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### Introduction

Acyclic ( $\pi$ -allyl)-*closo*-metallacarborane complexes of transition metals constitute an important class of compounds which are widely used in stoichiometric reactions in metallacarborane chemistry. Thus, much success has been achieved by Stone and co-workers by employing the anionic molybdenum and tungsten ( $\pi$ -allyl)-*closo*-metallacarboranes<sup>1</sup> and later on related complexes of other transition metals<sup>2</sup> in the development of a highly efficient synthetic route to a variety of neutral carborane-containing complexes of different compositions and structures. In particular, Stone's method relies on the displacement of the  $\pi$ -allyl ligand in the anionic 1,2-dicarborane- $(\pi$ -allyl)-metal complexes with different donor molecules, such as t-BuNC, CO, and PPh<sub>3</sub>, by treating the latter complexes with strong acids.<sup>1,2</sup> Closely related to the above stoichiometric reactions are the transformations of  $(\pi$ -allyl) nickel complexes  $[NEt_4][2-{(1-3-\eta^3)-C_3H_4R)}-closo-2,1,7-NiC_2B_9H_{11}]$  (R = H, Ph) derived from the "carbons apart" {nido-7,9-C<sub>2</sub>B<sub>9</sub>}-carborane ligand; the treatment of these species with HBF<sub>4</sub> Et<sub>2</sub>O in the

# Base-mediated transformation of the agostic $(\pi$ -allyl)-*closo*-rhodacarboranes into complexes with an open $(1-5-\eta^5)$ -pentadienyl ligand<sup>+</sup>

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The reactions of agostic (CH<sub>3</sub>...Rh) complexes  $[3-\{(1-3-\eta^3)-1,1,2-\text{trimethylallyl}\}-1-R-2-R'-closo-3,1,2-RhC_2B_9H_9]$  [**1**: R = R' = Me; **2**: R,R' =  $\mu$ -(ortho-xylylene); **3**: R = Ph, R' = Me] in a cooled (+5 °C) toluene solution with the strong non-nucleophilic base *N*,*N*,*N'*,*N'*-tetramethylnaphthalene-1,8-diamine (*tmnd*) formally involve a linear coupling of the  $\pi$ -allyl ligand of one molecule of the complex to the  $\pi$ -allyl ligand of the second molecule of the complex, ultimately forming the structurally novel mononuclear species  $[3-\{(1-5-\eta^5)-2,3-\text{dimethyl}-5-(3-\text{methylbuten}-2-yl)\text{pentadienyl}\}-1-R-2-R'-closo-3,1,2-RhC_2B_9H_9]$  (**4**, **5**) and (**6a**,**b**, a mixture of diastereomers). Complexes **5** and **6a**,**b** were also prepared using weaker bases such as PPh<sub>3</sub> or even EtOH instead of *tmnd*. All new complexes **4–6** were characterized by a combination of analytical and multinuclear NMR data, as well as by single-crystal X-ray diffraction studies of two selected species **5** and the major diastereomer of **6**, which revealed an open  $\eta^5$ -pentadienyl coordination mode of the hydrocarbon ligands in these complexes.

presence of cyclic dienes such as dcp, cod, chd, nbd, and C<sub>5</sub>Me<sub>5</sub>H was shown to afford a series of neutral ( $\eta^4$ -diene)*closo*-nickelacarboranes of the general formula [2-( $\eta^4$ -diene)*closo*-2,1,7-NiC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>].<sup>3</sup> Relevant to these studies<sup>4</sup> are investigations on the hydrogen activation by ( $\pi$ -allyl)-*closo*-rhodacarborane [3-{(1-3- $\eta^3$ )-C<sub>3</sub>H<sub>5</sub>}-3-PPh<sub>3</sub>-*closo*-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] that quantitatively produces either the known dimeric compound [3-PPh<sub>3</sub>-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sub>2</sub><sup>5</sup> or, in the presence of PPh<sub>3</sub>, the catalytically active hydrido complex [3,3-(PPh<sub>3</sub>)<sub>2</sub>-3-*H*-*closo*-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>].<sup>6</sup>

### **Results and discussion**

#### Synthesis of pentadienyl-type complexes 4-6

Recently, we have reported a convenient one-pot synthesis of a series of acyclic ( $\pi$ -allyl)-*closo*-rhodacarboranes of the general formula [3-{ $\pi$ -(R"-allyl)}-1-R-2-R'-*closo*-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>] (where R" is an aliphatic substituent), a new family of neutral metallacarborane complexes containing a relatively rare agostic (CH<sub>3</sub>...Rh) bonding system.<sup>7,8</sup> The facile and efficient synthesis of these  $\pi$ -allyl compounds allowed us to undertake the systematic exploration of their reactivity and catalytic properties.<sup>7</sup> Thus, in the present work we found that the treatment of [3-{(1-3- $\eta$ <sup>3</sup>)-1,1,2-trimethylallyl}-1-R-2-R'-*closo*-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>] [1: R = R' = Me;<sup>7</sup> 2: R,R' =  $\mu$ -(*ortho*-xylylene);<sup>7</sup> 3: R = Ph, R' = Me<sup>8</sup>] in a cooled (+5 °C) toluene solution with 2.5 equiv. of the

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<sup>&</sup>lt;sup>†</sup>Electronic supplementary information (ESI) available: Crystallographic data of 5 and 6a, and 2D  $[^{1}H^{-1}H]$ -COSY spectra of 4. CCDC 965360 and 965361. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c3dt52838c



Scheme 1 Synthesis of *closo*-rhodacarborane complexes with an open  $(1-5-\eta^5)$ -pentadienyl-type ligands in the presence of *tmnd*.

