exo-nido-Cyclooctadienerhodacarboranes: Synthesis, Reactivity, and Catalytic Properties in Alkene Hydrogenation

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Abstract: Reaction of [Rh(acac)(cod)] with 1 equivalent of $HClO_4$ and subsequent treatment with tetramethylammonium or cesium salts of [7-SR-8-R′-7,8-$C_2B_9H_{10}$]$^-$ anions affords [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(cod)] (**1**: R, R′ = Ph; **2**: R = Ph, R′ = Me; **3**: R = Et, R′ = Me). The structure of **1** has been determined by crystallographic studies. The Rh(I) has a normal four-coordinated square planar geometry and the carborane ligand is bonded to the metal by means of a S−Rh and a B(11)−H−Rh bond. The cod ligand fulfills the coordination sphere of the metal with two olefin−Rh bonds. Variable-temperature $^1H\{^{11}B\}$ NMR experiments indicate that **1** undergoes B−H/B−H−Rh exchange coupled with rotation of the [Rh(cod)]$^+$ moiety. This dynamic process appears to involve exclusively the B(11)−H group. The presence of two species that exchange at room temperature is detected for complexes **2** and **3**. A structure analogous to **1** is suggested for the major species, whereas the minor species appears to involve a [Rh(cod)]$^+$ fragment bonded to the cage by a single S−Rh bond. Complexes **1**−**3** rearrange in solution to give [*closo*-3-(η^3-C_8H_{13})-1-SR-2-R′-3,1,2-Rh$C_2B_9H_9$] (**4**: R, R′ = Ph; **5**: R = Ph, R′ = Me; **6**: R = Et, R′ = Me). The crystal structure of **4** reveals lack of bonding between C(1)−C(2) and the cluster adopts a pseudocloso geometry. The weighted average $^{11}B\{^1H\}$ NMR chemical shift of **5** and **6** suggests that these clusters have a normal closo structure. Kinetic studies of the reactions **2** → **5** and **3** → **6** showed a common first-order rate constant for the two reactions. Complexes **2** and **3** in the presence of 1 equivalent of PPh_3 present similar activity in the hydrogenation of cyclohexene to the parent diphosphine complexes [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$]. The *closo*-cyclooctenyl complexes **4** and **5** exhibit higher activity than the parent exo-nido isomers in the hydrogenation of cyclohexene.

Introduction

We have recently reported the synthesis of *exo-nido*-monophosphino and *exo-nido*-monothiorhodacarboranes of formula [Rh(7-X-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (X = PR_2, SR; R, R′ = alkyl, aryl).[1] The distinguishing feature associated with these complexes is the presence of a [Rh(PPh_3)$_2$]$^+$ fragment bonded to the carborane cage through a S−Rh or P−Rh and a B(11)−H−Rh bond. The types of B−H−M bonds are well documented both in icosahedral cages and in smaller borates. The necessary condition for them to take place is to have an electron-enriched B−H, as was recently demonstrated by using neutral boranes B_2H_4·2PMe_3,[2] or B_2H_4·(PMe_2)$_2$$CH_2$.[3] These compounds, although neutral, can be viewed as having a negative boron and a positive phosphorus. The negative charge is what makes BH_4^- so convenient for production of such a bond.[4] The B−H−M bonds have been definitely demonstrated in [7,8-$C_2B_9H_{12}$]$^-$ metal derivatives, although only a fraction of them contain the above-mentioned type of bond. In those compounds in which the B−H−M bond takes place it is said that the cluster presents a nonspectator behavior.[5] The formation of B−H−M bonds is, most probably, a first step in many reactions during which substitution on boron takes place, and in hydrogenation or hydroboration. With few exceptions the boron or boron atoms involved are farthest from the cluster carbon atoms. Thus, initial substitution usually takes place at position 10 in the ligand's nomenclature. It is convenient that when a single-cluster carbon is bonded to a coordinating element (e.g., sulfur) in [7,8-$C_2B_9H_{12}$]$^-$ derivatives, invariably a B(11)−H−M bond is formed upon coordination to M, where B(11) is the boron adjacent to C(7). The monothiorhodacarboranes of formula [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] (R, R′ = alkyl, aryl)[1a] incorporating the bond B(11)−H−M are very active catalysts in the hydrogenation of 1-alkenes under mild conditions (P = 1 bar, T = 25 °C), whereas the monophosphino compounds require higher temperatures and pressures. On the other hand, the activity of these systems is substantially decreased in the presence of added triphenylphosphine, which suggests that reversible dissociation of triphenylphosphine is an important step preceding the activation of hydrogen in the catalytic cycle. In addition, one feature of these rhodacarboranes and others reported earlier[6] is the relatively low activity in the hydrogena-

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tion of internal alkenes. A useful strategy to obtain enhanced hydrogenation rates, which was first developed by Schrock and Osborn,[7] consists of replacing the phosphine ligands by alkene ligands. Irreversible hydrogenation of the alkene ligand releases a noncoordinating alkane and produces an open coordination site on the metal. Hawthorne and co-workers first applied this method to a *closo*-rhodacarborane catalyst and enhanced rates were obtained.[8] However, we are not aware of the existence of *exo-nido*-rhodacarboranes in which B−H−Rh interactions and Rh-alkene bonds coexist in the same molecule other than our recent report on [Rh(7-PPh_2-8-Me-7,8-$C_2B_9H_{10}$)(cod)].[9] These considerations led us to explore the possibility of obtaining *exo-nido*-monothiorhodacarboranes which incorporates ancillary alkene ligands. In this paper, the preparation of cyclooctadienethiorhodacarborane complexes is described and the spectroscopic, chemical, and catalytic properties are reported.

Results and Discussion

Synthesis and Characterization of *exo-nido*-Cyclooctadienethiorhodacarborane Complexes. Initially, the dimer [RhCl(cod)]$_2$ was considered to be an acceptable material to produce the desired cyclooctadienerhodium complexes. However, no reaction was observed when [RhCl(cod)]$_2$ and [NMe_4][7-SPh-8-Me-7,8-$C_2B_9H_{10}$] were refluxed in a 1:1 mixture of MeOH/CH_2Cl_2. This was ascribed to the inability of [7-SR-8-R′-7,8-$C_2B_9H_{10}$]$^-$ anions to displace chloride ligand from the coordination sphere of transition metals.[1,10] For that reason, the use of the cesium salt of [7-SPh-8-Me-7,8-$C_2B_9H_{10}$]$^-$ to precipitate the chloride ligand as CsCl was attempted. Although this procedure had been successfully applied in the synthesis of other rhodacarboranes,[1,6c] no complex could be isolated from the reaction of Cs[7-SPh-8-Me-7,8-$C_2B_9H_{10}$] and [RhCl(cod)]$_2$ in an 8:1 toluene/ethanol mixture. These negative results prompted us to consider other rhodium complexes as starting materials. [Rh(acac)(cod)] has been long known to be an useful precursor to prepare a variety of cyclooctadienerhodium complexes.[7,11] The procedure commonly used involves acid-promoted removal[12] of the acetylacetonate ligand by an appropriate mineral acid such as $HClO_4$ or HBF_4. The reaction of [Rh(acac)(cod)] with 1 equivalent of $HClO_4$ in tetrahydrofuran (THF) and subsequent treatment with the cesium or tetramethylammonium salts of [7-SR-8-R′-7,8-$C_2B_9H_{10}$]$^-$ ligands led to the isolation of rhodium complexes **1**−**3** (**1**: R, R′ = Ph; **2**: R = Ph, R′ = Me; **3**: R = Et, R′ = Me) whose elemental analyses were consistent with the formula [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(cod)]. The $^{11}B\{^1H\}$ NMR spectra of the complexes presented seven resonances corresponding to nine boron atoms in the zone of −5 to −35 ppm. The IR spectra of **1**−**3** showed an absorption at 2119−2077 cm^{-1} attributable to B−H−Rh interactions. However, the negative zone of the $^1H\{^{11}B\}$ NMR spectra showed a broad resonance in the range −2.37 to −2.90 characteristic of B−H−B bridging protons, but no further resonances at higher field which could confirm the presence of B−H−Rh interactions. An X-ray crystallographic study of **1** was undertaken to obtain more information about the nature of the interaction between the [Rh(cod)]$^+$ fragment and the carborane cage. A simplified drawing of the complex unit is shown in Figure 1 and crystallographic data and selected bond parameters are given at Tables 1 and 2, respectively. The Rh(I) center has a distorted four-coordinated square planar geometry. The two bonds from the cage to Rh(I) are formed by the sulfur atom and the hydrogen atom bonded to B(11) at the C_2B_3 open face. Two olefin−Rh bonds from the cyclooctadiene ligand fulfill the coordination sphere of the metal. If we consider that the midpoint (M1) of the C(25)−C(26) bond and the midpoint (M2) of the C(29)−C(30) bond are the coordinating sites to Rh atom, then the coordination planes Rh, S, H(11) and Rh, M1, M2 are twisted 15.6(10)°.

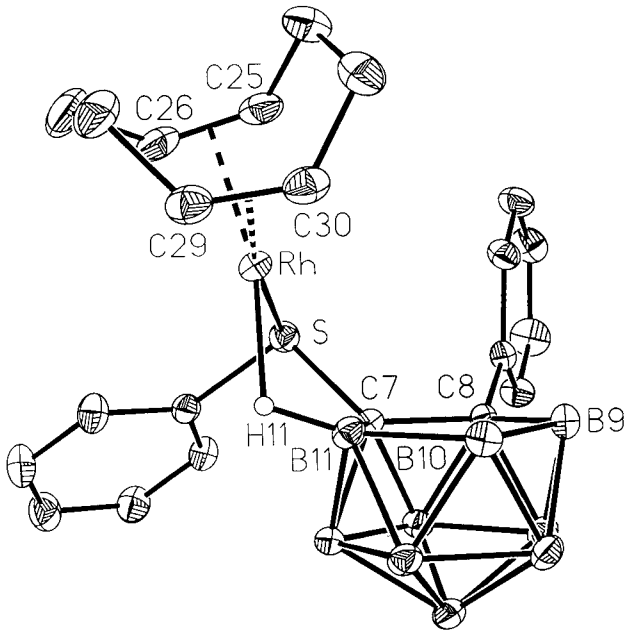

Figure 1. Crystal structure of **1**. Only H(11) is marked in the figure, all others are not displayed.

