3a**, **3b**, and **5a** were additionally supported by their $^{13}C\{^1H\}$ and ^{13}C NMR spectra (see the Experimental section). In the ^1H NMR spectra of individual diastereomeric complexes **2a**—**5a** and **2b**—**5b**, the resonances arising from the hydrocarbon ligands were well resolved multiplets, which allowed us to make the assignment of all signals by analogy with the spectra of the diastereomeric pair of **4a** and **4b** for which the assignment of all signals was performed based on the two-dimensional ^1H—^1H COSY NMR spectra. In the ^1H NMR spectra of complexes **2a**—**5a**, which are characterized by the same stereochemical configuration, the resonances due to the H(6β) protons involved in an agostic C—H...Rh interaction are observed at lower field ($\Delta\delta \approx 0.3$ ppm) compared to those from isomers **2b**—**5b**. On the contrary, the signals for the geminal H(6α) protons of isomers **2a**—**5a** are shifted upfield ($\Delta\delta \approx 0.3$—0.5 ppm) relative to the analogous signals of diastereomers **2b**—**5b**.

The $^{13}C\{^1H\}/^{13}C$ NMR spectra also proved to be exceptionally useful in confirming the nature of the metal—ligand bond in the diastereomeric complexes obtained. Thus, the resonances due to the carbon atoms of the vinyl substituents at the carborane cage in the spectra of diastereomeric complexes **3a** and **3b** are observed at very low field (δ_C 139.7 (=CH) and 112.1 ($=CH_2$) for **3a**; δ_C 138.7 (=CH) and 115.7 ($=CH_2$) for **3b**) and display the lack of coupling constants $J_{^{13}C,^{103}Rh}$. All the other resonances in the low-field portion of the spectra were doublets and the assignments were made taking into account the differences in their spin-spin coupling constants $J_{^{13}C,^{103}Rh}$. The coupling constants of the signals arising from coupling with the C(2) and C(3) atoms (5—9 Hz) and that from coupling with the C(5) atom (~15 Hz) agree well with the π- and σ-modes of coordination of the Rh atom by the C(2)=C(3) fragment and the C(5) atom of the hydrocarbon ligand, respectively (see, for example, Ref. 14). It should be noted that the signals for the C(6) atoms in the non-decoupled ^{13}C NMR spectra of diastereomeric complexes **3a** and **3b** are observed as doublets of doublets at δ_C 9.6 and 15.5, respectively. The observed multiplicities of these signals are due to the nonequivalence of the H(6α) ($J_{^{13}C,^1H} \approx 150$ Hz) and H(6β) ($J_{^{13}C,^1H} \approx 90$ Hz) protons of the CH_2 fragment since the latter is involved in an agostic bonding interaction.

Table 1. Principal bond lengths (*d*) and bond angles (φ) in complexes **3b** and **5a** (for two independent molecules (I and II) of both complexes)

Parameter	**3b**		**5a**	
	I	II	I	II
Bond:		*d*/Å		
Rh(3)—C(2)	2.259(5)	2.245(5)	2.237(5)	2.242(5)
Rh(3)—C(3)	2.223(5)	2.226(5)	2.214(5)	2.225(5)
Rh(3)—C(5)	2.058(5)	2.046(5)	2.061(5)	2.051(6)
Rh(3)...C(6)	2.378(6)	2.378(5)	2.359(5)	2.380(6)
Rh(3)—H(6B)	2.02(5)	1.98(4)	1.99(6)	1.96(9)
Rh(3)—C(01)	2.318(5)	2.350(4)	2.253(5)	2.252(5)
Rh(3)—C(02)	2.238(5)	2.263(5)	2.300(5)	2.290(5)
Rh(3)—B(4)	2.148(5)	2.146(5)	2.181(6)	2.209(6)
Rh(3)—B(7)	2.208(5)	2.199(5)	2.167(6)	2.167(7)
Rh(3)—B(8)	2.207(5)	2.194(5)	2.188(6)	2.218(6)
C(1)—C(2)	1.507(7)	1.485(8)	1.512(8)	1.502(8)
C(1)—C(7A)	1.536(7)	1.540(8)	1.531(8)	1.533(9)
C(2)—C(3)	1.372(7)	1.363(8)	1.382(8)	1.406(8)
C(3)—C(3A)	1.510(8)	1.494(7)	1.512(8)	1.493(8)
C(3A)—C(4)	1.529(9)	1.528(8)	1.529(8)	1.544(8)
C(3A)—C(7A)	1.557(8)	1.554(7)	1.556(8)	1.577(8)
C(4)—C(5)	1.516(8)	1.520(7)	1.542(7)	1.528(8)
C(4)—C(8)	1.529(11)	1.532(8)	1.543(9)	1.531(9)
C(5)—C(6)	1.490(8)	1.502(7)	1.506(8)	1.536(8)
C(6)—C(7)	1.556(8)	1.544(7)	1.551(8)	1.538(8)
C(6)—H(6A)	0.88(5)	0.92(4)	0.98(7)	0.98(6)
C(6)—H(6B)	0.99(5)	0.94(4)	1.14(6)	0.93(8)
C(7)—C(8)	1.512(9)	1.546(8)	1.524(9)	1.539(8)
C(7)—C(7A)	1.541(8)	1.525(7)	1.554(8)	1.550(8)
C(01)—C(02)	1.586(6)	1.570(6)	1.601(7)	1.584(7)
C(01)—B(4)	1.757(6)	1.751(7)	1.745(8)	1.746(7)
C(02)—B(7)	1.740(7)	1.743(8)	1.779(8)	1.755(9)
B(4)—B(8)	1.840(7)	1.836(8)	1.778(9)	1.798(8)
B(7)—B(8)	1.791(7)	1.813(8)	1.834(9)	1.846(9)
C(01)—C(13)	1.481(6)	1.479(7)	1.524(7)	1.517(7)
C(13)—C(14)	1.302(7)	1.295(9)	—	—
C(13)—O(1)	—	—	1.427(7)	1.423(7)
Angle:		φ/deg		
C(5)—Rh(3)—C(3)	78.5(2)	78.0(2)	78.3(2)	78.3(2)
C(5)—Rh(3)—C(2)	100.7(2)	100.2(2)	101.4(2)	101.7(2)
C(3)—Rh(3)—H(6B)	81(3)	82(3)	97(5)	95(6)
C(2)—Rh(3)—H(6B)	95(3)	95(3)	81(4)	82(6)
C(6)—H(6B)—Rh(3)	99(3)	103(3)	94(4)	105(6)
C(13)—C(01)—C(02)	119.4(4)	119.1(4)	120.2(4)	119.8(4)
C(13)—C(01)—B(4)	124.8(4)	125.1(4)	121.3(4)	120.9(4)
C(13)—C(01)—Rh(3)	109.5(3)	110.4(3)	108.5(3)	108.2(3)
C(02)—C(01)—B(4)	106.7(3)	106.8(4)	112.0(4)	110.0(4)
C(01)—C(02)—B(7)	115.8(4)	116.2(4)	109.2(4)	113.0(4)
C(01)—B(4)—B(8)	108.3(3)	108.9(4)	108.1(4)	106.5(4)
C(02)—B(7)—B(8)	105.2(3)	104.8(4)	106.9(4)	106.4(4)
B(7)—B(8)—B(4)	103.5(3)	102.8(4)	103.7(4)	103.9(4)
C(14)—C(13)—C(01)	126.5(5)	126.5(6)	—	—
O(1)—C(13)—C(01)	—	—	113.7(4)	110.3(4)