N,N,N',N'-tetramethylnaphthalene-1,8-diamine (tmnd is the non-nucleophilic base frequently used as the proton sponge) for 12 h afforded air-stable crystalline products  $[3-{(1-5-\eta^5)-2,3$ dimethyl-5-(3-methylbuten-2-yl)-pentadienyl}-1-R-2-R'-closo-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>] (4-6), respectively (Scheme 1). Each of these complexes was isolated from the reactions as the only metallacarborane product in reasonable to good yields based on onehalf of reacted complexes 1-3. They are air-stable in the solid state and in solutions of aromatic or chlorinated hydrocarbons, and their purification can be accomplished by column chromatography on silica gel. Based on the single-crystal X-ray diffraction data for 5 and the major diastereomer of 6 (vide infra) and on the multinuclear NMR data, all complexes 4-6 were assigned as having conventional 12-vertex closo geometry. However, a particularly noteworthy structural feature of molecules 4-6 is an open  $(1-5-\eta^5)$ -pentadienyl-type hydrocarbon ligand newly formed at their rhodium vertices.

Within the family of acyclic 18-electron ( $\pi$ -allyl)-*closo*-metallacarborane complexes of transition metals, several quite stable triphenylphosphine-containing rhodium species, such as  $[3-\{(1-3-\eta^3)-C_3H_4R\}-3-PPh_3-closo-3,1,2-RhC_2B_9H_{11}]$  (R = H, Me) and  $[2-PPh_3-2-\{(1-3-\eta^3)-C_3H_5\}-closo-2,1,7-RhC_2B_9H_{11}]$ , have been previously described.9 It seemed probable, therefore, that similar non-agostic 18-electron complexes of the general  $[3-{(1-3-\eta^3)-1,1,2-trimethylallyl}-3-PPh_3-1-R-2-R'-closo$ formula 3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>] might also be expected to be formed via simple treatment of agostic complexes 1-3 with the PPh<sub>3</sub> reagent. However, this turned out not to be the case. It was found that in the reaction of either 2 or 3 with PPh<sub>3</sub> the latter reagent serves as a non-nucleophilic base, again, giving rise to complexes 5 and 6, respectively. Moreover, complexes 5 and 6 can also be prepared by the treatment of a solution of 2 and 3, respectively, in toluene with a much weaker base (EtOH). Compared with the relatively short reaction time when using tmnd as a base, the duration of both these reactions of 2 or 3 with PPh<sub>3</sub> and/ or EtOH is greatly increased from 12 h to two days and one week, respectively, as can be seen from Table 1. Taking this into account and the fact that the reaction of 1 to form 4 failed to proceed in the presence of a base weaker than *tmnd*, the former route for preparing complexes 4-6 can be considered to be the most synthetically useful. A likely explanation for such a behavior of 1 is that the acidity of the agostic hydrogen atom in this complex is weaker compared to those in complexes 2 and 3, although we have no definite proof for this suggestion other than the above experimental fact.

 Table 1
 Reaction conditions and yields of compounds 4–6

Base-mediated formation of <b>4–6</b>	Base			
	<i>tmnd</i> (2.5 eq.)	PPh <sub>3</sub> (2.5 eq.)	EtOH (>50 eq.)	
	Reaction time/yield of <b>4–6</b> (%)			
$1 \rightarrow 4$ $2 \rightarrow 5$ $3 \rightarrow 6a,b$ (diastereomeric mixture)	12 h/49 12 h/75 12 h/78	No reaction 2 days/56 2 days/62	No reaction 1 week/14 1 week/15	