When this structure is compared to that of [Rh(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$],[1a] significant differences in the orientations of the Rh, S, H(11) plane and the C_2B_3 open-face plane are observed. In **1** the angle between those planes is 85.0(7)° and in [Rh(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] it is 51(2)°. The Rh(I) distance to the C_2B_3 plane in **1** is 2.116(3) Å, whereas the equivalent in [Rh(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] is 1.71(1) Å. Torsion angles C(8)−C(7)−S−C(13) and B(11)−C(7)−S−C(13) in **1** are 129.0(2)° and −93.1(2)°, respectively. Equivalent torsion angles in [Rh(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] are −102.0(7)° and 119.3(6)°. This means that two different conformers could be found in [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(PPh_3)$_2$] or [Rh(7-SR-8-R′-7,8-$C_2B_9H_{10}$)(cod)] assuming that H(11) and S are bonded to Rh(I). The nature of R and

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Table 1. Crystallographic Data and Structural Refinement Details for Compounds **1** and **4**

	1	**4**
empirical formula	$C_{22}H_{32}B_9RhS$	$C_{22}H_{32}B_9RhS$
formula weight	528.74	528.74
crystal system	triclinic	monoclinic
space group	P−1 (no. 2)	$P2_1/n$ (no. 14)
crystal habit, color	prism, pale yellow	plate, red
a (Å)	11.364(1)	9.698(1)
b (Å)	11.895(2)	16.420(2)
c (Å)	10.767(2)	15.938(1)
α (deg)	107.92(1)	90
β (deg)	100.74(1)	97.088(9)
γ (deg)	64.830(9)	90
V (Å^3)	1250.7(3)	2518.6(4)
Z	2	4
T (°C)	21	21
λ (Å)	0.71069	0.71069
ρ (g cm^{-3})	1.404	1.394
μ (cm^{-1})	7.76	7.71
goodness-of-fit	1.002	1.067
R1[a] [$I > 2\sigma(I)$]	0.0283	0.0270
wR2[b]	0.0639	0.0562

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Rh−C(25)	2.132(3)	Rh−S	2.3694(8)
Rh−C(26)	2.127(3)	Rh−H(11)	1.85(3)
Rh−C(29)	2.182(3)	S−C(7)	1.809(3)
Rh−C(30)	2.170(3)	C(7)−C(8)	1.570(3)
C(25)−Rh−S	94.4(1)	C(29)−Rh−S	168.7(1)
C(26)−Rh−S	94.9(1)	S−Rh−H(11)	88.0(9)
C(30)−Rh−S	154.4(1)	C(7)−S−Rh	83.98(9)

R′ in [7-SR-8-R′-7,8-$C_2B_9H_{10}$]$^-$ and the ancillary ligands PPh_3 or cod are important factors in the formation of these conformers. For steric reasons the lower belt B−H hydrogens are not coordinated to Rh(I) in the complexes under discussion.

Exo-nido Species. (a) Dynamic Behavior in Solution. The ^{1}H NMR resonances corresponding to the cyclooctadiene olefinic protons of **1**−**3** appeared as two broad signals in the range of 4.85−4.50 ppm. The respective $^{13}C\{^1H\}$ NMR spectra also showed two broad signals at 84−82 ppm. These observations were intriguing given the asymmetric nature of [7-SR-8-R′-7,8-$C_2B_9H_{10}$]$^-$ ligands, where four different olefinic resonances would be expected. For this reason, the variable-temperature $^1H\{^{11}B\}$ NMR spectra were recorded which provided useful information about the structure of the complexes in solution. Unfortunately, the poor solubility of **1** in common solvents and the instability of **2** and **3** (see next section) precluded the study of the variable-temperature $^{13}C\{^1H\}$ NMR spectra, for which a relatively high number of scans is required.

On cooling **1** in CD_2Cl_2 the two broad olefinic resonances in the $^1H\{^{11}B\}$ NMR spectrum decoalesced at −25 °C and resolved at −94 °C to give four resonances at 5.43, 5.09, 4.37, and 3.96 ppm corresponding to the four olefinic protons of the cod ligand (Figure 2). Focusing the negative zone of the spectrum, a new broad resonance centered at −2.78 ppm appeared at −25 °C which, on further cooling to −94 °C, shifted to −3.05 ppm (Figure 3). Although this signal could correspond to a B−H−Rh interaction, B−H−B resonances at ca. −3 ppm are not rare.[13] To rule out this last possibility, the bridge-deuterated complex [Rh(10-D-7-SPh-8-Ph-7,8-$C_2B_9H_9$)(cod)] (**9**) was synthesized from [NMe_4][10-D-7-SPh-8-Ph-7,8-$C_2B_9H_9$] and [Rh(acac)(cod)], and the variable $^1H\{^{11}B\}$ NMR spectra were recorded (Figure 4). The $^1H\{^{11}B\}$ NMR spectrum at room temperature showed no signal in the negative zone, indicating that the B−D−B deuterium label of the carborane ligand was retained in the complex. On cooling to −94 °C only a signal at −3.05 ppm integrating one proton appeared, thus supporting the B−H−Rh assignment for this resonance. Therefore, rapid rotation of the cod ligand coupled to rapid exchange between B−H−Rh and terminal B−H hydrogens in the NMR time scale occurs at room temperature. Nevertheless, only one isomer appears to be involved in this dynamic process because only one set of four olefinic resonances, one B−H−B signal, and one B−H−Rh interaction are observed at low temperature. Thus, although **1** is evidently fluxional, the stereochemistry observed in solid state seems to be essentially retained in solution.

Complexes **2** and **3** also exhibited similar fluxional behavior. However, the variable-temperature $^1H\{^{11}B\}$ NMR spectra indicated the presence of two isomers in solution. For instance, complex **2** in CD_2Cl_2 at −94 °C exhibited three resonances at

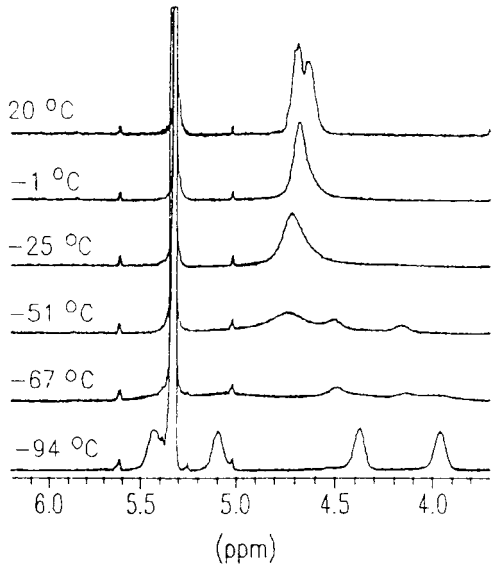

Figure 2. Olefinic zone of the variable-temperature $^1H\{^{11}B\}$ NMR spectra of **1** in CD_2Cl_2.

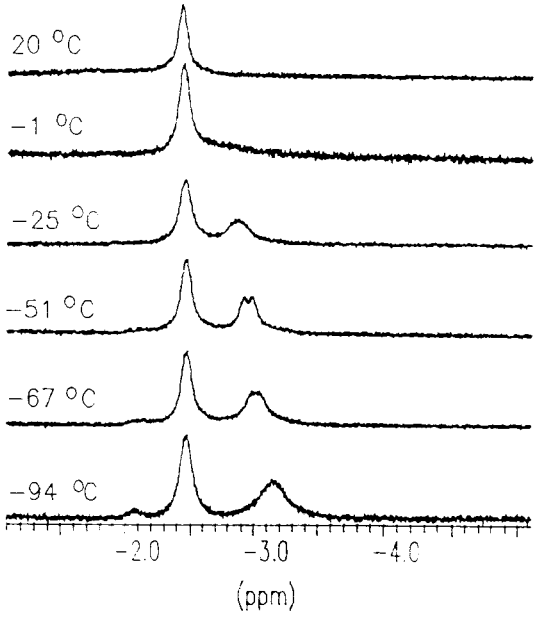

Figure 3. Negative zone of the variable-temperature $^1H\{^{11}B\}$ NMR spectra of **1** in CD_2Cl_2.

(13) For instance, several monophosphinorhodacarboranes of formula [Rh(7-PR_2-8-R′-$C_2B_9H_{10}$)(PPh_3)$_2$] typically exhibit ^{1}H NMR B−H−B resonances at ca. −3 ppm.[b]

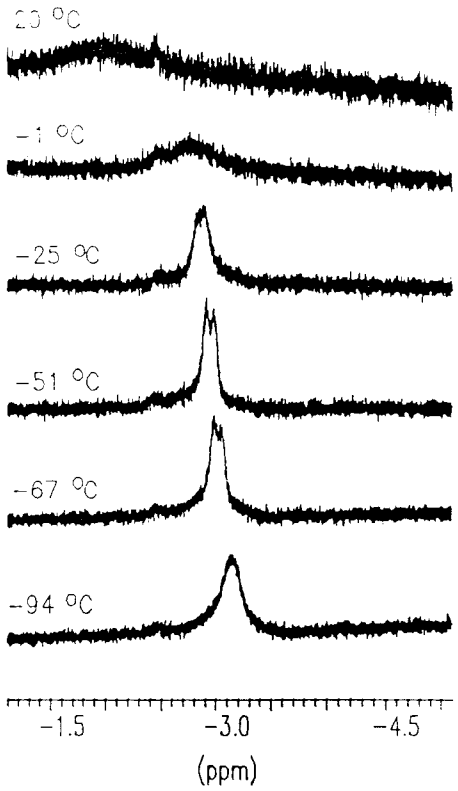

Figure 4. Negative zone of the variable-temperature $^1H\{^{11}B\}$ NMR spectra of **9** in CD_2Cl_2.

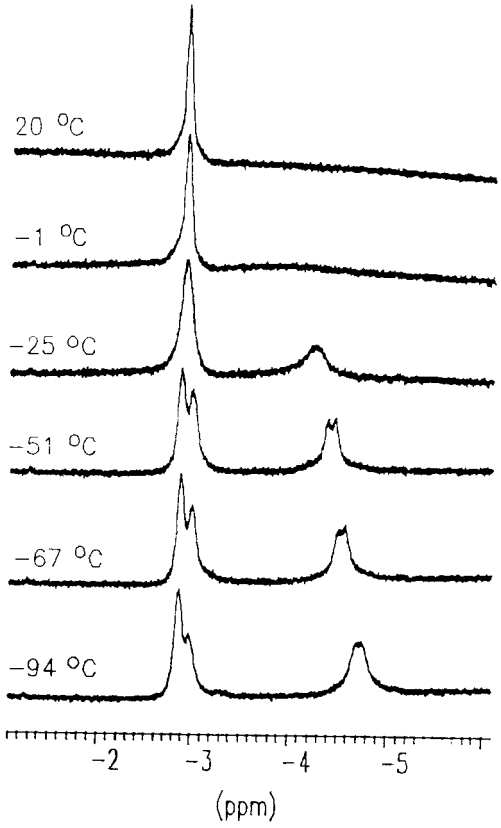

Figure 5. Negative zone of the variable-temperature $^1H\{^{11}B\}$ NMR spectra of **2** in CD_2Cl_2.

−2.78, −2.88, and −4.67 ppm (Figure 5). In addition, the methyl resonance decoalesced at −25 °C and resolved at −94 °C to give two resonances at 1.58 and 1.33 ppm. The two broad olefinic resonances also resolved at −94 °C to give four

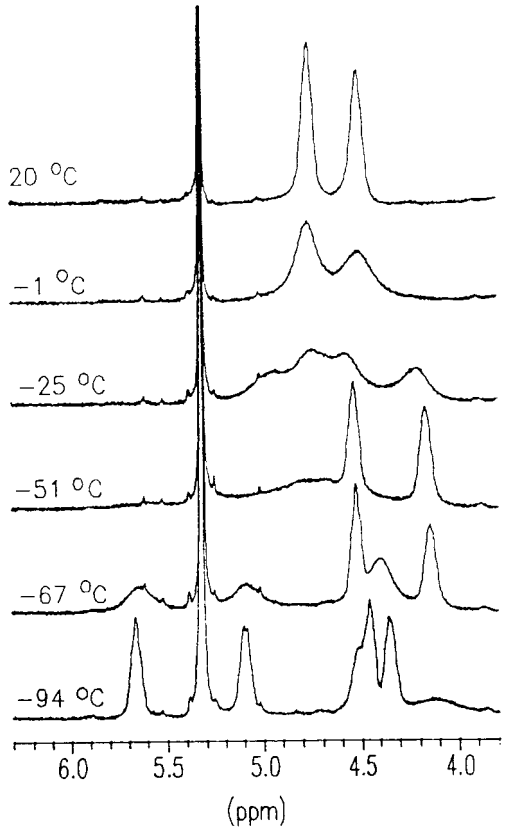

Figure 6. Olefinic zone of the variable-temperature $^1H\{^{11}B\}$ NMR spectra of **2** in CD_2Cl_2.