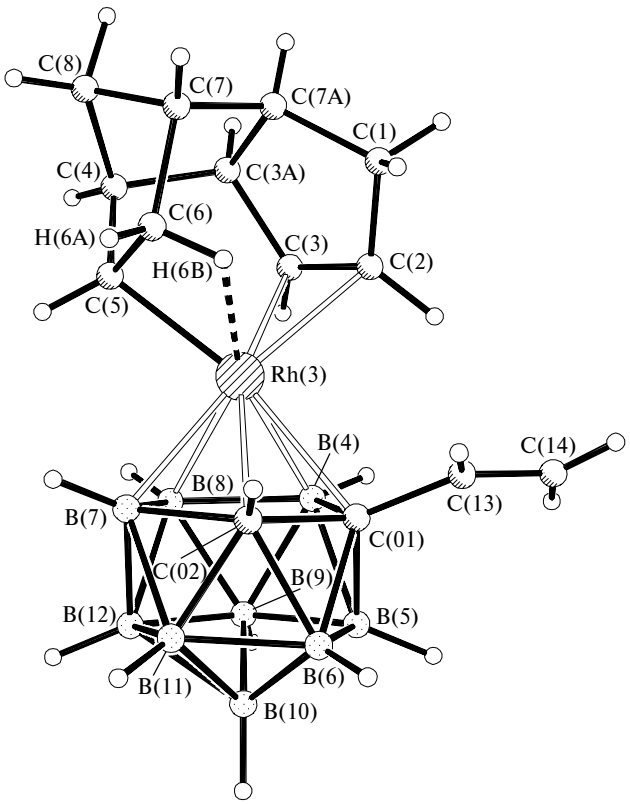

Fig. 2. Molecular structure of diastereomeric complex (*S*,*R*/*R*,*S*)-**3b**. The (*S*,*R*) enantiomer is presented.

The geometrical and configurational isomerism of two individual diastereomeric complexes **3b** and **5a** was investigated by X-ray diffraction analysis. The molecular structures of complexes **3b** and **5a** (both crystal structures contain two crystallographically independent molecules) are shown in Figs. 2 and 3, respectively. The principal geometric characteristics (the bond lengths and bond angles) are given in Table 1. It should be noted that two independent molecules revealed in the crystal structure of isomer **5a** are optical antipodes linked to each other through O—H...O hydrogen bonds (O(1)...O(1′), 2.754(6) Å; O(1)...H(10′), 2.16(7) Å; the O(1)...H(10′)—O(1′) angle is 171(10°)).

According to the X-ray diffraction data, the configurations of the arbitrarily chosen chiral centers at position 1 of the carborane moiety (C(01)) and at position 7 of the hydrocarbon ligand (C(7)) in diastereomers **3b** and **5a** are determined as (*S*,*R*/*R*,*S*) and (*S*,*S*/*R*,*R*), respectively. However, it should be noted that the application of the Cahn—Ingold—Prelog rule for establishing the configurations of these complexes may involve at first glance particular difficulties associated with the formally six-coordinate states of the boron and carbon atoms in the dicarbollyl ligands. However, due to the specificity of the geometric characteristics of the mono-*C*-substituted dicarbollyl ligands, the consideration of the C(01) atom as one of the chiral centers leads to the fact that any one of the adjacent boron atoms is always located only on one side of the triangular plane, which is formed by the Rh(3) and C(02) atoms and the exopolyhedral carbon C(13) atom, and is always a formally lower substituent in the series of the above-mentioned atoms. Taking into account this regularity, the absolute (*S*,*R*) configuration of the chosen chiral C(01) and C(7) centers, respectively, was assigned to the enantiomer of complex **3b** shown in Fig. 2. Therefore, the configuration of the racemate studied by X-ray diffraction analysis