Although at this point there is insufficient experimental evidence for the exact pathway of this coupling reaction, we can suggest a possible mechanism by which pentadienyl-type complexes 4-6 are formed (Scheme 2). Since the agostic hydrogen atom in 1-3 possesses an acidic character, the likely pathway for the first stage of the reaction may involve the agostic hydrogen abstraction either from complexes 1-3 or their dienehydride isomers [3,3-(η<sup>4</sup>-diene)-3-hydrido-1-R-2-R'-closo-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>] (not shown in Scheme 2). Under base-mediated conditions, both these species may yield the reactive anionic Rh(1) species A with the 1,3-diene ligand at the rhodium vertex,<sup>10</sup> which may slowly transform in solution to give the  $\sigma$ -allylic complex **B** having a potential electrophilic reactivity. This complex B may further get alkylated at the rhodium center by the nucleophilic anion **A** to give the allylic  $\pi$ , $\sigma$ -binuclear complex C, which may become agostic in nature after the migration of the Rh-bound moiety to the diene ligand. Again, the doubly agostic complex D, through complex E, can ultimately convert to products 4-6 via the diene-hydride mechanism and through the migration of the β-hydrogen to the nearest allylic function. The latter route should be accompanied by the loss of one of the Rh carborane moieties, presumably in the form of  $[R, R'C_2B_9H_9RhH(base)_n]$  (n = 1 or 2), as proposed in Scheme 2.

# Single-crystal X-ray diffraction study of 5 and 6a (the major diastereomer)

The rather unusual result obtained in the reactions of 1–3 that produce a short series of  $\eta^5$ -pentadienyl-type complexes 4–6 was confirmed by a single-crystal X-ray diffraction study of species 5 and the major diastereomer of 6, complex 6a. Single crystals of both 5 and 6a suitable for X-ray diffraction were

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Scheme 2 Possible mechanism of the formation of  $(1-5-\eta^5)$ -pentadienyl-type complexes 4-6 under base-mediated conditions.

grown from dichloromethane–*n*-hexane mixtures at room temperature. The molecular structures of both complexes are shown in Fig. 1. Selected geometric parameters (bond distances and bond angles) are listed in Table 2. Although numerous examples of transition metal complexes with  $(1-5-\eta^5)$ -pentadienyl ligands are known and structurally characterized in organometallic chemistry,<sup>11</sup> we are aware of only several structurally studied smaller-cage metallacarborane mixed-sandwich dimeric complexes reported by Hosmane and coworkers, such as  $[(1-5-\eta^5)-2,4-(Me)_2C_5H_5)(\eta^5-2\cdot R-3\cdot(Me_3Si)-2,3-C_2B_4H_4)M]_2$  [M = lanthanides (Y, Dy, Gd, Tb, Ho, Er, Tm, Lu); R = Me\_3Si or Me],<sup>12</sup> in which the 2,4-pentadienyl ligands are coordinated symmetrically by lanthanide metals.

The overall geometry of 5 and 6a clearly confirmed that these complexes can be considered as neutral *closo*-

metallacarborane species with a pseudooctahedral 18-electron configuration of the Rh(m) center. The rhodium atoms in both species are  $\eta^5$ -coordinated in a symmetric fashion by *C*,*C*'-di-substituted *nido*-carborane cage ligands with the Rh–C(1,2) and Rh–B(4,7,8) distances averaging for 5 at 2.258 and 2.181 Å and for **6a** at 2.249 and 2.182 Å, respectively, and are rather asymmetrically bound to the same type  $\eta^5$ -pentadienyl ligand terminally substituted by the isopenten-2-yl function. Indeed, the Rh–C(01) separation of 2.122(5) and 2.148(2) Å in 5 and **6a**, respectively, proved to be considerably shorter than the other four Rh–C(02···05) distances, which range from 2.213(3) to 2.447(2) Å in 5 and from 2.221(4) to 2.372(5) Å in **6a**. Interestingly, despite the U-shaped  $\eta^5$ -pentadienyl ligand in 5 and **6a**, the carbon atoms C(01···05) are not all coplanar. In molecule **6a**, the carbon atom C(05) is 0.22 Å above the plane defined by



Fig. 1 ORTEP drawings of the molecular structures of compounds 5 (left) and 6a (right) with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

Table 2 Selected interatomic distances (Å) and angles (°) of complexes 5 and 6a

Complexes	5	6a
Rh(3)-C(1)	2.253(5)	2.227(2)
Rh(3)-C(2)	2.262(5)	2.271(2)
Rh(3)-B(4)	2.159(5)	2.164(3)
Rh(3)–B(7)	2.179(6)	2.170(3)
Rh(3)–B(8)	2.206(5)	2.213(3)
Rh(3)-C(01)	2.122(5)	2.148(2)
Rh(3)-C(02)	2.221(4)	2.230(2)
Rh(3)-C(03)	2.286(4)	2.251(3)
Rh(3)-C(04)	2.226(5)	2.243(3)
Rh(3)-C(05)	2.372(5)	2.447(2)
C(1)-C(2)	1.593(7)	1.624(3)
C(01) - C(02)	1.426(7)	1.425(3)
C(02)-C(03)	1.424(6)	1.417(3)
C(02)-C(09)	1.501(6)	1.518(4)
C(03)-C(04)	1.431(7)	1.455(4)
C(03)-C(010)	1.514(6)	1.510(3)
C(04)-C(05)	1.385(7)	1.375(3)
C(05)-C(06)	1.473(7)	1.476(3)
C(06)-C(07)	1.353(7)	1.351(3)
C(06)-C(011)	1.507(6)	1.516(4)
C(07)–C(08)	1.499(7)	1.502(4)
C(07)–C(012)	1.495(7)	1.509(4)
C(03)-C(02)-C(01)	120.9(4)	121.3(2)
C(03)-C(02)-C(09)	122.2(4)	120.5(2)
C(01)-C(02)-C(09)	116.8(4)	117.9(2)
C(02)-C(03)-C(04)	123.6(4)	123.2(2)
C(02)-C(03)-C(010)	119.8(4)	121.5(2)
C(04)-C(03)-C(010)	116.3(4)	115.2(2)
C(05)-C(04)-C(03)	127.1(5)	129.6(2)
C(04)-C(05)-C(06)	124.5(4)	123.1(2)
C(07)-C(06)-C(05)	118.8(4)	120.1(2)
C(07)-C(06)-C(011)	122.6(4)	121.0(2)
C(05)-C(06)-C(011)	118.6(4)	118.6(2)
C(06)-C(07)-C(08)	124.5(5)	123.3(2)
C(06)-C(07)-C(012)	121.8(4)	123.0(2)
C(08)-C(07)-C(012)	113.7(4)	113.7(2)