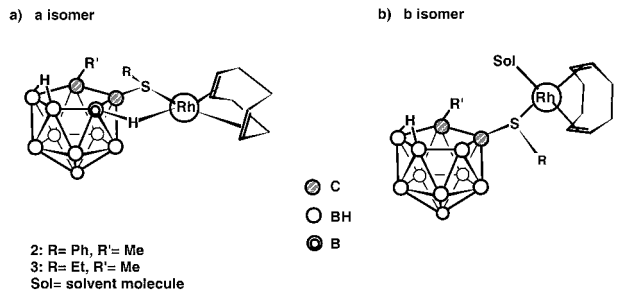

Figure 7. Structures proposed for **a** and **b** isomers of complexes **2** and **3**.

resonances at 5.69, 5.14, 4.49, and 4.15 ppm and other additional resonances of minor intensity (some of them overlaped) (Figure 6). The integration of the spectrum allowed the signals at 1.58 (C_{cage}−Me), −2.78 (B−H−B), −4.67 (B−H−Rh) ppm and the four olefinic resonances to be associated with one species (**2a**) and the signals at 1.33 (C_{cage}−Me), −2.88 (B−H−B) ppm and the rest of olefinic resonances to be associated with a different species (**2b**). Furthermore, the ratio of integrals indicated an aproximate relative proportion of **2a**/**2b** = 70:30. The distribution of the **2a** set of signals resembles that found in complex **1** and suggests an analogous structure for this species (Figure 7a). The structure proposed for the **2b** species is an isomer of **2a** in which the $[Rh(cod)]^+$ fragment is bonded to the carborane ligand through a single S−Rh bond (Figure 7b). A solvent molecule would occupy the fourth coordination site on the metal. Alternatively, the **2b** set could correspond to free [7-SPh-8-Me-7,8-$C_2B_9H_{10}]^-$ arising from dissociation of **2**. However, this second alternative can be confidently rejected because the B−H−B and C_{cage}−Me chemical shifts of free [7-SPh-8-Me-7,8-$C_2B_9H_{10}]^-$ ligand are significantly different from those of the **2b** species (−2.30 and 1.53 ppm, respectively).

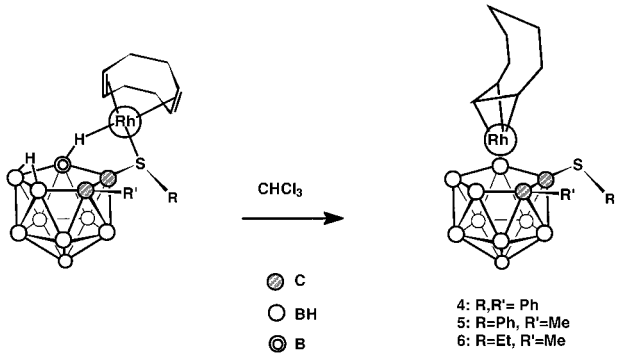

Figure 8. Formation of *closo*-cyclooctenilthiorhodacarboranes.

The variable-temperature $^1H\{^{11}B\}$ NMR spectra of **3** were similar to those of **2**. In this case the resonances belonging to the major isomer **3a** appeared at 5.53, 4.86, 4.42 (olefinic), 1.44 (C_{cage}−Me), −2.72 (B−H−B), and −4.51 (B−H−Rh), whereas those of the minor isomer **3b** appeared at 4.86 (overlaped), 4.22, 3.96 (olefinic), 1.51 (C_{cage}−Me), and −3.04 (B−H−B).[14] The structures proposed for **3a** and **3b** are analogous to those proposed for **2a** and **2b**, respectively. The ratio of isomers was found to be **3a**/**3b** = 82:18. The fact that B−H−B resonances as well as C_{cage}−Me resonances in complexes **2** and **3** decoalesced at intermediate temperatures indicates that there exists interconversion between **a** and **b** isomers.

***Closo*-η^3-Cyclooctenylthiorhodacarboranes.** Solutions of complexes **1**−**3** in CH_2Cl_2 or $CHCl_3$ at room temperature gradually change their color from yellow to orange-red. Analytical thin-layer chromatography (TLC) (CH_2Cl_2) shows a new spot at R_f = 0.74−0.78 which indicates the formation of a new compound. The rate of the transformation depends on the starting complex considered: While **2** and **3** show complete reaction after 24 h, complex **1** reacts more slowly and the reaction must be accelerated by refluxing the solution to obtain comparable yields. After isolation by preparative TLC, orange solids are obtained whose elemental analyses coincide with those of the respective starting compounds. However, the spectroscopic features of the new complexes are completely different. For instance, the $^{11}B\{^1H\}$ NMR resonances appear in a different zone (20 to −19 ppm.) and the absorptions at ca. 2100 cm^{-1} in the IR spectra and the B−H−B resonances in the $^1H\{^{11}B\}$ NMR spectra are no longer present. Moreover, the $^{13}C\{^1H\}$ NMR spectra show three doublets at ca. 108, 85, and 83 ppm (^1J(Rh,C) = 6−8 Hz) and the $^1H\{^{11}B\}$ NMR spectra display two quadruplets and a triplet in the zone of 5.8−4.6 ppm (^3J(H,H) = 8−9 Hz), which are characteristic of a η^3-allyl moiety bound to rhodium. Hence, the spectroscopic and elemental analyses strongly suggest that the *exo-nido*-cyclooctadienerhodium complexes **1**−**3** rearrange in solution to give the respective isomeric *closo*-η^3-cyclooctenylrhodacarboranes **4**−**6** (Figure 8). Also, in the solid state and at room temperature, complexes **2** and **3** slowly undergo the isomerization process, whereas solid **1** is kinetically stable. Nevertheless, the isomerization of compounds **2** and **3** in the solid state can be considerably retarded provided they are stored below −20 °C.

An X-ray crystallographic study of **4** provided additional interesting features of these compounds. A simplified drawing of the complex unit is shown in Figure 9, crystallographic data are shown in Table 1, and selected geometrical parameters are shown in Table 3.

(14) No mention is made of the resonances corresponding to the S−CH_2−CH_3 fragment because they were fully overlapped with those of the CH_2 cyclooctadiene ligand.

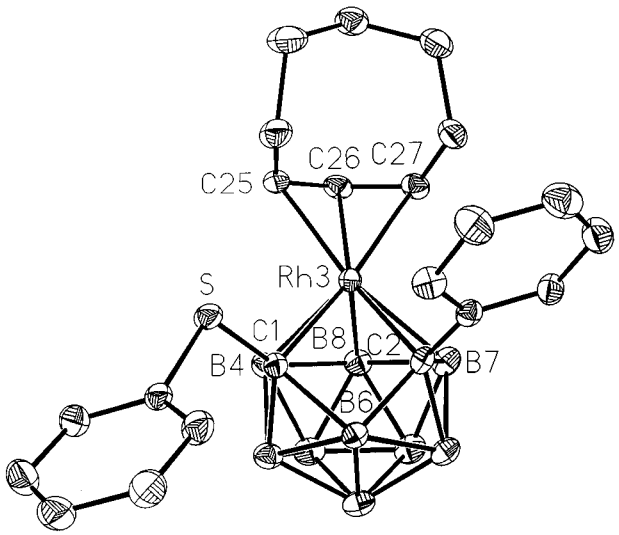

Figure 9. Crystal structure of the *pseudocloso* compound **4**, facing at the diamond open face.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for **4**

S−C(1)	1.755(3)	Rh(3)−B(7)	2.243(3)
C(1)−C(2)	2.427(4)	Rh(3)−B(8)	2.138(3)
C(1)−Rh(3)	2.156(3)	Rh(3)−C(25)	2.168(3)
C(2)−Rh(3)	2.120(3)	Rh(3)−C(26)	2.143(3)
Rh(3)−B(4)	2.191(3)	Rh(3)−C(27)	2.208(3)
Rh(3)−B(6)	3.003(3)		
C(1)−Rh(3)−C(2)	69.2(1)	C(1)−Rh(3)−C(27)	173.2(1)
C(1)−Rh(3)−C(25)	106.5(1)	C(2)−Rh(3)−C(27)	114.0(1)
C(2)−Rh(3)−C(25)	159.3(1)		

The metal is coordinated to the C_2B_3 pentagonal open face and to the three allylic carbons of a cyclooctenyl ligand. Skeletal electron counting formalisms[15] suggest that **4** contains 12 electron pairs for skeletal bonding and should exhibit a hypercloso geometry.[16] However, a modification of these rules[17] suggests that the effective atomic number of the metal center must be considered in order to determine the geometry of the polyhedron. This approach suggests that **4** with a formally 16-electron Rh(III) might possess 13 skeletal electron pairs available for cage bonding and thus exhibit closo geometry.

Interestingly, the C(1)−C(2) distance (2.427(4) Å) reveals lack of bonding between the two carbon atoms. The lengthening of the C(1)−C(2) distance produces a tetragonal open face formed by C(1)−C(2)−Rh(3)−B(6). Thus, in the process from **1** to **4**, two main steps have taken place: the oxidation of Rh(I) to Rh(III), and hydrogen transfer to C_8H_{12} to produce $C_8H_{13}^-$. It may be the consequence of these two steps that the C−C cluster distance has lengthened to a value long enough to indicate that there is no C−C bond. The cluster adopts a so-called pseudocloso structure.[18] The name refers to those clusters which, despite having a closo electron count, present an open-cage structure. Figure 10 shows geometrical details (angstroms and degrees) in the open face of the pseudocloso compound **4**.

(15) a) Mingos, D. M. P. *Nature (London), Phys. Sci.* **1972**, *236*, 99. (b) Wade, K. *Prog. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (c) Rudolph, R. W. *Acc. Chem. Res.* **1976**, 9, 446.

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(17) Nishura, E. K. *J. Am. Chem. Soc.* **1980**, *102*, 5782.

(18) (a) Mingos, M. P.; Forsyth, M. I.; Welch, A. J. *Chem. Commun.* **1977**, 605. (b) Thomas, R. L.; Welch, A. J. *J. Chem. Soc., Dalton Trans* **1997**, 631. (c) Welch, A. J.; Weller, A. S. *Inorg. Chem.* **1996**, *35*, 4548. (d) Thomas, R. L.; Rosair, G. M.; Welch, A. J. *Chem. Commun.* **1996**, 1327. (e) Kim, J.-H.; Lamrani, M.; Hwang, J.-W.; Do, Y. *Chem. Commun.* **1997**, 1761.

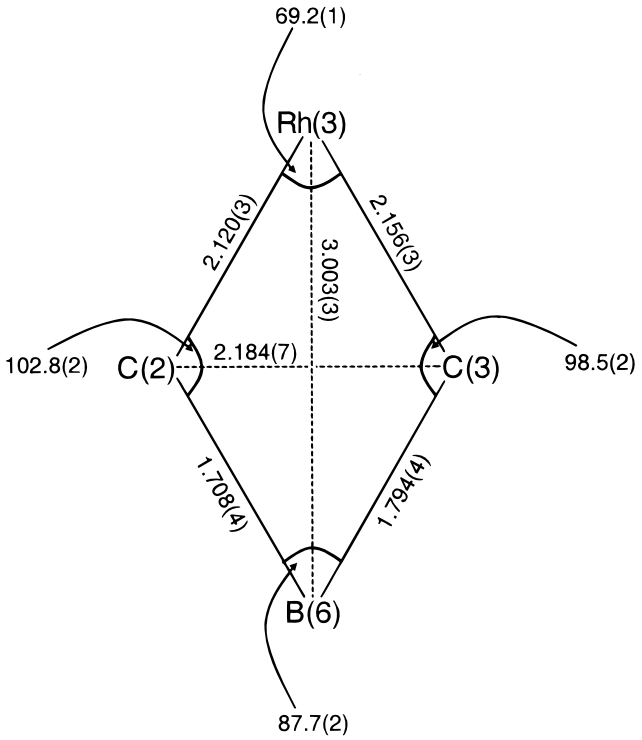

Figure 10. Geometrical details (angstroms and degrees) in the open face of the pseudocloso compound **4**.