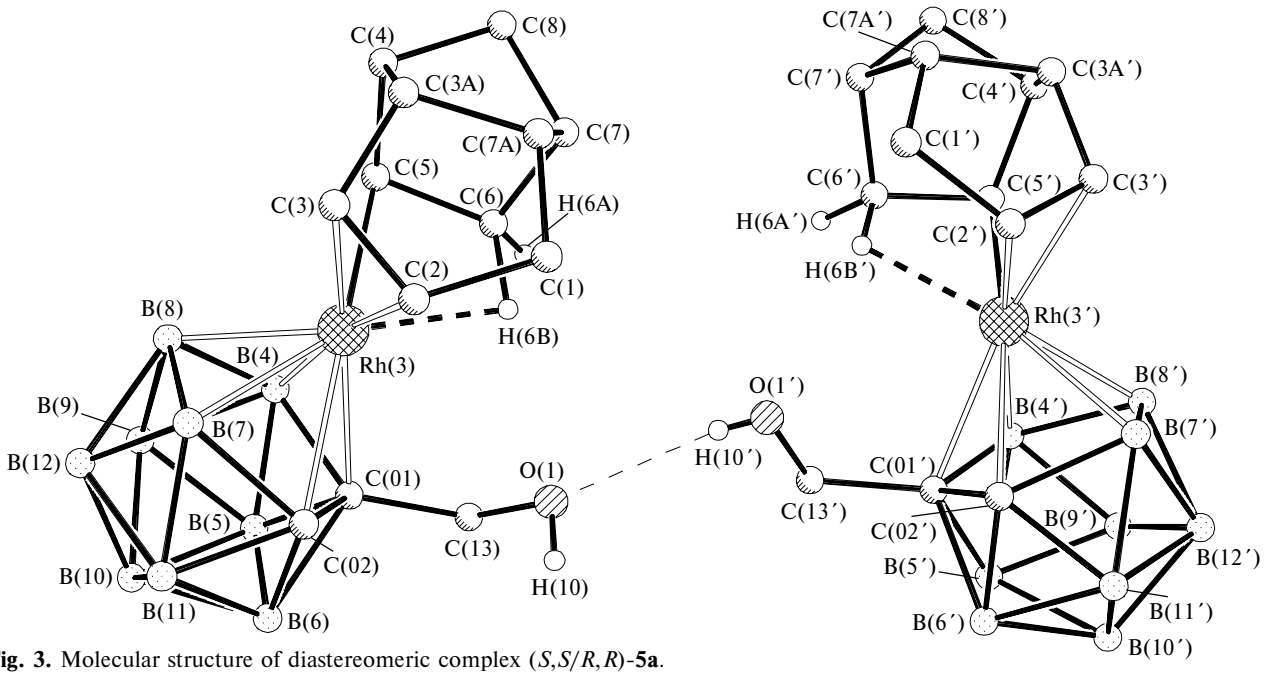

Fig. 3. Molecular structure of diastereomeric complex (*S*,*S*/*R*,*R*)-**5a**.

was determined as (*S,R/R,S*). Analogously, the relative (*S,S/R,R*) configuration was assigned to the same asymmetric centers of diastereomer **5a**.

In complexes **3b** and **5a**, the hydrocarbon ligand is π,σ-coordinated to the Rh atom through the C(2)=C(3) fragment and the C(5) atom, respectively. The Rh(3)—C(5) distances (the average value is 2.054 Å) correspond to the Rh—C σ-bond (2.092 Å),[15] which agrees well also with the coupling constants observed in the $^{13}C\{^1H\}$ NMR spectra of complexes **3b** ($J_{^{13}C(5),^{103}Rh}$ = 15.3 Hz) and **5a** ($J_{^{13}C(5),^{103}Rh}$ = 16 Hz). The formation of the Rh(3)—C(5) σ-bond in complexes **3b** and **5a** is also supported by the fact that the C(5)—C(6) bond in the $\eta^{1,2}$-dicyclopentenyl ligand is elongated (the bond length averaged over four independent molecules is 1.59 Å), whereas the average length of the C(2)=C(3) double bond involved in π-coordination to the Rh atom is 1.381 Å. The high quality of single crystals of **3b** and **5a** allowed us to reveal the positions of all hydrogen atoms, including the terminal H(6α) atom and the agostic H(6β) atom (these atoms are denoted H(6A) and H(6B), respectively, in Figs. 2 and 3). However, the accuracy of the hydrogen atom positions determined by X-ray diffraction, in particular, in the presence of heavy metal atoms, is apparently inadequate to use the observed differences in the C(6)—H(6A) and C(6)—H(6B) bond lengths (see Table 1 for all independent molecules) as a basis for the discussion of the effect of the agostic interaction on the elongation of the C(6)—H(6B) bond caused by the transfer of the electron pair from the C—H(β) bond to the electron-deficient metal atom.[1] The carborane ligands in complexes **3b** and **5a** are π-coordinated to the metal atom without a noticeable deviation of the metal atom from the center of the pentagonal C_2B_3 plane. The geometric parameters of these ligands are typical of *closo*-metallacarborane systems of the semi-sandwich type.[16] It should be emphasized that, according to the X-ray diffraction data, the same **A** type of the geometrical isomerism is realized in diastereomeric complexes **3b** and **5a** possessing opposite relative configurations. In these complexes, the C(2)=C(3) bond coordinated to the metal atom and the C(H)—H...Rh fragment are located on the opposite sides of the plane passing through the midpoint of the C(5)=C(6) bond and the C(2) and C(8) atoms.