the C(01…C04) atoms, whereas C(04) is only 0.003 Å above it. The carbon atoms C(04) and C(05) in 5 do not lie in the plane of the C(01)–C(02)–C03) atoms, the deviations from this plane toward and away from the rhodium atom being 0.11 and 0.08 Å, respectively. Moreover, the C–C bond lengths in the  $\eta^5$ coordinated pentadienyl moiety of the ligand are highly different; the C(03)-C(04) distances in both complexes are longer (1.431(7) Å for 5 and 1.455(4) Å for 6a), whereas C(04)-C(05) are shorter (1.385(7) Å for 5 and 1.375(3) Å for 6a) than the other two carbon-carbon bonds in this part of the ligand. Note that the latter distances are similar to the C(05)-C(06)and C(06)-C(07) bond lengths in the uncoordinated isopenten-2-yl substituent, which have average values of 1.4745 and 1.352 Å for complexes 5 and 6a, respectively. The X-ray diffraction data suggest some contribution of the  $\eta^{3,2}$ -allylolefinic form into the total pentadienyl structure of the hydrocarbon ligand in these complexes where the carbon atoms C(01...03)define the allyl moiety and the C(04...05) atoms define the olefin moiety of the ligands. In fact, this description may be applied at least to 5, where the deviation of the pentadienyl ligand from planarity is more pronounced. Note that more or less the same structural pattern is observed in the

known 2,4-pentadienyl-type rhenium complex  $[(\eta^5-C_5Me_5)ReCl \{\eta^5-(3,4-diphenylhexa-2,4-diene-6-yl)\}]$ <sup>13</sup> where the  $\eta^5$ -coordinated pentadienyl skeleton composed of five carbon atoms is not planar.

# Multinuclear NMR spectroscopic characterization of compounds 4-6

The detailed examination of the room-temperature <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **4–6** reveals their solution structures. Standard homo- and heteronuclear 2D correlation techniques were successfully used to assign the proton and carbon resonances in their <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra. Two correlation spectra of **4**: 2D [<sup>1</sup>H–<sup>1</sup>H]-COSY and [<sup>13</sup>C–<sup>1</sup>H]-HMBC are given as ESI,†

The <sup>1</sup>H NMR spectra of all η<sup>5</sup>-pentadienyl rhodacarborane complexes are somewhat similar in that they all display a set of two pairs of characteristic proton resonances in the range from 2.3 to 5.5 ppm along with five upfield methyl resonances and resonances corresponding to arene and methyl substituents at the carborane cage ligand. Of these sets of resonances, the first two for complexes 4 and 5, a sharp doublet at ca. 4.0 ppm with  $J_{\text{gem}} \sim 3.9$  Hz and a broad triplet-like signal at *ca*. 2.5 ppm, share a cross-peak in the 2D  $[^{1}H^{-1}H]$ -COSY spectra. In the 2D  $[^{13}C^{-1}H]$ -HSQC spectra of 4 and 5 (see, for example, Fig. 2) both these resonances are also connected by a crosspeak to the single carbon resonance at ca. 58.0 ppm originating from the terminal CH<sub>2</sub> groups of the pentadienyl ligands. The fact that the resonances of this pair observed at higher field split into triplets can reasonably be explained by an additional coupling arising from  $J(^{103}Rh-^{1}H) = 2.6$  Hz. Based on this observation, the resonances at ca. 2.5 ppm in the spectra of 4 and 5 can be assigned to the protons H(1-anti), and the other resonances at ca. 4.0 ppm can be assigned to H(1-syn). Both proton resonances in the lower field region of the <sup>1</sup>H NMR spectra of 4 and 5 exhibit doublet structures due to the *transoid* couplings of J(H,H) = 12.9 Hz; the higher-field doublet is somewhat broadened again due to the additional coupling  $J(^{103}Rh-^{1}H)$ , which is, however, smaller than 1.0 Hz in this case. These doublet resonances at 5.32 and 4.68 ppm (in the case of 4) and at 4.96 and 4.45 ppm (in the case of 5) share a cross-peak between themselves in the 2D [<sup>1</sup>H-<sup>1</sup>H]-COSY spectra of 4 and 5, whereas these doublets in the 2D [<sup>13</sup>C-<sup>1</sup>H]-HSQC spectra are connected by cross-peaks to different carbon resonances (see, for instance, Fig. 2). Based on these spectroscopic data, the above doublet resonances were assigned to the protons H(4) and H(5) of the 2,3dimethylpentadienyl moiety of the ligand in 4 and 5. Taking all these facts into account and based on the observed crosspeaks between other signals in the 2D [13C-1H]-HSQC, 2D  $[^{13}C-^{1}H]$ -HMBC, as well as 2D  $[^{1}H-^{1}H]$ -COSY spectra of 4 and 5, we made the remaining assignments in their <sup>1</sup>H and <sup>13</sup>C NMR spectra as shown in the Experimental section.