Oxidation of Rh(I) to Rh(III) causes several changes in the geometry of the molecule. In compound **1**, orientation of the phenyl group at C(8) is almost perpendicular to the C_2B_3 open face (see Figure 1), but during metal's coordination to the C_2B_3 open face, compound **4**, the orientation changes. This new orientation would cause a short S....C(phenyl) contact (see Figure 9) and, consequently, a repulsion. To minimize the repulsion the molecule enlarges the C(1)−C(2) distance to such an extent that no C(1)−C(2) bond can be considered.

The unexpected finding of a pseudocloso structure for **4** requires some comments. Welch and co-workers recently reported several metallacarboranes which adopt pseudocloso structures.[19] There it is considered that the presence of two bulky phenyl substituents at the cage carbon atoms induces the breaking of the C−C cage bond. The pseudocloso metallacarbaboranes are characterized by a weighted average ^{11}B NMR chemical shift, ($\delta(^{11}B)$), of the order of ca. +6 ppm, at a higher frequency than those of related closo metallacarboranes (ca. −10 ppm).[20] The weighted averages of **4**, **5**, and **6** are +3.1, −3.9, and −3.6 ppm, respectively, which do not coincide with either of the two typical values. Note that those reference figures correspond to metallacarboranes with no electron-rich substituents on the carbon-cage atoms and thus some discrepancy is expected. Nevertheless, if we assume a weighted average of ca. +3.1 ppm for any C_{cage}−SR-substituted pseudocloso cluster, then the weighted averages calculated for **5** and **6** suggest normal closo structures for the two compounds. Of more interest is, however, the relationship between C_{cage} substituents and pseudocloso geometry. All C_2B_9 pseudocloso metallacarboranes reported hitherto are C_{cage}−Ph-disubstituted compounds and the typical features of these compounds (lengthening of C(1)−C(2) distances and shortening of M(3)−B(6) distances) have been regarded as the result of intramolecular steric crowding between the cage-bound phenyl groups and the conical transition-metal-containing fragments such as {(η^5-L)M}, {(η^6-L)M}, and {(κ^3-L)M} bonded at the vertex (3). Compound **4** is the first pseudocloso which does not incorporate two phenyl substituents on cluster carbons, although it incorporates one C_{cage}−Ph and one C_{cage}−SPh. The explanation of why it is formed or whether a C_{cage}−SPh could be considered as a C_{cage}−Ph is difficult to answer; however, it is certain that when no phenyl group is present on carbon cluster atom, compounds **5** and **6**, such C−C lengthening has not occurred.

Few *closo*-cyclooctenylrhodacarboranes have been reported to date. They were obtained by protonation of the respective anionic *closo*-cyclooctadienerhodacarboranes [*closo*-3,3-(η^4-1,5-C_8H_{12})-1-R-2-R′-3,1,2-$RhC_2B_9H_9$]$^-$ and their stability was found to depend on the C_{cage} substituents.[21] Hence, while the disubstituted C_{cage}−Me compound was isolated, the monosubstituted C_{cage}−Ph and the unsubstituted C_{cage}−H compounds decomposed rapidly upon formation. In contrast, compounds **4**−**6** are air stable both in CH_2Cl_2 or $CHCl_3$ solutions and in the solid state.

Exo-nido to Closo Isomerization. (a) Kinetic Investigations. According to an earlier mechanistic study[6] on alkene hydrogenation reactions catalyzed by rhodacarboranes of the type [Rh(7-R-8-R′-$C_2B_9H_{10}$)(PPh_3)$_2$] (R,R′ = alkyl, aryl), phosphine dissociation and subsequent alkene coordination are the first steps ocurring in the catalytic cycle. If we assume similar initial steps for the alkene hydrogenation reactions catalyzed by monothiorhodacarboranes, then the *exo-nido*-cyclooctadienerhodacarboranes reported here can be viewed as intermediates in these catalytic reactions. Moreover, the isomerization reactions which complexes **1**, **2**, and **3** undergo involve the formal addition of hydride to a double bond and hence can be regarded as the following step after coordination of alkene in the catalytic cycle. In this regard, the study of the exo-nido to closo transformations reported here could reveal important information pertinent to the alkene catalytic hydrogenation reaction, and was studied further.

Isomerization of **2** and **3** at 23 °C as monitored by ^{1}H{^{11}B} NMR spectroscopy at the diene and allyl region. A representative series of spectra for the reaction of **3** is shown in Figure 11. Both systems were found to be first-order with respect to concentration of the diene complex. In addition, no other species different from the starting diene and the final allyl derivatives were detected. The calculated rate constants are 2.66×10^{-5} and 5.5×10^{-5} for compounds **2** and **3**, respectively. This behavior is consistent with the simple mechanism proposed below, in which [Rh*] would be a reactive intermediate.

$$\text{Exo-nido} \xrightarrow{K_1} [\text{Rh}^*] \xrightarrow{K_2\ (\text{fast})} \text{closo}$$

Considering these results and the hitherto known chemistry of rhodacarboranes, two different pathways appear to be most plausible. The first is depicted in Scheme 1a and involves initial oxidative addition of the B−H−B bridge to the [Rh(cod)]$^+$ fragment to give the *closo*-cyclooctadienerhodacarborane intermediate **I**. Compound **I** would undergo hydride transfer from the metal to an olefin carbon and, after a series of rapid 1,3-hydrogen shifts, would yield the final *closo*-cyclooctenyl complex. In the alternative proposed pathway, Scheme 1b, a

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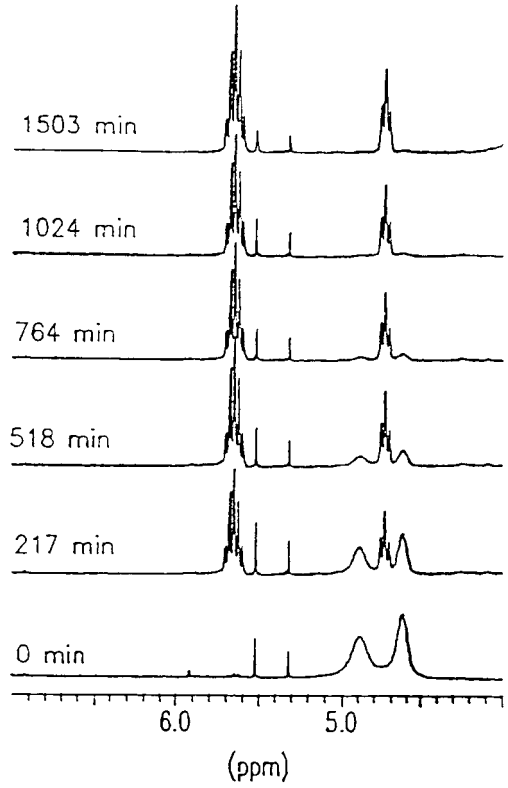
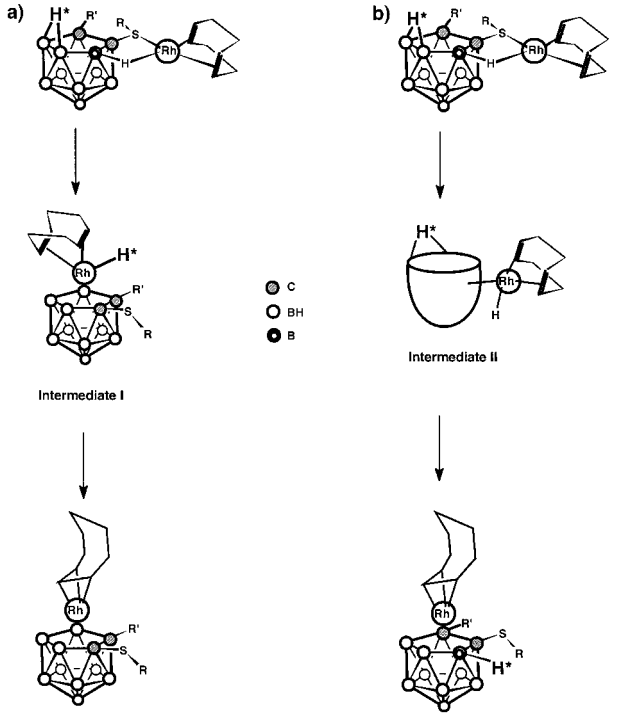


Figure 11. $^1H\{^{11}B\}$ NMR spectra at 23 °C, at the diene and allyl region, of the transformation of **3** to **6** in CD_2Cl_2.

Scheme 1. Proposed Mechanisms for the Exo-nido to Closo Isomerization Reaction



terminal B−H bond (possibly B(11)−H) would undergo B−Rh(III)−H oxidative addition to the $[Rh(cod)]^+$ fragment to give intermediate **II**. Again, transfer of hydride followed by 1,3-hydrogen shifts would result in an *exo-nido*-cyclooctenyl complex which rapidly would rearrange to a closo structure while the B−H−B bridging proton would rearrange to a terminal B(11)−H position.

Both pathways proposed are based in thoroughly studied reaction mechanisms of related rhodacarborane compounds. Intermediate **I** has been proposed in the disproportionation reaction of $[RhCl(cod)(PPh_3)]$ with nido carborane anions,[22] whereas an intermediate analogous to **II** is the key in the rhodacarborane-catalyzed isomerization and hydrogenation reactions.[6h] The main difference between the two pathways lies in the source of hydride. In the first, the B−H−B bridging proton is the one transferred to the cyclooctadiene ligand, whereas in the second the proton is transferred to a terminal B−H hydrogen. When we tried to discern which pathway, Scheme 1a or b, was the most pausible, the deuterated complexes $[Rh(10\text{-}D\text{-}7\text{-}SPh\text{-}8\text{-}Ph\text{-}7,8\text{-}C_2B_9H_9)(cod)]$ (**9**) and $[Rh(10\text{-}D\text{-}7\text{-}SPh\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_9)(cod)]$ **(10)** were also prepared by the reaction of $[Rh(acac)(cod)]$, $HClO_4$ in THF with the corresponding deuterated ligands $[NMe_4][10\text{-}D\text{-}7\text{-}SPh\text{-}8\text{-}Ph\text{-}7,8\text{-}C_2B_9H_9]$ (**7**) and $[NMe_4][10\text{-}D\text{-}7\text{-}SPh\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_9]$ (**8**).

Deuteration studies on $[Rh(10\text{-}D\text{-}7\text{-}SR\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_9)(cod)]$ and $[closo\text{-}3\text{-}(\eta^3\text{-}C_8H_{13})\text{-}1\text{-}SR\text{-}2\text{-}R'\text{-}3,1,2\text{-}RhC_2B_9H_8D]$. The preparation of nido monothioether monodeuterated ligands was accomplished by reaction of $[7\text{-}SR\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_9]^{2-}$ [23] with D_2O to give $[7\text{-}SR\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_9D]^-$ (R, R′ = Ph in **7** and R = Ph, R′ = Me in **8**) which were isolated as their tetramethylammonium salts.[24] The ^{11}B NMR spectrum of the compounds are quite similar to those of the undeuterated ligands, however, the fine structure on the resonance of area 1 centered at −32.86 for **7** and −33.26 for **8** has been removed by deuteration, thus establishing that this fine structure is indeed due to the H bridge. ^2H NMR spectra show a broad singlet at −2.01 for **7** and −2.50 ppm for **8** that would confirm the presence of deuterium at the B−D−B bridge position. There is no evidence from the ^{11}B NMR spectrum that any of the terminal hydrogen atoms have been exchanged with deuterium during the reaction.