In our opinion, the fact that π,σ-dicyclopentenyl complexes **2**—**7** are readily and stereospecifically formed exclusively as geometrical isomers of the **A** type is attributable to the characteristic features of the geometry of the DCPD ligand in transition-metal complexes. It is known that coordination of the DCPD ligand to the metal atom leads to substantial geometric distortions. For example, the C(2)=C(3) bond in the complex (η^4-$C_{10}H_{12}$)$PdCl_2$ [17] retains its coplanarity with the $PdCl_2$ plane and the Pd atom is located at equal distances from both carbon atoms involved in this bond (Pd—C(2), 2.20(2) Å; Pd—C(3), 2.21(2) Å). On the contrary, the C(5)=C(6) is substantially shifted from the metal center along its axis in the $PdCl_2$ plane, and the metal—π-bond angle also deviates essentially (13°) from the standard value (90°). As a result, the distance between the C(5) atom in the norbornene moiety of the coordinated DCPD ligand and the Pd atom (2.19(1) Å) is shorter than the distance between the C(6) and Pd atoms (2.28(1) Å). This deformation analogous to the deformation $\eta^2 \rightarrow \eta^1$ should lead to a change in the charge density at the C(5) and C(6) atoms, *i.e.*, to activation of the C=C double bond *via* π-coordination.[18] Actually, nucleophilic addition reactions involving dicyclopentadiene π-complexes are generally highly regioselective and proceed at the C(6) atom, which is more remote from the metal atom and, therefore, bears a certain positive charge (δ+).[11—13] However, as demonstrated above and exemplified by other π-dicyclopentadiene complexes of the platinum-group metals,[19] the electrophilic addition of the proton also occurs at the same C(6) atom of the DCPD ligand. Hence, the above-considered data are in obvious contradiction. We believe that this contradiction can be resolved by considering the ricochet mechanism of protonation, which involves the initial attack of the proton on the metal center followed by rapid migration of the hydrogen atom as a hydride ion from the metal atom to the C(6) atom of the DCPD ligand resulted in the formation of the agostic C—H...Rh bond in complexes **2**—**7**.

Apparently, the electronic structure of dicarbollyl ligands is responsible for the high thermodynamical stability of neutral π,σ-dicyclopentenyl Rh^{III} complexes **2**—**7**. Although hypothetical zwitterionic complexes of the *closo*-3,3-(η^4-DCPD)-1-C^+R_2-3,1,2-$RhC_2B_9^-H_{10}$ type and protonation products **2**—**7** studied in the present work belong to a group of complexes with a 18-electron configuration, the rhodium atoms in the former complexes are formally Rh^I, whereas these atoms in the synthesized complexes are Rh^{III}, which is in better agreement with the known tendency of double-charged dicarbollyl ligands to stabilize transition metals in higher oxidation states.[20]

In summary, a series of diastereomeric *closo*-(π,σ-dicyclopentenyl)rhodacarborane complexes containing the agostic C—H...Rh bond were synthesized by the new procedure. The conditions for the preparative separation of diastereomeric mixtures were found and the mixtures were successfully separated into individual isomers. The structures and stereochemistry of new complexes were studied by ^1H and ^{13}C NMR spectroscopy in detail. The configurations of two key diastereomers were established based on the X-ray diffraction data.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer; the chemical shifts of protons are given relative to Me_4Si. Anionic complexes **1a**—**f** were synthesized according to a procedure reported previously[5] under an atmo-

sphere of argon. The protonation reactions were carried out in air. Chromatography was performed with the use of silica gel L 40—100 μm (Czech Republic) and Silpearl (Czech Republic); CH_2Cl_2 distilled over CaH_2 was used as the eluent. The separation of diastereomeric mixtures by HPLC was performed on a Beckman-165 liquid chromatograph (Germany) equipped with a SZ (3.3×150 mm) column packed with silica gel Separon SGX (5 μm; Czech Republick); the rate of elution was 1 mL min^{-1}; the detection was based on absorption at 370 nm.

Preparation of ($\eta^{1,2}$-dicyclopentenyl)-*closo*-rhodacarboranes by protonation of anionic complexes on silica gel (general procedure). A solution of the PPN^+ salt of anionic *closo*-(η^4-dicyclopentadiene)rhodacarborane in CH_2Cl_2 was applied on a column with silica gel and the colored band was eluted with CH_2Cl_2. The solvent was evaporated *in vacuo*. The products were additionally purified by recrystallization from a CH_2Cl_2—*n*-hexane mixture.

***Closo*-3,3,3-(2,3-η^2,5-η^1-3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-inden-5-yl)-1-methyl-3,1,2-dicarbollylrhodium (2).** Complex **2** was prepared according to the general procedure from PPN^+ salt **1a** (0.72 g, 0.78 mmol) as orange crystals (a mixture of the diastereomers in a ratio of 1 : 1) in a yield of 0.21 g (69%). Found (%): C, 40.58; H, 6.51; B, 25.80. $C_{13}H_{26}B_9Rh$. Calculated (%): C, 40.82; H, 6.80; B, 25.43. Column chromatography on silica gel Silpearl (a 1 : 2 ether—*n*-hexane mixture as the eluent) afforded (*S,S/R,R*)-diastereomer **2a** and (*S,R/R,S*)-diastereomer **2b** in yields of 0.08 g (27%) and 0.07 g (23%), respectively. ^{1}H NMR of (*S,S/R,R*)-isomer **2a** (CD_2Cl_2), δ:* 6.56 (m, 1 H, H(2)); 6.32 (m, 1 H, H(5)); 5.51 (m, 1 H, H(3)); 4.09 (br.s, 1 H, CH_{carb}); 3.89 (t*, 1 H, H(4)); 2.94 (m, 1 H, H(3a)); 2.73 (m, 4 H, H(7), H(7a), H(1)); 2.20 (dq*, 1 H, H(8α), J_{AB} = 9.7 Hz); 2.08 (s, 3 H, Me); 2.05 (dm, 1 H, H(8β), J_{AB} = 9.7 Hz); 0.70 (dddd, 1 H, H(6α))**; −3.14 (d, 1 H, H(6β), $J_{H(6\beta),H(6\alpha)}$ = 19.0 Hz). ^{1}H NMR of (S,*R/R,S*)-isomer **2b** (CD_2Cl_2), δ: 6.30 (m, 1 H, H(2)); 6.03 (m, 1 H, H(5)); 5.53 (m, 1 H, H(3)); 3.85 (t*, 1 H, H(4), J = 4.8 Hz); 3.64 (br.s, 1 H, CH_{carb}); 3.04 (m, 2 H, H(3a), H(7a)); 2.73 (m, 1 H, H(7)); 2.57 (s, 3 H, Me); 2.45 (m, 2 H, H(1)); 2.18 (dm, 1 H, H(8α), J_{AB} = 10.2 Hz); 2.08 (dm, 1 H, H(8β), J_{AB} = 10.2 Hz); 0.87 (dddd, 1 H, H(6α)); -3.31 (d, 1H, H(6β), $J_{H(6\beta),H(6\alpha)}$ = 16.3 Hz).