By analogy with 4 and 5, we also assigned the resonances in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of diastereomeric complexes **6a,b**, in which double sets of all principal proton and carbon resonances of both the pentadienyl and carborane ligands are

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Fig. 2 The 2D [<sup>13</sup>C-<sup>1</sup>H]-HSQC spectrum of 5 in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C showing the assignment of the proton and some carbon resonances.

clearly observed (see the Experimental section). Based on the integration of the resonances associated with the pentadienyl ligand, such as well-resolved signals originating from the terminal  $CH_2$  groups, the relative ratio of diastereomers **6a** and **6b** was estimated as *ca.* 2 : 1.

The examination of the <sup>11</sup>B/<sup>11</sup>B{<sup>11</sup>B} NMR spectra of compounds **4–6** provided additional confirmation of their structures. These spectra of **4** and **5** revealed a set of resonances corresponding to nine cage boron atoms of these molecules, all of which are observed in the expected integral ratio. The <sup>11</sup>B {<sup>1</sup>H} NMR spectrum of the diastereomeric mixture **6a,b** proved, however, to be more complicated. Thus, it displays, along with resonances of the major diastereomer **6a**, a set of more weak boron signals consistent with the presence of the minor isomeric product which, due to overlapping, were only partly presented in the Experimental section.

#### Conclusions

The unusual base-mediated linear coupling reactions of the agostic (CH<sub>3</sub>…Rh) ( $\pi$ -allyl)rhodacarborane complexes have been described. The products of these reactions (compounds **4**, **5** and **6a,b**, a mixture of diastereomers) were characterized by a combination of analytical and multinuclear NMR data, as well as by single-crystal X-ray diffraction studies of two selected species **5** and **6a**. A particularly noteworthy structural feature of molecules **4–6** is an open  $\eta^5$ -pentadienyl-type hydrocarbon ligand newly formed at their rhodium vertices.

#### **Experimental**

#### Materials and methods

All reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques. Solvents including those used for the column chromatography were distilled from appropriate drying agents under argon prior to use. Chromatography columns (ca. 12-15 cm in length and 1.8 cm in diameter) were packed with silica gel (Acros, 230-400 Mesh). NMR spectra were recorded in CD<sub>2</sub>Cl<sub>2</sub> (5.32 ppm vs. Me<sub>4</sub>Si) with a Bruker AMX-400 spectrometer at the following frequencies: 400.13 MHz (<sup>1</sup>H), 100.61 MHz (<sup>13</sup>C) and 128.33 MHz (<sup>11</sup>B). Proton and boron chemical shifts were referenced to residual protons in CD2Cl2 or to external BF3·Et2O, respectively, with downfield shifts taken as positive. IR spectra in KBr were obtained using a Nicolet Magna-750 spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Institute of Organoelement Compounds of the RAS. Starting rhodium allylic complexes (1-3)7,8 were prepared according to the literature methods. All other reagents were supplied commercially.

#### Synthetic procedures

General method for the synthesis of  $\{(1-5-\eta^5)-2,3-dimethyl-5-(3-methylbutene-2-yl)pentadienyl}rhodacarborane complexes (4-6). To a solution of complexes 1-3 (0.2 mmol) in 8 ml of degassed toluene was added either$ *tmnd*(0.6 mmol) or PPh<sub>3</sub> (0.6 mmol) or EtOH (*ca*. 2 ml). The resulting mixture was then stirred at 5 °C overnight, 2 days or 1 week, respectively. After the reactions were completed (TLC control using the CH<sub>2</sub>Cl<sub>2</sub>-

*n*-hexane (1:4) mixture as an eluent), the resulting dark suspension was treated by column chromatography eluting a colored fraction with  $CH_2Cl_2$ –*n*-hexane (1:2). The solvent was evaporated under reduced pressure, and the residue was treated with *n*-hexane to afford **4–6a**,**b** as crystalline solids. Recrystallization of crude solids from a dichloromethane–*n*-hexane mixture resulted in analytically pure complexes **4–6a**,**b**.