The IR spectra of **9** and **10** showed an absorption at 2547 and 2533 cm^{-1}, respectively. The $^{11}B\{^1H\}$ NMR spectra of **9** and **10** presented seven resonances corresponding to nine boron atoms in the range −4 to −35 ppm characteristic of a nido cluster. However, the $^1H\{^{11}B\}$ NMR spectra at room temperature showed no resonance in the negative zone. This means that the B−D−B bridge has been retained at the C_2B_3 open face in the complexes. On cooling to −94 °C, a resonance at −3.05 ppm integrating one proton appeared at the $^1H\{^{11}B\}$ NMR spectrum of **9**, which supports the B−H−Rh agostic interaction in the deuterated complex. Exo-nido complexes **9** and **10** rearrange in solution to give the closo complexes **11** and **12** respectively. In the IR spectra of **11** and **12** the ν(B−H) occur at 2550 and 2532 cm^{-1}, respectively. The $^{11}B\{^1H\}$ NMR spectra pattern 1:1:1:1:2:1:1:1 in the range +19/−19 ppm and +8/−20 ppm is found for **11** and **12**, respectively. This chemical shift range is in agreement with the η^5 rhodium coordination to the C_2B_3 open face. ^2H NMR spectra show a broad singlet at 0.64 ppm for **11** and at 0.69 ppm for **12**. These spectroscopic data concerning the deuterated species are in total agreement with their hydrogen analogues, however, they bring relevant information concerning the fate of the hydrogen bridge B−H−B. It has been proven that the hydrogen bridge B−H−B does

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not scatter through the cluster, so there is no exchange between bridge hydrogen and boron terminal hydrogen atoms in compounds **7** and **8**. On complexation to the $[Rh(cod)]^+$ fragment the hydrogen bridge B−H−B remains on the open face, thus not participating in bonding to metal. In the exo-nido to closo isomerization process the bridging B−H−B hydrogen must be shifted to a new position, which can be either on the alkene or on the cluster (most probably on the B(11) position, the one involved in the process). The ^2H NMR data on **11** and **12** are very informative and they prove that the deuterium is on a boron atom, most probably B(11). Thus, if we refer to the two pathways shown in Scheme 1, we can conclude that the isomerization process takes place according to pathway b in Scheme 1.

Catalytic Hydrogenation. In contrast to the high activity exhibited by the monothiorhodacarborane complexes $[Rh(7\text{-}SR\text{-}8\text{-}R'\text{-}C_2B_9H_{11})(PPh_3)_2]$ in the catalytic hydrogenation of 1-hexene, they were shown to be much less active when an internal olefin such as cyclohexene was used. By replacing the PPh_3 ligands by a diene ligand we sought to enhance the activity in the hydrogenation of internal alkenes. It was nevertheless of interest to previously determine whether the *exo-nido*-cyclooctadiene rhodacarborane complexes reported here could activate molecular hydrogen and undergo hydrogenolysis of the diene ligand.

Complex **2** was allowed to react with H_2 (25 °C) in the presence of 1 equiv of PPh_3. By using 1 equiv of PPh_3 we intended to preclude the isomerization of **2** to its closo isomer. After ca. 1 h of H_2 bubbling, the $^{31}P\{^1H\}$ NMR spectrum of the solution showed a broad doublet at 41.9 ppm ($^1J(Rh, P) = 169$ Hz) and the $^1H\{^{11}B\}$ NMR displayed broad resonances at −2.70 (B−H−B) and −4.46 ppm (B−H−Rh). In addition, a broad signal at 4.56 ppm indicated the presence of alkene. These spectroscopic observations strongly suggest that the species formed in solution consist of a $[Rh(PPh_3)(alkene)]^+$ fragment coordinated to the carborane cage via S−Rh and B−H−Rh bonds. This is supported by the $^{11}B\{^1H\}$ NMR spectrum of the solution, which closely resembles that of the parent compound $[Rh(7\text{-}SPh\text{-}8\text{-}Me\text{-}C_2B_9H_{11})(PPh_3)_2]$. The broadness of the $^{31}P\{^1H\}$ NMR doublet is indicative of the existence of a dynamic process similar to that observed in $[Rh(7\text{-}SR\text{-}8\text{-}R'\text{-}C_2B_9H_{11})(PPh_3)_2]$ complexes. However, the observation of the olefinic signal in the $^1H\{^{11}B\}$ NMR spectrum indicates that the hydrogenolysis of the diene ligand proceeds very slowly at ambient temperatures and pressures.

Hydrogenation experiments using **2** and **3** as catalyst precursors in the presence of 1 equiv of PPh_3 and using cyclohexene as substrate were performed in order to investigate the catalytic activity of the species generated in situ. Similar experiments were also conducted with the parent diphosphine complexes $[Rh(7\text{-}SPh\text{-}8\text{-}Me\text{-}C_2B_9H_{11})(PPh_3)_2]$ and $[Rh(7\text{-}SEt\text{-}8\text{-}Me\text{-}C_2B_9H_{11})(PPh_3)_2]$ under the same experimental conditions for comparison. The results are gathered in Table 4. Surprisingly, comparison of entries 1 and 2 indicate that there is no significant difference in activity between the diphosphine complex $[Rh(7\text{-}SPh\text{-}8\text{-}Me\text{-}C_2B_9H_{11})(PPh_3)_2]$ or the monophosphine complex generated in situ from **2** and 1 equiv of PPh_3. In addition, although complex **3** in the presence of 1 equiv of PPh_3 exhibits higher conversion than $[Rh(7\text{-}SEt\text{-}8\text{-}Me\text{-}C_2B_9H_{11})(PPh_3)_2]$, the difference is small (entries 3 and 4). Therefore, contrary to what we expected, the elimination of a phosphine ligand from the coordination sphere of the metal in monothiorhodacarborane complexes does not result in a marked increase in the catalytic activity.

Table 4. Percent Conversion of Cyclohexene to Cyclohexane[a]

entry	complex	% hydrogenation
1	$[Rh(7\text{-}SPh\text{-}8\text{-}Me\text{-}C_2B_9H_{11})(PPh_3)_2]$	32
2[b]	**2**	30
3	$[Rh(7\text{-}SEt\text{-}8\text{-}Me\text{-}C_2B_9H_{11})(PPh_3)_2]$	8
4[b]	**3**	12
5	**5**	82
6[b]	**5**	98
7	**4**	76

[a] Experimental conditions: [complex] = 7×10^{-3} M; [cyclohexene] = 1.5 M; $P = 20$ atm $T = 25$ °C; $t = 1$ h. [b] Experiment performed with 1 equivalent of PPh_3.

The catalytic activity of the *closo*-cyclooctenil complexes **4** and **5** in the hydrogenation of cyclohexene was also investigated. Note that the turnover number (TON) obtained using **4** and **5** in the absence of added PPh_3 was far superior to that exhibited by the exo-nido complexes (entries 7 and 5). The addition of 1 equiv of PPh_3 to system **5** (entry 6) resulted in a moderate increase in activity. These results suggest that different reaction mechanisms are operating in the exo-nido and closo systems. Earlier, the *closo*-rhodacarborane complex (*closo*-3-(PPh_3)−$(\eta^3$-$C_3H_5)$-3,1,2-$RhC_2B_9H_{10}$), which bears an η^3-allyl moiety at the metal vertex, was shown to activate molecular hydrogen.[25] The hydrogen reaction was tentatively proposed to occur through a η^3 to η^1 rearrangement of the η^3-allyl ligand followed by oxidative addition of H_2 to produce an unstable Rh(V) alkyl dihydride species or alternatively by a concerted four-center transition state involving the η^1-allyl-Rh moiety and H_2. Regardless of the detailed mechanism of this process, the enhanced activity exhibited by **4** and **5** compared to the isomeric *exo-nido*-rhodacarboranes allows one to consider the *closo*-cyclooctenylrhodacarboranes reported here as potentially useful catalyst precursors whose scope is currently under investigation in our research group.

Experimental Section

Instrumentation. Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded with KBr pellets on a Nicolet 710 FT spectrophotometer. ^1H and $^1H\{^{11}B\}$ NMR (300.13 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz), ^{11}B NMR (96.29 MHz), and ^2H NMR (46.07 MHz) spectra were recorded with a Bruker ARX 300 instrument equipped with the appropriate decoupling accessories. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$ and those for ^1H, $^1H\{^{11}B\}$, and $^{13}C\{^1H\}$ NMR spectra were referenced to $SiMe_4$. ^2H NMR spectra were recorded relative to the solvent resonance. Chemical shifts are reported in units of parts per million downfield from tetramethylsilane, and all coupling constants are reported in Hz. GC analyses were performed using a Shimadzu GC-15A, SPB-1 capillary column (Supelco) 30 m long, inner diameter 0.25 mm, 1-μm-thick stationary phase. Catalytic hydrogenations were conducted in a 35-mL autoclave built at the workshop facility of the Universitat Autònoma de Barcelona. The autoclave was equipped with a water jacket, a rupture disk, a manometer, and sample and gas inlets.

Materials. Unless otherwise noted, all manipulations (except the preparative TLC separations) were carried out under a dinitrogen atmosphere using standard vacuum line techniques. THF was distilled from sodium benzophenone prior to use and the rest of the solvents were of reagent grade quality and were used without further purification. Cyclohexene was distilled from CaH_2 prior to use. PPh_3 (Aldrich) was recrystallized from ethanol prior to use. $RhCl_3{\cdot}3H_2O$ (Johnson Matthey), acetylacetone (Aldrich), and cod (Aldrich), were purchased from commercial sources and used as received. $HClO_4$ 70% solutions (Panreac) were titrated before use. Deuterium oxide (99.8% isotopic purity) was obtained from Aldrich. Tetramethylammonium chloride used to precipitate deuterated anions was dried in vacuo over P_2O_5

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before use. $[RhCl(cod)]_2$,[26] [Rh(acac)(cod)],[27] and trimethylammonium, tetramethylammonium, or cesium salts of $[7\text{-SR-8-R}'\text{-}7,8\text{-}C_2B_9H_{10}]^-$ were prepared according to the literature methods.[28]