***Closo*-3,3,3-(2,3-η^2,5-η^1-3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-inden-5-yl)-1-vinyl-3,1,2-dicarbollylrhodium (3).** Complex **3** was synthesized according to the general procedure from PPN^+ salt **1b** (0.80 g, 0.85 mmol) as red-orange crystals (a mixture of the diastereomers in a ratio of 1 : 1) in a yield of 0.29 g (0.73 mmol, 85%). Found (%): C, 42.60; H, 6.64; B, 24.60. $C_{14}H_{26}B_9Rh$. Calculated (%): C, 42.64; H, 6.60; B, 24.62. The mixture of the diastereomers (0.2 g) was separated by HPLC (a 1 : 3 ether—*n*-hexane mixture as the eluent) to obtain (*S,S/R,R*)-diastereomer **3a** and (*S,R/R,S*)-diastereomer **3b** in yields of 0.09 g (45%) and 0.09 g (45%), respectively. ^{1}H NMR of (*S,S/R,R*)-isomer **3a** ($CDCl_3$), δ: 6.51 (m, 1 H, H(5)); 6.45 (m, 1 H, H(2)); 6.19 (dd, 1 H, C<u>H</u>=CH_2, J_{cis} = 10.5 Hz, J_{trans} = 16.9 Hz); 5.51 (q*, 1 H, H(3)); 5.09 (d, 1 H, =CH<u>H</u>$_{trans}$, J = 16.9 Hz); 4.79 (d, 1 H, =CH<u>H</u>$_{cis}$, J = 10.5 Hz); 4.01 (br.s, 1 H, CH_{carb}); 3.90 (t*, 1 H, H(4), J = 4.7 Hz); 2.91 (m, 1 H, H(3a)); 2.69 (q*, 1 H, H(7a)); 2.42 (m, 1 H, H(7)); 2.39 (m, 2 H, H(1)); 2.12 (d, 1 H, H(8α), J_{AB} = 10.2 Hz); 2.01 (d, 1 H, H(8β), J_{AB} = 10.2 Hz); 0.24 (dddd, 1 H, H(6α)); −3.10 (d, 1 H, H(6β), $J_{H(6\beta),H(6\alpha)}$ = 18.8 Hz). ^{13}C{^{1}H} NMR of (*S,S/R,R*)-isomer **3a** (CD_2Cl_2), δ (J^* = $J_{^{13}C,^{103}Rh}$): 139.7 (<u>C</u>H = CH_2); 112.1 (CH=<u>C</u>H_2); 107.2 (d, C(2) or C(3), J^* = 9.0 Hz); 104.6 (d, C(3) or C(2), J^* = 6.0 Hz); 75.1 (d, C(5), J^* = 15.3 Hz), 61.8 (C(3a) or C(7a)); 58.7 (br.s, CH_{carb}); 52.0 (C(8)); 51.8 (C(7a) or C(3a)); 44.2 (br.s, C_{carb}); 42.7 (C(7) or C(4)); 39.6 (C(4) or C(7)); 31.9 (C(1)); 9.6 (C(6)). ^{13}C NMR of (*S,S/R,R*)-isomer **3a** (CD_2Cl_2), δ (J = $J_{^{13}C,^1H}$, J^* = $J_{^{13}C,^{103}Rh}$): 139.7 (d, <u>C</u>H=CH_2, J = 162.6 Hz); 112.1 (dd, CH=<u>C</u>H_2, $J_{C,H(1)}$ = 157.1 Hz, $J_{C,H(2)}$ = 161.6 Hz); 107.2 (br.d, C(2) or C(3), J = 167.2 Hz); 104.6 (br.d, C(3) or C(2), J = 173.7 Hz); 75.1 (br.d, C(5), J = 162.2 Hz); 61.8 (d, C(3a) or C(7a), J = 152.3 Hz); 58.7 (br.d, CH_{carb}, J = 166.8 Hz); 52.0 (td, C(8), J = 134.7 Hz, J^* = 6.8 Hz); 51.8 (d, C(7a) or C(3a), J = 132.9 Hz); 44.2 (br.s, C_{carb}); 42.7 (d, C(7) or C(4), J = 136.5 Hz); 39.6 (d, C(4) or C(7), J = 145.6 Hz); 31.9 (t, C(1), J = 125.8 Hz); 9.6 (dd, C(6), $J_{C,H(\alpha)}$ = 151.9 Hz, $J_{C,H(\beta)}$ = 91.8 Hz). ^{1}H NMR of (*S,R/R,S*)-isomer **3b** ($CDCl_3$), δ: 6.40 (dd, 1 H, C<u>H</u>=CH_2, J_{cis} = 10.5 Hz, J_{trans} = 16.9 Hz); 6.14 (m, 1 H, H(2)); 5.71 (m, 1 H, H(5)); 5.55 (q*, 1 H, H(3)); 5.15 (d, 1 H, =CH<u>H</u>$_{trans}$, J = 16.9 Hz); 5.03 (d, 1 H, =CH<u>H</u>$_{cis}$, J = 10.5 Hz); 3.86 (t*, 1 H, H(4), J = 4.7 Hz); 3.67 (br.s, 1 H, CH_{carb}); 3.02 (m, 1 H, H(3a)); 2.70 (q*, 1 H, H(7a)); 2.34 (m, 1 H, H(7)); 2.29 (m, 2 H, H(1)); 2.20 (dt, 1 H, H(8α), J_{AB} = 10.2 Hz, J_t = 4.7 Hz); 2.10 (dm, 1 H, H(8β), J_{AB} = 10.2 Hz); 0.77 (dddd, 1 H, H(6α)); −3.43 (d, 1 H, H(6β), $J_{H(6\beta),H(6\alpha)}$ = 18.6 Hz). ^{13}C{^{1}H} NMR of (*S,R/R,S*)-isomer **3b** (CD_2Cl_2), δ (J^* = $J_{^{13}C,^{103}Rh}$): 138.7 (<u>C</u>H=CH_2); 115.7 (CH=<u>C</u>H_2); 108.7 (d, C(2) or C(3), J^* = 9.0 Hz); 91.9 (d, C(3) or C(2), J^* = 5.9 Hz); 79.2 (br.s, C_{carb}); 76.6 (d, C(5), J^* = 15.6 Hz); 63.5 (C(3a or 7a)); 51.3 (br.s, C(8), J^* = 5.3 Hz); 50.4 (C(7a) or C(3a)); 45.5 (br.s, CH_{carb}); 42.7 (C(7) or C(4)); 39.7 (C(4) or C(7)); 32.7 (C(1)); 15.5 (C(6)). ^{13}C NMR of (*S,R/R,S*)-isomer **3b** (CD_2Cl_2), δ (J = $J_{^{13}C,^1H}$, J^* = $J_{^{13}C,^{103}Rh}$): 138.7 (d, <u>C</u>H=CH_2, J = 163.1 Hz); 115.7 (t, CH=<u>C</u>H_2, J = 160.2 Hz); 108.7 (br.d, C(2) or C(3), J = 170.7 Hz); 91.9 (br.d, C(3 or 2), J = 164.6 Hz); 79.2 (br.s, C_{carb}); 76.6 (dm, C(5), J = 153.9 Hz); 63.5 (d, C(3a) or C(7a), J = 146.6 Hz); 51.3 (td, C(8), J = 146.6 Hz, J^* = 5.3 Hz); 50.4 (d, C(7a) or C(3a), J = 136.9 Hz); 45.5 (br.d, CH_{carb}, J = 176.5 Hz); 42.7 (d, C(7) or C(4), J = 141.4 Hz); 39.7 (d, C(4) or C(7), J = 146.0 Hz); 32.7 (t, C(1), J = 146.6 Hz); 15.5 (dd, C(6), $J_{C,H(\alpha)}$ = 149.7 Hz, $J_{C,H(\beta)}$ = 91.6 Hz).