[3-{(1-5-η<sup>5</sup>)-2,3-Dimethyl-5-(3-methylbuten-2-yl)pentadienyl}- $1,2-(CH_3)_2$ -closo- $3,1,2-RhC_2B_9H_9$  (4). The general method described above was employed: 1 (100 mg, 0.29 mmol), tmnd (161 mg, 0.87 mmol), degassed toluene (8 ml), reaction time, 12 h. Yield of 4 (orange microcrystals) after recrystallization from a mixture of CH<sub>2</sub>Cl<sub>2</sub>-n-hexane: 30 mg (49%). IR spectrum (KBr, cm<sup>-1</sup>): 2549 ( $\nu_{BH}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  5.33 (d, 1H, <sup>3</sup>J<sub>HH</sub> = 12.9 Hz, H4), 4.68 (br.d, 1H,  ${}^{3}J_{HH}$  = 12.9 Hz, H5), 4.09 [d, 1H,  ${}^{2}J_{HH}$  = 3.9 Hz, H(1-syn)], 2.45 [br.t,  ${}^{2}J_{HH}$  = 3.9 Hz,  $J_{RhH}$  = 2.6 Hz, 1H, H(1-anti)], 2.12 [s, 3H, 3-CH<sub>3</sub>], 2.01 (s, 3H, CH<sub>3</sub>-carb), 2.00 (s, 3H, CH<sub>3</sub>-carb), 1.95 (s, 3H, 2-CH<sub>3</sub>), 1.84, 1.81 (s, 2 × 3H, 7-CH<sub>3</sub>), 1.75 (s, 3H, 6-CH<sub>3</sub>).  ${}^{13}C{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  143.4 (C7), 127.1 (C6), 112.3 (d, J<sub>RhC</sub> = 3.7 Hz, C2), 111.0 (d, J<sub>RhC</sub> = 3.0 Hz, C3), 104.0 (d,  $J_{RhC}$  = 3.7 Hz, C4), 100.3 (d,  $J_{RhC}$  = 5.3 Hz, C5), 72.2 (m, C-carb), 69.5 (m, C-carb), 58.0 (d, J<sub>RhC</sub> = 14.0 Hz, C1), 29.8 (s, 3H, CH3-carb), 27.6 (s, 3H, CH3-carb), 23.6, 22.8 (7-CH<sub>3</sub>), 21.4 (2-CH<sub>3</sub>), 20.1 (3-CH<sub>3</sub>), 14.8 (6-CH<sub>3</sub>). <sup>11</sup>B NMR  $(CD_2Cl_2, J = J_{BH})$ :  $\delta$  5.7 (d, 1B, J = 143 Hz), 3.2 (d, 1B, J =154 Hz), 0.2 (d, 1B, J = 146 Hz), -2.9 (d, 1B, J = 146 Hz), -7.3 (d, 2B, J = 136 Hz), -11.7 (d, 2B, J = 156 Hz), -13.9 (d, 1B, J = 151 Hz). Anal. calcd for C16H34B9Rh: C 45.04; H 8.03; B 22.81%; found: C 45.25; H 8.29; B 22.88%.