Synthesis of [Rh(7-SPh-8-Ph-7,8-$C_2B_9H_{10}$)(cod)] (1). [Rh(acac)(cod)] (0.167 g, 0.538 mmol) was dissolved in THF (5 mL) and 65 μL of $HClO_4$ 8.372 M (0.54 mmol) was added with stirring. After the mixture was stirred for 15 min, a solution of Cs[7-SPh-8-Ph-7,8-$C_2B_9H_{10}$] (0.242 g, 0.537 mmol) in 6 mL of CH_2Cl_2/THF (5:1) was added and a white solid precipitated. The suspension was filtered through Celite, the filtrate was concentrated in vacuo to ca. 5 mL, and a yellow precipitate formed. MeOH (20 mL) was added to complete precipitation and the solid was isolated by filtration, washed with MeOH (2 × 5 mL) and then ethyl ether (2 × 5 mL), and vacuum-dried. Yield 0.215 g (76%). Recrystalization from dichloromethane/*n*-heptane (1:1) gave pale yellow microcrystals. Anal. Calcd. for $C_{22}H_{32}B_9SRh$: C, 49.97; H, 6.10; S, 6.06. Found: C, 49.60; H, 5.73; S, 5.83. IR: ν [cm^{-1}] = 2547 (B−H), 2077 (B−H−Rh). ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.40−7.20 (m, H_{aryl}, 10H), 4.68, 4.64 (br s, $H_{olefinic}$,4H), 2.52 (m, CH_2, 4H), 1.97 (m, CH_2, 4H), −2.37 (br s, B−H−B, 1H).^{1}H NMR (CD_2Cl_2, −94 °C): δ = 7.40−7.20 (m, H_{aryl}, 10H), 5.43 (br s, $H_{olefinic}$,1H), 5.09 (br s, $H_{olefinic}$,1H), 4.37 (br s, $H_{olefinic}$,1H), 3.96 (br s, $H_{olefinic}$,1H), 2.52 (m, CH_2, 4H), 1.97 (m, CH_2, 4H), −2.37 (br s, B−H−B, 1H), −3.05 (br s, B−H−Rh, 1H). ^{1}H{^{11}B} NMR (CD_2Cl_2, 25 °C): δ = 7.40−7.20 (m, H_{aryl}, 10H), 4.68, 4.64 (br s, $H_{olefinic}$,4H), 2.52 (m, CH_2, 4H), 2.25 (br s, B−H), 2.09 (br s, B−H), 1.97 (m, CH_2, 4H), 1.07 (br s, B−H), 0.95 (br s, B−H), −2.37 (br s, B−H−B, 1H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 131.2, 130.4, 128.6, 127.5, 127.1 (C_{aryl}), 83.5 (br s, $C_{olefinic}$), 81.8 (br s, $C_{olefinic}$), 31.0 (CH_2), 29.9 (CH_2). ^{11}B NMR (CD_2Cl_2, 25 °C): δ = −4.9 (d, ^1J(B,H) = 135, 1B), −12.4 (2B), −15.1 (1B), −18.8 (d, ^1J(B,H) = 106, 1B), −26.3 (1B), −27.5 (2B), −34.8 (d, ^1J(B,H) = 147, 1B).

Synthesis of [Rh(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(cod)] (2). [Rh(acac)(cod)] (0.093 g, 0.30 mmol) was dissolved in THF (5 mL) and 36 μL of $HClO_4$ 8.372 M (0.30 mmol) was added with stirring. After the mixture was stirred for 15 min, a solution of Cs[7-SPh-8-Me-7,8-$C_2B_9H_{10}$] (0.116 g, 0.299 mmol) in 6 mL THF was added and a white solid precipitated. The suspension was filtered through Celite and the filtrate was concentrated in vacuo to 1 mL. Ether was added (10 mL), the solution was cooled to −78 °C, and a yellow-orange precipitate formed which was isolated by filtration, washed with ethyl ether (2 × 5 mL), and vacuum-dried. Yield 0.125 g (89%). Anal. Calcd. for $C_{17}H_{30}B_9SRh\cdot 1/2(Et_2O)$: C, 45.30; H, 7.00; S, 6.37. Found: C, 45.27; H, 7.00; S, 5.98. IR: ν [cm^{-1}] = 2535 (B−H), 2098 (B−H−Rh). ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.7−7.4 (m, H_{aryl}, 5H), 4.76 (br s, $H_{olefinic}$, 2H), 4.50 (br s, $H_{olefinic}$, 2H), 3.46 (q, ^3J(H,H) = 7, CH_3-CH_2-O), 2.51 (m, CH_2, 4H), 1.90 (m, CH_2, 4H), 1.47 (s, CH_3, 3H), 1.19 (t, ^3J(H,H) = 7, CH_3-CH_2-O, 0.5 H), −2.84 (br s, B−H−B, 1H). ^{1}H NMR (CD_2Cl_2, −94 °C): δ = 7.7−7.4 (m, H_{aryl}, 5H), 5.69 (br s, $H_{olefinic}$, 1H), 5.14 (br s, $H_{olefinic}$, 1H), 4.49 (br s, $H_{olefinic}$, 1H), 4.15 (br s, $H_{olefinic}$, 1H), 2.51 (m, CH_2, 4H), 1.90 (m, CH_2, 4H), 1.58 (s, CH_3, (**2a**)), 1.33 (s, CH_3, (**2b**)), −2.78 (br s, B−H−B (**2a**)), −2.88 (br s, B−H−B (**2b**)), −4.67 (br s, B−H−Rh, (**2a**)). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 136.2, 129.9, 129.3, 128.7 (C_{aryl}), 82.9 (br s, $C_{olefinic}$), 81.7 (br s $C_{olefinic}$), 65.3 (CH_3-CH_2-O), 30.8 (CH_2), 30.1 (CH_2), 20.3 (CH_3), 14.8 (CH_3-CH_2-O). ^{11}B NMR ($CDCl_3$, 25 °C): δ = −4.3 (d, ^1J(B,H) = 147, 1B), −8.7 (1B), −11.9 (2B), −18.1 (d, ^1J(B,H) = 106, 1B), −24.9 (1B), −26.5 (2B), −34.1 (d, ^1J(B,H) = 146, 1B).

Synthesis of [Rh(7-SEt-8-Me-7,8-$C_2B_9H_{10}$)(cod)] (3). The procedure was as for **2** using the salt $[NMe_4][7\text{-SEt-8-Me-7,8-}C_2B_9H_{10}]$ (0.067 g, 0.236 mmol), [Rh(acac)(cod)] (0.0730 g, 0.235 mmol), 29 μL of $HClO_4$ 8.372 M (0.24 mmol). Yield 37 mg (37%). Anal. Calcd. for $C_{22}H_{32}B_9SRh$: C, 37.30; H, 7.22; S, 7.66. Found: C, 36.90; H, 6.94; S, 7.28. IR: ν [cm^{-1}] = 2538 (B−H), 2119 (B−H−Rh). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 4.85 (br s, $H_{olefinic}$, 2H), 4.58 (br s, $H_{olefinic}$, 2H), 2.58 (m, CH_2, 4H), 1.98 (m, CH_2, 4H), 1.54 (s, CH_3, 3H), 1.26 (br s, $S-CH_2-CH_3$), −2.90 (br s, B−H−B). ^{1}H NMR ($CDCl_3$, −94 °C): δ = 5.53, 4.86, 4.42 (br s, $H_{olefinic}$, (**3a**)), 4.86 (overlaped), 4.22, 3.96 (br s, $H_{olefinic}$, (**3b**)), 2.58 (m, CH_2, 4H), 1.98 (m, CH_2, 4H), 1.51 (s, CH_3, (**3b**)), 1.44 (s, CH_3, (**3a**)), 1.26 (br s $S-CH_2-CH_3$), −2.72 (br s, B−H−B, (**3a**)), −3.04 (br s, B−H−B), (**3b**)), −4.51 (br s, B−H−Rh, (**3a**)). ^{1}H{^{11}B} NMR($CDCl_3$, 25 °C): δ = 4.85 (br s, $H_{olefinic}$, 2H), 4.58 (br s, $H_{olefinic}$, 2H), 2.58 (m, CH_2, 4H), 2.10 (br s, B−H), 1.98 (m, CH_2, 4H), 1.75 (br s, B−H), 1.54 (s, CH_3, 3H), 1.32 (br s, B−H), 1.26 (br s, $S-CH_2-CH_3$), 0.97 (br s, B−H), 0.71 (br s, B−H), −2.90 (br s, B−H−B). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 82.5 (br s, $C_{olefinic}$), 35.5 ($-S-CH_2-$), 31.2 (CH_2), 30.6 (CH_2), 21.4 ($C_{cage}-CH_3$), 13.8 ($-S-CH_2-CH_3$). ^{11}B NMR ($CDCl_3$, 25 °C): δ = −5.3 (d, ^1J(B,H) = 141, 1B), −8.9 (d, ^1J(B,H) = 157, 1B), −12.5 (d, ^1J(B,H) = 148, 2B), −19.1 (d, ^1J(B,H) = 95, 1B), −25.2 (1B), −26.8 (2B), −34.5 (d, ^1J(B,H) = 145, 1B).

Synthesis of [*closo*-3-(η^3-C_8H_{13})-1-SPh-2-Ph-3,1,2-$RhC_2B_9H_9$] (4). A suspension of **1** (0.153 g, 0.289 mmol) in CH_2Cl_2 (25 mL) was heated to reflux and the reaction was monitored by TLC. The yellow solid dissolved within a few minutes and the color of the solution gradually changed from yellow to deep red. After 15 h the solution was allowed to cool to room temperature and concentrated to ca. 2 mL. Preparative TLC (CH_2Cl_2) revealed two mobile bands, but only the most mobile of them (R_f = 0.74) was present in sufficient amount for collection. After isolation, the solvent was removed in vacuo and the residue was treated with petroleum ether. The resulting orange solid was filtered, washed with petroleum ether, and vacuum-dried. Recrystallization from chloroform/*n*-heptane gave red microcrystals. Yield: 86 mg (56%). Anal. Calcd. for $C_{22}H_{32}B_9SRh$: C, 49.97; H, 6.10; S, 6.06. Found: C, 49.63; H, 5.92; S, 5.81. IR: ν [cm^{-1}] = 2550 (B−H). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.90−7.30 (m, H_{aryl}, 10H), 5.60 (q, J(H,H) = 8.1, $H_{allylic}$, 1H), 5.38 (q, J(H,H) = 8.5, $H_{allylic}$, 1H), 4.72 (t, J(H,H) = 7.6, $H_{allylic}$, 1H), 2.76 (m, CH_2, 2H), 1.75 (m, CH_2, 4H), 1.47 (m, CH_2, 2H), 1.31-(m, CH_2, 2H).^{1}H{^{11}B} NMR ($CDCl_3$, 25 °C): δ = 7.90−7.30 (m, H_{aryl}, 10H), 5.56 (q, J(H,H) = 7.6, $H_{allylic}$, 1H), 5.34 (q, J(H,H) = 8.2, $H_{allylic}$, 1H), 4.68 (t, J(H,H) = 7.6, $H_{allylic}$, 1H), 4.20 (br s, B−H), 3.60 (br s, B−H), 3.18 (br s, B−H), 2.56 (br s, B−H), 2.29 (br s, B−H), 2.72 (m, CH_2, 2H), 1.67 (m, CH_2, 4H), 1.47 (m, CH_2, 2H), 1.31(m, CH_2, 2H), 0.66 (br s, B−H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 145.5, 137.2, 135.8, 131.0, 130.2, 129.1, 128.4, 128.2, 127.0 (C_{aryl}), 118.1, 116.6 (C_{cage}), 107.8 (d, ^1J(Rh,C) = 6, $C_{allylic}$), 85.8 (d, ^1J(Rh,C) = 7, $C_{allylic}$), 84.3 (d, ^1J(Rh,C) = 7, $C_{allylic}$), 33.8, 31.6, 29.7, 29.3, 22.3 (CH_2). ^{11}B NMR ($CDCl_3$, 25 °C): δ = 20.1 (d, ^1J(B,H) = 122, 1B), 14.3 (d, ^2J(B,H) = 146, 1B), 6.4 (1B), 4.6 (1B), 2.4 (2B), 0.4 (1B), −4.6 (d, ^1J(B,H) = 141, 1B), −18.5 (d, ^1J(B,H) = 145, 1B).