***Closo*-3,3,3-(2,3-η^2,5-η^1-3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-inden-5-yl)-1-isopropenyl-3,1,2-dicarbollylrhodium (4).** Complex **4** was synthesized according to the general procedure from PPN^+ salt **1c** (0.86 g, 0.9 mmol) as a red-orange resin in a yield of 0.23 g (65%) (a mixture of the diastereomers in a ratio of 1 : 1). Column chromatography on silica gel (a 1 : 3 ether—*n*-hexane mixture as the eluent) afforded (*S,S/R,R*)-diastereomer **4a** as red-orange crystals in a yield of 0.07 g (20%) and (*S,R/R,S*)-diastereomer **4b** as a red-orange resin in a yield of 0.08 g (23%). ^{1}H NMR of (*S,S/R,R*)-isomer **4a** ($CDCl_3$), δ: 6.46 (m, 1 H, H(5)); 6.39 (m, 1 H, H(3)); 5.54 (m, 1 H, H(2)); 4.96 (br.s, 1 H, =CH_2); 4.69 (br.s, 1 H, =CH_2); 4.14 (br.s, 1 H, CH_{carb}); 3.90 (t*, 1 H, H(4), J_t = 5.6 Hz); 2.91 (m, 1 H, H(3a)); 2.70 (q*, 1 H, H(7a)); 2.49—2.30 (m, 5 H, H(7), H(1), H(8)); 2.04 (m, 3 H, Me); 0.22 (dddd, 1 H, H(6α)); −3.32 (d, 1 H, H(6β), $J_{H(6\beta),H(6\alpha)}$ = 17.6 Hz). ^{1}H NMR of (*S,R/R,S*)-isomer **4b** ($CDCl_3$), δ: 6.15 (m, 1 H, H(2)); 5.55 (m,

* Hereinafter, t* and q* are triplet- and quadruplet-like multiplet signals; J_t and J_d are the spin-spin coupling constants for triplets and doublets, respectively.