{(1-5-ŋ<sup>5</sup>)-2,3-Dimethyl-5-(3-methylbutene-2-yl)pentadienyl}- $1,2-\mu-(1',2'-xylylene)-closo-3,1,2-RhC_2B_9H_9$  (5). The general method described above was employed: 2 (100 mg, 0.24 mmol), degassed toluene (8 ml), tmnd (133 mg, 0.72 mmol; reaction time, 12 h), PPh<sub>3</sub> (189 mg, 0.72 mmol; reaction time, 48 h) or EtOH (2 ml; reaction time, one week). Yield of 5 (yellow microcrystals) after recrystallization from a mixture of CH<sub>2</sub>Cl<sub>2</sub>-n-hexane: 45 mg (75%) (in the presence of *tmnd*); 33 mg (56%) (in the presence of  $PPh_3$ ); 8 mg (14%) (in the presence of EtOH). IR spectrum (KBr, cm<sup>-1</sup>): 2549 ( $\nu_{BH}$ ). <sup>1</sup>H NMR ( $CD_2Cl_2$ ):  $\delta$  7.28–7.19 (m, 2H, H-aryl), 7.09 (br. d, 1H, H-aryl), 7.05 (br. d, 1H, H-aryl), 4.96 (d, 1H,  ${}^{3}J_{HH} = 12.8$  Hz, H4), 4.45 (d, 1H,  ${}^{3}J_{HH}$  = 12.8 Hz, H5), 4.08 [d, 1H,  ${}^{2}J_{HH}$  = 3.8 Hz, H(1-syn)], 3.98 (d, 1H, J<sub>AB</sub> = 19.2 Hz, CHH-aryl), 3.81 (d, 1H, J<sub>AB</sub> = 18.7 Hz, CHH-aryl), 3.59 (d, 1H, J<sub>AB</sub> = 18.7 Hz, CHHaryl), 3.49 (d, 1H,  $J_{AB}$  = 19.2 Hz, CH*H*-aryl), 2.34 [br. t,  ${}^{2}J_{HH}$  = 3.8 Hz, J<sub>RhH</sub> = 2.7 Hz, 1H, H(1-anti)], 1.89 (s, 3H, 7-CH<sub>3</sub>), 1.86 (s, 3H, 2-CH<sub>3</sub>), 1.82 (s, 3H, 7-CH<sub>3</sub>), 1.78 (s, 3H, 6-CH<sub>3</sub>), 1.06 (s, 3H, 3-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  143.9 (C7), 131.2, 131.2 (Cipso), 130.5, 129.3, 127.8, 127.6 (C-aryl), 126.5 (C6), 115.4 (d,  $J_{\rm RhC}$  = 2.1 Hz, C2), 111.0 (d,  $J_{\rm RhC}$  = 3.5 Hz, C3), 101.6 (d,  $J_{\rm RhC}$  = 3.6 Hz, C4), 98.3 (br. s, C5), 70.9 (m, C-carb), 65.9 (m, C-carb), 58.0 (d,  $J_{RhC}$  = 14.4 Hz, C1), 43.6 (CH<sub>2</sub>-carb), 42.2 (CH<sub>2</sub>-carb), 23.7, 23.0 (7-CH<sub>3</sub>), 21.1 (2-CH<sub>3</sub>), 19.6 (3-CH<sub>3</sub>), 15.1 (6-CH<sub>3</sub>). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $J = J_{BH}$ ):  $\delta$  7.7 (d, 1B, J = 135 Hz), 4.2 (d, 1B, J =139 Hz), 1.1 (d, 1B, J = 144 Hz), -4.2 (d, 1B, J = 153 Hz), -7.0 (d, 1B, J = 138 Hz), -8.0 (d, 1B, J = 132 Hz), -10.7 (d, 1B, J =

136 Hz), -13.3 (m, 2B). Anal. calcd for C<sub>22</sub>H<sub>36</sub>B<sub>9</sub>Rh: C 52.77; H 7.25; B 19.43%; found: C 52.76; H 7.35; B 19.58%.