Synthesis of [*closo*-3-(η^3-C_8H_{13})-1-SPh-2-Me-3,1,2-$RhC_2B_9H_9$] (5). (a) [Rh(acac)(cod)] (0.229 g, 0.738 mmol) was dissolved in THF (5 mL) and 88 μL of $HClO_4$ 8.372 M (0.737 mmol) was added with stirring. Inmediately after, a solution of Cs[7-SPh-8-Me-7,8-$C_2B_9H_{10}$] (0.287 g, 0.739 mmol) in 10 mL of THF was added and a white solid precipitated. The suspension was filtered through Celite, the filtrate was concentrated to dryness, and CH_2Cl_2 was added (8 mL). The solution was stirred at room temperature and the reaction was monitored by TLC. The color of the solution gradually changed from orange to deep red. After 24 h analytical TLC revealed only a single mobile band (R_f = 0.78, CH_2Cl_2) which was isolated by preparative TLC. After isolation, the solvent was removed in vacuo and the residue was treated with petroleum ether. The resulting orange solid was isolated by filtration, washed with petroleum ether, and vacuum-dried. Yield: 326 mg (95%). Anal. Calcd. for $C_{17}H_{30}B_9SRh$: C, 43.75; H, 6.48; S, 6.87. Found: C, 43.55; H, 6.24; S, 6.53. IR: ν [cm^{-1}] = 2532 (B−H). ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.50−7.30 (m, H_{aryl}, 5H), 5.75 (q, J(H,H) = 8.8, $H_{allylic}$, 1H), 5.68 (q, J(H,H) = 8.8, $H_{allylic}$, 1H), 4.75 (t, J(H,H) = 7.1, $H_{allylic}$, 1H), 2.72 (m, CH_2, 2H), 2.52 (m, CH_2, 2H), 2.28 (s, CH_3, 3H), 1.80 (m, CH_2, 6H). ^{1}H{^{11}B} NMR (CD_3Cl, 25 °C): δ = 7.5−7.3 (m, H_{aryl}, 5H), 5.77 (q, J(H,H) = 8.5, $H_{allylic}$, 1H), 5.70 (q, J(H,H) = 8.5, $H_{allylic}$, 1H), 4.77 (t, J(H,H) = 7.7, $H_{allylic}$, 1H), 3.80 (br s, B−H), 3.20 (br s, B−H), 2.72 (m, CH_2, 2H), 2.52 (m, CH_2, 2H), 2.30 (s, CH_3, 3H), 2.17−1.93 (br s, B−H), 1.85 (m, CH_2, 6H), 0.71 (br s, B−H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 136.6, 130.6, 130.2, 129.0 (C_{aryl}), 107.6 (d, ^1J(Rh,C) = 5.6, $C_{allylic}$), 85.5 (d, ^1J(Rh,C) = 8.3, $C_{allylic}$), 82.5 (d, ^1J(Rh,C) = 8.3, $C_{allylic}$), 33.1, 32.2, 29.8, 29.8, 29.6, 22.5 (CH_2, 5C; CH_3, 1C). ^{11}B NMR ($CDCl_3$, 25 °C): δ = 9.0 (d,

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^1J(B,H) = 141, 2B), −1.1 (2B), −7.3 (d, ^1J(B,H) = 142, 3B), −9.6 (1B), −19.9 (d, ^1J(B,H) = 153, 1B. (b) Starting from **2** (0.105 g, 0.225 mmol), the procedure was as for **4** but at room temperature (24 h). The yield was similar to that of method (a).

Synthesis of [*closo*-3-(η^3-C_8H_{13})-1-SEt-2-Me-3,1,2-$RhC_2B_9H_9$] (6). (a) The procedure was as for **5** but the isolation was performed by decanting the petroleum ether at −78 °C. [Rh(acac)(cod)] (0.091 g, 0.293 mmol), Cs[7-SEt-8-Me-7,8-$C_2B_9H_{10}$] (0.100 g, 0.294 mmol), 35 μL of $HClO_4$ 8.372 M (0.293 mmol). R_f = 0.75 (CH_2Cl_2). Yield 56 mg (46%). Anal. Calcd. for $C_{22}H_{32}B_9SRh$: C, 37.30; H, 7.22; S, 7.66. Found: C, 37.57; H, 7.14; S, 7.26. IR: ν [cm^{-1}] = 2542 (B−H). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 5.63 (q, J(H,H) = 7.6, $H_{allylic}$, 1H), 5.60 (q, J(H,H) = 7.6, $H_{allylic}$, 1H), 4.70 (t, J(H,H) = 7.6, $H_{allylic}$, 1H), 2.91 (m, CH_2−CH_3, 2H), 2.63 (m, CH_2, 2H), 2.46 (m, CH_2, 2H), 2.17 (s, C_{cage}−CH_3, 3H), 1.77 (m, CH_2, 6H), 1.25 (t, ^3J(H,H) = 7.7, CH_2−CH_3, 3H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 113.7, 112.3 (C_{cage}), 107.6 (d, ^1J(Rh,C) = 5.6, $C_{allylic}$), 84.9 (d, ^1J(Rh,C) = 6.9, $C_{allylic}$), 82.5 (d, ^1J(Rh,C) = 8.3, $C_{allylic}$), 33.1, 32.1, 29.8 (2C, overlapped), 29.7, 29.3, 22.5 (CH_2, 5C; CH_2−CH_3, 1C; C_{cage}−CH_3, 1C), 13.8 (CH_2−CH_3). ^{11}B NMR ($CDCl_3$, 25 °C): δ = 9.2 (d, ^1J(B,H) = 147, 2B), −1.0 (2B), −5.8 (1B), −7.0 (1B), −7.6 (1B), −8.6 (1B), −19.6 (d, ^1J(B,H) = 156, 1B). (b) Starting from **3**, the procedure was as for **5** (24 h). The yield was similar to that of method (a).

Synthesis of [NMe_4][10-D-7-SPh-8-Ph-7,8-$C_2B_9H_9$] (7). A solution of Na_2[7-SPh-8-Ph-7,8-$C_2B_9H_{11}$] in THF was prepared from [$HNMe_3$]-[7-SPh-8-Ph-7,8-$C_2B_9H_{10}$] (0.350 g., 0.927 mmol) by the method of Hawthorne et al.[23] and then treated with D_2O (2 mL) and stirred under nitrogen for 15 min. The bulk of the THF was evaporated under reduced pressure and tetramethylammonium chloride (0.155 g., 1.423 mmol) dissolved in D_2O (1.5 mL) was added to the residual solution.[24] The white precipitate of [NMe_4][10-D-7-SPh-8-Ph-7,8-$C_2B_9H_9$] was isolated by filtration, washed with D_2O, and recrystallized from acetone/D_2O to give 0.356 mg (98%) of compound **7**. Anal. Calcd. for $C_{18}H_{31}B_9$-DNS: C, 55.07; H, 7.90; N, 3.57; S, 8.17. Found: C, 54.78; H, 8.21; N, 3.50; S, 7.82. IR: ν [cm^{-1}] = 2538, 2517 (B−H). ^{1}H NMR ((CD_3)$_2$O, 25 °C): δ = 7.34−7.30 (m, H_{aryl}, 2H), 7.20−7.10 (m, H_{aryl}, 4H), 7.03−6.91 (m, H_{aryl}, 4H), 3.45 (s, N(CH_3)$_4$, 12 H). ^{1}H{^{11}B} NMR ((CD_3)$_2$O, 25 °C): δ = 7.34−7.30 (m, H_{aryl}, 2H), 7.20−7.10 (m, H_{aryl}, 4H), 7.03−6.91 (m, H_{aryl}, 4H), 3.45 (s, N(CH_3)$_4$, 12 H), 2.52 (br s, B−H), 2.35 (br s, B−H), 1.71 (br s, B−H), 0.80 (br s, B−H), 0.40 (br s, B−H). ^{2}H NMR ((CD_3)$_2$O, 25 °C): −2.01 (br s, B−D−B). ^{13}C-{^{1}H} NMR ((CD_3)$_2$O, 25 °C): δ = 141.6, 132.4, 127.5, 127.4, 126.1, 125.4, 124.0 (C_{aryl}), 72.5 (C_{cage}), 61.1 (C_{cage}), 55.1 (N(CH_3)$_4$). ^{11}B NMR ((CD_3)$_2$O, 25 °C): δ = −6.35 (d, ^1J(B,H) = 143, 1B), −8.47 (d, ^1J(B,H) = 142, 1B), −13.19 (d, ^1J(B,H) = 74, 1B), −13.78 (1B), −17.66 (d, ^1J(B,H) = 145, 3B), −32.86 (d, ^1J(B,H) = 142, 1B), −35.63 (d, ^1J(B,H) = 133, 1B).

Synthesis of [NMe_4][10-D-7-SPh-8-Me-7,8-$C_2B_9H_9$] (8). Starting from [$HNMe_3$][7-SPh-8-Me-7,8-$C_2B_9H_{10}$] (0.350 g, 1.109 mmol), the procedure was the same as for **7**; 0.363 g (99%) of compound **8** was obtained. Anal. Calcd. for $C_{13}H_{29}B_9$DNS: C, 47.24; H, 8.77; N, 4.24; S, 9.70. Found: C, 46.86; H, 9.05; N, 3.96; S, 9.46. IR: ν [cm^{-1}] = 2524 (B−H). ^{1}H NMR ((CD_3)$_2$O, 25 °C): δ = 7.30−7.19 (m, H_{aryl}, 4H), 7.06 (tt, J(H,H) = 7.1, J(H,H) = 1.5, H_{aryl}, 1H), 3.43 (s, N(CH_3)$_4$, 12H), 1.53 (s, C_{cage}−CH_3, 3H). ^{1}H{^{11}B} NMR ((CD_3)$_2$O, 25 °C): δ = 7.30−7.19 (m, H_{aryl}, 4H), 7.06 (tt, J(H,H) = 7.1, J(H,H) = 1.5, H_{aryl}, 1H), 3.43 (s, N(CH_3)$_4$, 12H), 2.28 (br s, B−H), 2.19 (br s, B−H), 1.76 (br s, B−H), 1.68 (br s, B−H), 1.53 (s, C_{cage}−CH_3, 3H), 1.38 (br s, B−H), 0.65 (br s, B−H), 0.26 (br s, B−H). ^{2}H NMR ((CD_3)$_2$O, 25 °C): −2.50 (br s, B−D−B). ^{13}C{^{1}H} NMR ((CD_3)$_2$O, 25 °C): δ = 143.6, 128.1, 126.0, 123.6 (C_{aryl}), 55.2 (N(CH_3)$_4$), 22.5 (C_{cage}−CH_3). ^{11}B NMR ((CD_3)$_2$O, 25 °C): δ = −7.07 (d, ^1J(B,H) = 124, 1B), −8.25 (d, ^1J(B,H) = 130, 1B), −10.31 (d, ^1J(B,H) = 169, 1B), −16.99 (d, ^1J(B,H) = 148, 4B), −33.26 (d, ^1J(B,H) = 134, 1B), −35.91 (d, ^1J(B,H) = 138, 1B).