** The pattern of this signal in the spectra of complexes **2a**,**b**—**5a**,**b** is analogous to that observed in the spectra of complexes **6** and **7** reported previously.[5] The detailed analysis of the spin-spin coupling constants has been performed previously.[5]

1 H, H(5)); 5.41 (m, 1 H, H(3)); 4.98 (s, 1 H, $=CH_2$); 4.94 (m, 1 H, $=CH_2$); 3.86 (t*, 1 H, H(4), J_t = 4.5 Hz); 3.79 (br.s, 1 H, CH_{carb}); 3.00 (m, 1 H, H(3a)); 2.70 (m, 1 H, H(7a)); 2.46 (dm, 1 H, H(1α), J_{AB} = 9.8 Hz); 2.42 (dm, 1 H, H(1β), J_{AB} = 9.8 Hz), 2.27 (m, 1 H, H(7)); 2.22 (d, 1 H, H(8α), J_{AB} = 10.4 Hz); 2.12 (s, 3 H, Me); 2.10 (d, 1 H, H(8β), J_{AB} = 10.4 Hz); 0.79 (dddd, 1 H, H(6α)); −3.50 (d, 1 H, H(6β), $J_{H(6\beta),H(6\alpha)}$ = 17.8 Hz).

***Closo*-3,3,3-(2,3-η²,5-η¹-3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-inden-5-yl)-1-hydroxymethyl-3,1,2-dicarbollylrhodium (5).** Complex **5** was prepared according to the general procedure from PPN^+ salt **1d** (0.80 g, 0.85 mmol) as red-orange crystals in a yield of 0.28 g (82%) (a mixture of the diastereomers in a ratio of 1 : 1). Found (%): C, 39.17; H, 6.53; B, 24.41. $C_{13}H_{26}B_9ORh$. Calculated (%): C, 39.89; H, 6.47; B, 24.84. (*S*,*S*/*R*,*R*)-Diastereomer **5a** was isolated in the pure form by threefold recrystallization from $CHCl_3$ in a yield of 0.09 g (67% with respect to one isomer). Its structure and stereochemistry were established by X-ray diffraction analysis (Fig. 3). We failed to isolate (*S*,*R*/*R*,*S*)-diastereomer **5b** from the mother liquor in the individual state. ^{1}H NMR of (*S*,*S*/*R*,*R*)-isomer **5a** (CD_2Cl_2), δ: 6.41 (m, 1 H, H(2)); 6.22 (m, 1 H, H(5)); 5.54 (q*, 1 H, H(3)); 4.17 (br.s, 1 H, CH_{carb}); 3.95 (dd, 1 H, J_{AB} = 12.2 Hz, J_d = 3.7 Hz, $C\underline{H}_ACH_BOH$); 3.89 (m, 1 H, H(4)); 3.56 (dd, 1 H, J_{AB} = 12.2 Hz, J_d = 3.7 Hz, $CH_AC\underline{H}_BOH$); 3.31 (br.t, 1 H, OH); 2.96 (m, 1 H, H(3a)); 2.71 (m, 1 H, H(7a)); 2.45 (m, 3 H, H(7)+H(1)); 2.20 (dt, 1 H, H(8α), J_{AB} = 9.0 Hz, J_t = 1.6 Hz); 2.10 (dm, 1 H, H(8β), J_{AB} = 9.0 Hz); 0.60 (dddd, 1 H, H(6α)); −2.84 (d, 1 H, H(6β), $J_{H(6\beta),H(6\alpha)}$ = 19.0 Hz). $^{13}C\{^1H\}$ NMR of (*S*,*S*/*R*,*R*)-isomer **5a** (CD_2Cl_2), δ (J^* = $J_{^{13}C,^{103}Rh}$): 109.5 (d, C(2) or C(3), J^* = 8.7 Hz); 93.1 (d, C(3) or C(2), J^* = 5.8 Hz); 74.5 (d, C(5), J^* = 16.0 Hz); 68.6 (CH_2OH); 63.3 (C(3a) or C(7a)); 62.1 (br.s, CH_{carb}); 51.9 (C(8)); 50.5 (C(7a) or C(3a)); 45.4 (br.s, C_{carb}); 42.9 (C(7) or C(4)); 39.8 (C(4) or C(7)); 32.0 (C(1)); 9.3 (C(6)). ^{1}H NMR of (*S*,*R*/*R*,*S*)-isomer **5b** (CD_2Cl_2), δ: 6.36 (m, 1 H, H(2)); 5.97 (m, 1 H, H(5)); 5.46 (q*, 1 H, H(3)); 4.33 (dd, 1 H, $C\underline{H}_ACH_BOH$, J_{AB} = 11.9 Hz, J_D = 2.9 Hz); 4.07 (dd, 1 H, $CH_AC\underline{H}_BOH$, J_{AB} = 11.9 Hz, J_D = 5.8 Hz); 3.89 (m, 1 H, H(4)); 3.59 (br.s, 1 H, CH_{carb}); 3.04 (m, 1 H, H(3a)); 2.71 (m, 2 H, OH, H(7a)); 2.48 (m, 3 H, H(7), H(1)); 2.20 (dt, 1 H, H(8α), J_{AB} = 10.0 Hz, J_t = 1.6 Hz); 2.13 (dm, 1 H, H(8β), J_{AB} = 10.0 Hz); 0.80 (dddd, 1 H, H(6α)); −2.96 (dm, 1 H, H(6β), $J_{H(6\beta),H(6\alpha)}$ = 19.0 Hz).