{(1-5-η<sup>5</sup>)-2,3-Dimethyl-5-(3-methylbutene-2-yl)pentadienyl}-1-CH<sub>3</sub>-2-Ph-closo-3,1,2-RhC<sub>2</sub>B<sub>9</sub>H<sub>9</sub>] (6a,b). The general method described above was employed: 3 (80 mg, 0.2 mmol), degassed toluene (6 ml), tmnd (112 mg, 0.6 mmol; reaction time, 12 h), PPh<sub>3</sub> (154 mg, 0.6 mmol; reaction time, 48 h) or EtOH (1.5 ml; reaction time, one week). Yield of 6a,b (deep-red microcrystals): 38 mg (78%) (in the presence of *tmnd*), 30 mg (62%) (in the presence of  $PPh_3$ ), 7 mg (15%) (in the presence of EtOH). IR spectrum (KBr, cm<sup>-1</sup>): 2547 ( $\nu_{BH}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, \*major diastereomer): 8 7.22-7.21 (10H, H-aryl\*, H-aryl), 5.38 (d, 2H,  ${}^{3}J_{\rm HH}$  = 14.0 Hz, H5\*, H5), 4.83 (d, 2H,  ${}^{3}J_{\rm HH}$  = 14.0 Hz, H4\*, H4), 4.13 [d, 1H,  ${}^{2}J_{HH}$  = 3.9 Hz, H(1-anti)\*], 4.08 [d, 1H,  ${}^{2}J_{HH}$  = 4.0 Hz, H(1-anti)], 2.97 [d, 1H,  ${}^{2}J_{HH}$  = 3.9 Hz, H(1-syn)\*], 2.80 [d, 1H,  ${}^{2}J_{HH}$  = 3.6 Hz, H(1-syn)], 2.23 (s, 3H, CH<sub>3</sub>-carb\*), 2.13 (s, 3H, CH<sub>3</sub>-carb), 1.86 (s, 3H, 2-CH<sub>3</sub>\*), 1.83 (s, 3H, 2-CH<sub>3</sub>), 1.81 (s, 3H, 3-CH<sub>3</sub>), 1.77 (s, 3H, 3-CH<sub>3</sub>\*), 1.75 (s, 3H, 7-CH<sub>3</sub>), 1.74 (s, 6H, 7-CH<sub>3</sub>\*, 7-CH<sub>3</sub>), 1.69 (s, 3H, 7-CH<sub>3</sub>\*), 1.51 (s, 3H, 6-CH<sub>3</sub>\*), 1.27 (s, 3H, 6-CH<sub>3</sub>).  ${}^{13}C{}^{1}H$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  145.3 (C3\*), 145.0 (C3), 142.2 (Cipso\*), 142.0 (Cipso), 128.8, 128.5, 128.3, 128.1, 128.1, 128.1, 127.9 (C-aryl\*, C-aryl), 127.6 (C6\*), 127.3 (C6), 119.6 (C5\*, C5), 114.6 (d,  $J_{RhC}$  = 3.7 Hz, C3), 114.1 (d,  $J_{RhC}$  = 4.4 Hz, C2\*, C2), 106.3 (d,  $J_{RhC}$  = 4.2 Hz, C3\*), 105.3 (d,  $J_{RhC}$  = 12.5 Hz, C4\*, C4), 84.6, 78.5 (C-carb\*), 79.0 (C-carb), 58.6 (d, J<sub>RbC</sub> = 12.5 Hz, C1\*), 58.2 (d, J<sub>RhC</sub> = 12.9 Hz, C1), 32.1 (CH<sub>3</sub>-carb, CH<sub>3</sub>carb\*), 23.8 (7-CH<sub>3</sub>\*), 23.7 (7-CH<sub>3</sub>), 22.9 (7-CH<sub>3</sub>\*, 7-CH<sub>3</sub>), 22.2 (2-CH<sub>3</sub>\*, 2-CH<sub>3</sub>), 20.2 (3-CH<sub>3</sub>), 19.4 (3-CH<sub>3</sub>)\*, 14.8 (6-CH<sub>3</sub>\*), 14.0 (6-CH<sub>3</sub>). <sup>11</sup>B NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $J = J_{BH}$ ):  $\delta$  7.2 (d, J = 143 Hz), 6.2 (d, J = 114 Hz), 3.3 (d, J = 142 Hz), 1.8 (d, J = 225 Hz), 1.5 (d, *J* = 150 Hz), 0.3 (d, *J* = 162 Hz), -2.3 (d, *J* = 139 Hz), -5.2 (d, *J* = 125 Hz), -6.2 (d, J = 131 Hz), -7.3 (d, J = 136 Hz), -8.4 (d, J = 143 Hz), -10.2 (d, J = 160 Hz), -11.5 (d, J = 162 Hz), -12.7 (d, J = 165 Hz), -13.1 - -15.9 (m). Anal. calcd for  $C_{21}H_{36}B_9Rh$ : C 51.61; H 7.42; B 19.91%; found: C 50.89; H 7.15; B 19.86%.

#### X-Ray diffraction studies

Crystals of 5 and 6a suitable for X-ray diffraction study were obtained by recrystallization of purified complexes from a methylenechloride-n-hexane mixture at ambient temperature. Single-crystal X-ray diffraction studies were carried out using a Bruker SMART APEX II diffractometer (graphite monochromated Mo-K<sub> $\alpha$ </sub> radiation,  $\lambda = 0.71073$  Å,  $\omega$ -scan technique, T =100 K). The APEX II software<sup>14</sup> was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction, and SHELXTL<sup>15</sup> for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against  $F^2$ with the anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms at the cage boron atoms as well as at the C(01), C(04), C(05) atoms of the pentadienyl ligands were located from difference Fourier maps and refined isotropically without restraints; the rest of the hydrogen atoms were placed in the geometrically calculated positions and included

 Table 3
 Crystal data, data collection and structure refinement parameters for 5 and 6a

Compound	5	6a
Molecular formula	C22H36B9Rh	C <sub>21</sub> H <sub>36</sub> B <sub>9</sub> Rh
Formula weight	500.71	488.70
Dimension, mm <sup>3</sup>	0.16  imes 0.11  imes 0.08	$0.27 \times 0.10 \times 0.07$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_{1}2_{1}2_{1}$
a (Å)	9.3802(7)	9.575(5)
b (Å)	17.295(1)	15.128(9)
c (Å)	14.8261)	16.401(9)
$\alpha$ (°)	90	90
$\beta(\hat{o})$	93.867(2)	90
γ(°)	90	90
$V(A^3)$	2399.6(3)	2376(2)
Z	4	4
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.386	1.366
$2\theta_{\max}(\circ)$	56	60
Linear absorption $(\mu)$ (cm <sup>-1</sup> )	7.21	7.26
No. unique refl. $(R_{int})$	5771 (0.1174)	6881(0.0400)
No. observed refl. $(I > 2\sigma(I))$	3489	6505
No. parameters	346	337
$R_1$ (on F for observed refl.) <sup>a</sup>	0.0511	0.0284
$wR_2$ (on $F^2$ for all refl.) <sup>b</sup>	0.1268	0.0649
GOOF	0.995	1.002

in the structure factor calculations in the riding motion approximation. The Flack parameter value 0.46 (2) found for **6a** shows a racemic mixture in this case. The principal experimental and crystallographic parameters are presented in Table 3.

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