Synthesis of [Rh(10-D-7-SPh-8-Ph-7,8-$C_2B_9H_9$)(cod)] (9). The complex was synthesized from [NMe_4][10-D-7-SPh-8-Ph-7,8-$C_2B_9H_9$] (0.120 g, 0.306 mmol), using the same procedure as that corresponding to nondeuterated complex **1**; 0.121 g (75%) of compound (**9**) was obtained. Anal. Calcd. for $C_{22}H_{31}B_9$DSRh·0.6 CH_2Cl_2: C, 46.76; H, 5.54; S, 5.52. Found: C, 47.06; H, 5.37; S, 5.59. IR: ν [cm^{-1}] = 2547 (B−H). IR: ν [cm^{-1}] = 2550 (B−H). ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.40−7.20 (m, H_{aryl}, 10H), 4.67, 4.62 (br s, $H_{olefinic}$, 4H), 2.52 (m, CH_2, 4H), 1.97 (m, CH_2, 4H). ^{1}H NMR (CD_2Cl_2, −94 °C): δ = 7.40−7.20 (m, H_{aryl}, 10H), 5.43 (br s, $H_{olefinic}$, 1H), 5.09 (br s, $H_{olefinic}$, 1H), 4.37 (br s, $H_{olefinic}$, 1H), 3.96 (br s, $H_{olefinic}$, 1H), 2.52 (m, CH_2, 4H), 1.97 (m, CH_2, 4H), −3.05 (br s, B−H−Rh). ^{11}B NMR (CD_2Cl_2, 25 °C): δ = −4.4 (d, ^1J(B,H) = 146, 1B), −11.2 (1B), −12.6 (1B), −15.1 (1B), −19.3 (d, ^1J(B,H) = 105, 1B), −26.6 (3B), −34.7 (d, ^1J(B,H) = 148, 1B).

Synthesis of [Rh(10-D-7-SPh-8-Me-7,8-$C_2B_9H_9$)(cod)] (10). The complex was synthesized from [NMe_4][10-D-7-SPh-8-Me-7,8-$C_2B_9H_9$] (99 mg, 0.30 mmol), as for **2**; 112 mg (80%) of compound **10** was obtained. Anal. Calcd. for $C_{17}H_{29}B_9$DSRh: C, 43.68; H, 6.20; S, 6.86. Found: C, 43.59; H, 6.15; S, 6.84. IR: ν [cm^{-1}] = 2533 (B−H). ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.58−7.42 (m, H_{aryl}, 5H), 4.66 (br s, $H_{olefinic}$, 2H), 4.40 (br s, $H_{olefinic}$, 2H), 3.46 (q, ^3J(H,H) = 7, CH_3−CH_2−O), 2.51 (m, CH_2, 4H), 1.90 (m, CH_2, 4H), 1.43 (s, CH_3, 3H), 1.19 (t, ^3J(H,H) = 7, CH_3−CH_2−O, 0.5H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 136.2, 129.9, 129.3, 128.7 (C_{aryl}), 82.9 (br s, $C_{olefinic}$), 81.7 (br s, $C_{olefinic}$), 65.3 (CH_3-CH_2−O), 30.8 (CH_2), 30.1 (CH_2), 20.3 (CH_3), 14.8 (CH_3−CH_2−O). ^{11}B NMR ($CDCl_3$, 25 °C): δ = −4.1 (d, ^1J(B,H) = 148, 1B), −8.5 (d, ^1J(B,H) = 142, 1B), −12.1 (d, ^1J(B,H) = 144, 2B), −18.1 (d, ^1J(B,H) = 107, 1B), −24.9 (d, ^1J(B,H) = 140, 1B), −26.3 (2B), −34.1 (d, ^1J(B,H) = 143, 1B).

Synthesis of [*closo*-3-(η^3-C_8H_{13})-1-SPh-2-Ph-3,1,2-$RhC_2B_9H_8D$] (11). Starting from [Rh(10-D-7-SPh-8-Ph-7,8-$C_2B_9H_9$)(cod)] (118 mg, 0.30 mmol) compound **11** was obtained as for the synthesis of **4**. Anal. Calcd. for $C_{22}H_{31}B_9$DSRh·0.6 CH_2Cl_2: C, 46.76; H, 5.54; S, 5.52. Found: C, 47.06; H, 5.37; S, 5.59. IR: ν [cm^{-1}] = 2550 (B−H). ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.89−7.33 (m, H_{aryl}, 10H), 5.64−5.55 (m, $H_{allylic}$, 1H), 5.44−5.35 (m, $H_{allylic}$, 1H), 4.71 (t, J(H,H) = 7, $H_{allylic}$, 1H), 2.72 (m, CH_2, 2H), 1.68 (m, CH_2, 4H), 1.49 (m, CH_2, 2H), 1.33-(m, CH_2, 2H). ^{1}H{^{11}B} NMR (CD_2Cl_2, 25 °C): δ = 7.89−7.33 (m, H_{aryl}, 10H), 5.64−5.55 (m, $H_{allylic}$, 1H), 5.44−5.35 (m, $H_{allylic}$, 1H), 4.71 (t, J(H,H) = 7, $H_{allylic}$, 1H), 4.10 (br s, B−H), 3.84 (br s, B−H), 3.57 (br s, B−H), 2.45 (br s, B−H), 2.72 (m, CH_2, 2H), 1.68 (m, CH_2, 4H), 1.49 (m, CH_2, 2H), 1.33 (m, CH_2, 2H). ^{2}H NMR (CD_3Cl/CH_2Cl_2, 25 °C): 0.64 (br s, B−D). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ = 145.6, 137.5, 136.1, 131.5, 130.6, 129.5, 128.8, 128.2, 127.3 (C_{aryl}), 118.4, 116.6 (C_{cage}), 108.2, 86.7, 85.3 ($C_{allylic}$), 34.1, 32.1, 29.9, 29.6, 22.6 (CH_2). ^{11}B NMR (CD_2Cl_2, 25 °C): δ = 19.4 (d, ^1J(B,H) = 127, 1B), 13.5 (d, ^1J(B,H) = 140, 1B), 5.9 (1B), 4.4 (1B), 2.1 (2B), 0.0 (1B), −4.9 (d, ^1J(B,H) = 138, 1B), −18.6 (d, ^1J(B,H) = 148, 1B).

Synthesis of [*closo*-3-(η^3-C_8H_{13})-1-SPh-2-Me-3,1,2-$RhC_2B_9H_8D$] (12). Starting from [Rh(10-D-7-SPh-8-Me-7,8-$C_2B_9H_9$)(cod)], the procedure was as for **4** to get compound **12**. Anal. Calcd. for $C_{17}H_{29}B_9$-DSRh: C, 43.68; H, 6.20; S, 6.86. Found: C, 43.59; H, 6.15; S, 6.84. IR: ν [cm^{-1}] = 2532 (B−H). ^{1}H NMR (CD_2Cl_2, 25 °C): δ = 7.51−7.36 (m, H_{aryl}, 5H), 5.79 (q, J(H,H) = 8.5, $H_{allylic}$, 1H), 5.72 (q, J(H,H) = 8.5, $H_{allylic}$, 1H), 4.77 (t, J(H,H) = 7, $H_{allylic}$, 1H), 2.71 (m, CH_2, 1H), 2.53 (m, CH_2, 1H), 2.29 (s, CH_3, 3H), 1.81 (m, CH_2, 4H), 1.51 (m, CH_2, 4H). ^{1}H{^{11}B} NMR (CD_2Cl_2, 25 °C): δ = 7.51−7.36 (m, H_{aryl}, 5H), 5.79 (q, J(H,H) = 8.5, $H_{allylic}$, 1H), 5.72 (q, J(H,H) = 8.5, $H_{allylic}$, 1H), 4.77 (t, J(H,H) = 7, $H_{allylic}$, 1H), 3.66 (br s, B−H), 3.22 (br s, B−H), 2.71 (m, CH_2, 1H), 2.53 (m, CH_2, 1H), 2.29 (s, CH_3, 3H), 2.07 (br s, B−H), 1.81 (m, CH_2, 4H), 1.51 (m, CH_2, 4H), 0.67 (br s, B−H/B−D). ^{2}H NMR (CD_3Cl/CH_2Cl_2, 25 °C): 0.69 (br s, B−D). ^{13}C{^{1}H} NMR (CD_3Cl, 25 °C): δ = 136.9, 131.0, 130.6, 129.3 (C_{aryl}), 107.9 ($C_{allylic}$), 86.5 (d, ^1J(Rh,C) = 5.6, $C_{allylic}$), 83.5 (d, ^1J(Rh,C) = 5.6, $C_{allylic}$), 33.4, 32.5, 30.1, 30.0, 29.7, 22.8 (CH_2, 5C; CH_3, 1C). ^{11}B NMR ($CDCl_3$, 25 °C): δ = 8.2 (d, ^1J(B,H) = 142, 2B), −0.8 (d, ^1J(B,H) = 67, 1B), −1.3 (d, ^1J(B,H) = 57, 1B), −7.7 (d, ^1J(B,H) = 139, 3B), −10.0 (d, ^1J(B,H) = 78, 1B), −20.0 (d, ^1J(B,H) = 156, 1B).

Kinetic Experiments. A weighted amount of **2** or **3** was placed in a small container, 0.5 mL of $CDCl_3$ was added, and the time counter was reset. The mixture was stirred until dissolution and the solution was transferred to an NMR tube. The NMR spectrometer was configured to obtain the ^{1}H{^{11}B}NMR spectra at preselected time intervals. After the experiment was finished the spectra were integrated and the percent composition of the mixture was calculated. The reaction

times were taken as the elapsed time from mixing to the middle of each spectral adquisition.

General Procedure for the Hydrogenation of Cyclohexene. (a) Hydrogenation without Added PPh_3. THF and cyclohexene were previously freeze−pump−thawed three times under H_2. To a Schlenck flask was added 4.2×10^{-2} mmol of rhodium complex and a magnetic stirring bar, and the system was evacuated and filled with H_2 three times. THF (5 mL) was added and the system was stirred until dissolution of the solid. Then cyclohexene (1 mL) was added. Meanwhile the autoclave had been evacuated and filled with H_2, and fitted with hoses supplying water maintained at 25 °C from the constant-temperature bath, and the gas inlet had been connected to the H_2 line. The solution was rapidly transferred to the autoclave through the sample inlet via syringe, the gas inlet was opened, and the system was pressurized to 20 atm of H_2. The magnetic stirring was started and the timing counter was reset. From the addition of the alkene to the resetting of the timing counter no more than 3 min passed. After 1 h, the autoclave was vented and dismantled, and the composition of the solution was analyzed by capillary GC.

(b) Hydrogenation with Added PPh_3. The procedure used was as for (a) but the complex was previously treated as follows: To a Schlenck flask was added 4.2×10^{-2} mmol of rhodium complex and a magnetic stirring bar, and the system was evacuated and filled with H_2 three times. Then 5 mL of a 8.34 M solution of PPh_3 (1 equivalent) in THF was added and H_2 was bubbled through the solution with stirring for ca. 40 min. After this time the solvent was removed in vacuo and 5 mL of THF followed by 1 mL of cyclohexene were added to the residue. The solution was then transferred to the autoclave as in (a).

X-ray Structure Determinations of 1 and 4. Single-crystal data collections were performed at room temperature on a Rigaku AFC5S diffractometer using graphite monochromatized Mo Kα radiation. A total of 4405 and 4439 independent reflections were collected by $\omega/2\theta$ scan mode ($2\theta_{max} = 50°$) for **1** and **4**, respectively. Crystallographic data are presented in Table 1.

The structures were solved by direct methods by using the SHELXS86 program[29] and refined on F^2 by the SHELXL-93 program.[30] Non-hydrogen atoms were refined with anisotropic displacement parameters and positional parameters for the hydrogen atoms with fixed isotropic displacement parameters.

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Supporting Information Available: (1) Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** and **4**; (2) the ^2H NMR spectrum (46.07 MHz) of [*closo*-3-(η^3-C_8H_{13})-1-SPh-2-Me-3,1,2-$RhC_2B_9H_8D$] (**12**) in $CHCl_3$; and (3) figures illustrating the plot of material vs time for the isomerization of compounds [Rh(7-SPh-8-Me-7,8-$C_2B_9H_{10}$)(cod)] (**2**) and [Rh(7-SEt-8-Me-7,8-$C_2B_9H_{10}$)(cod)] (**3**), respectively, and figures illustrating the first-order kinetic plot for their isomerization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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