***Closo*-3,3,3-(2,3-η²,5-η¹-3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-inden-5-yl)-3,1,2-dicarbollylrhodium (6).** Complex **6** was prepared according to the general procedure from PPN^+ salt **1e** (0.70 g, 0.77 mmol) as orange crystals in a yield of 0.23 g (79%). The ^{1}H NMR spectrum was identical with that published in the literature.[5]

***Closo*-3,3,3-(2,3-η²,5-η¹-3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-inden-5-yl)-1,2-dimethyl-3,1,2-dicarbollylrhodium (7).** Complex **7** was prepared according to the general procedure from PPN^+ salt **1f** (0.80 g, 0.86 mmol) as dark-red crystals in a yield of 0.27 g (81%). The ^{1}H NMR spectrum was identical with that published in the literature.[5]

X-ray diffraction study of complexes 3b and 5a. Single crystals of complex **3b** were prepared by crystallization from a CH_2Cl_2—*n*-hexane mixture. Single crystals of complex **5a** were obtained by crystallization from $CHCl_3$. The crystallographic data and the principal details of the refinement of complexes **3b** and **5a** are given in Table 2. Both structures were solved by the direct method. The positions and the thermal parameters of the nonhydrogen atoms were refined first isotropically and then anisotropically by the full-matrix least-squares method. The positions of the hydrogen atoms in complexes **3b** and **5a** were located from difference electron density syntheses and refined isotropically. All calculations were carried out on a personal computer with the use of the SHELXTL PLUS 5 program package.[21] The complete tables of the atomic coordinates, thermal parameters, bond lengths, and bond angles were deposited with the Cambridge Structural Database.

Table 2. Crystallographic data and details of the refinement of the crystal structures of **3b** and **5a**

Parameter	**3b**	**5a**
Molecular formula	$C_{14}H_{26}B_9Rh$	$C_{13}H_{26}B_9ORh$
Molecular weight	394.55	398.54
Space group	$P\bar{1}$	*Pbca*
T/K	293(2)	143(2)
a/Å	10.919(3)	13.375(5)
b/Å	12.439(4)	20.031(9)
c/Å	13.910(4)	26.088(9)
α/deg	92.64(2)	
β/deg	107.42(2)	
γ/deg	91.84(3)	
V/Å^3	1798.6(9)	6990(5)
Z	4	16
d_{calc}/g cm^{-3}	1.457	1.515
Diffractometer	Siemens P3/PC	
Radiation	Mo-Kα (λ = 0.71073 Å)	
μ/cm^{-1}	9.40	9.72
Scanning mode	θ/2θ	θ/2θ
$2\theta_{max}$/deg	54	58
Number of independent reflections (R_{int})	7358 (0.0374)	9022
R_1 (based on *F* for reflections with $I > 2\sigma(I)$)	0.0484 (5209 refl.)	0.0557 (6014 refl.)
wR_2 (based on F^2 for all reflections)	0.0882	0.1278
Number of parameters in the refinement	641	641
Weighting scheme	$w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$, where $P = 1/3(F_0^2 + 2F_0^2)$	
a	0.0272	0.0599
b	0.8625	5.4281

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References

1. M. Brookhart and M. L. H. Green, *J. Orgamomet. Chem.*, 1983, **250**, 395.
2. A. G. Ginzburg, *Usp. Khim.*, 1988, **57**, 2046 [*Russ. Chem. Rev.*, 1988, **57** (Engl. Transl.)].
3. D. M. Speckman, C. B. Knobler, and M. F. Hawthorne, *Organometallics*, 1985, **4**, 426.

4. D. M. Speckman, C. B. Knobler, and M. F. Hawthorne, *Organometallics*, 1985, **4**, 1692.
5. I. T. Chizhevskii, T. V. Zinevich, P. V. Petrovskii, V. A. Antonovich, and L. I. Zakharkin, *Metalloorg. Khim.,* 1991, **4**, 1416 [*Organomet. Chem. USSR*, 1991, **4**, 706 (Engl. Transl.)].
6. I. T. Chizhevskii, T. V. Zinevich, P. V. Petrovskii, V. I. Bregadze, F. M. Dolgushin, A. I. Yanovsky, and Yu. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, **4**, 776 [*Russ. Chem. Bull.*, 1995, **4**, 758 (Engl. Transl.)].
7. L. I. Zakharkin, I. T. Chizhevsky, G. G. Zhigareva, P. V. Petrovskii, A. V. Polyakov, A. I. Yanovsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1988, **358**, 449.
8. I. T. Chizhevskii, T. V. Zinevich, P. V. Petrovskii, and V. I. Bregadze, *Metalloorg. Khim.,* 1992, **5**, 1088 [*Russ. Organomet. Chem.*, 1992, **5**, 530 (Engl. Transl.)].
9. I. T. Chizhevskii, T. V. Zinevich, P. V. Petrovskii, V. A. Antonovich, and L. I. Zakharkin, *Metalloorg. Khim.,* 1991, **4**, 1411 [*Organomet. Chem. USSR*, 1991, **4**, 703 (Engl. Transl.)].
10. J. D. Littlehailes, in *Rodd's Chemistry of Carbon Compounds*, Ed. S. Coffey, Elsevier, Amsterdam, 1969, Vol. **II**, Part C, Ch. 11, p. 99.
11. J. K. Stille and R. A. Morgan, *J. Am. Chem. Soc.*, 1966, **88**, 5135.
12. J. K. Stille and D. B. Fox, *J. Am. Chem. Soc.*, 1970, **92**, 1274.
13. W. A. Whitla, W. A. Powell, and L. M. Venanzi, *Chem. Commun.*, 1966, 310.
14. A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
15. J. Evans, B. F. J. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1977, **6**, 510.
16. I. T. Chizhevsky, A. I. Yanovsky, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1997, **536—537**, 51.
17. L. L. Wright, R. M. Wing, and M. F. Rettig, *J. Am. Chem. Soc.*, 1982, **104**, 610.
18. O. Eisenstein and R. Hoffmann, *J. Am. Chem. Soc.*, 1981, **103**, 4308.
19. M. A. Bennett, J. I. McMalon, S. Pelling, G. B. Robertson, and W. A. Wickramasinghe, *Organometallics*, 1985, **4**, 754.
20. A. K. Saxena and N. S. Hosmane, *Chem. Rev.*, 1993, **93**, 1081.
21. G. M. Sheldrick, *SHELXTL Plus, Version 5, Software Reference Manual*, Siemens Industrial Automation, Inc., Madison, 1994.

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