Influence of S-Aryl Groups in the Coordination and Reactivity of (*nido*-Thiocarborane)ruthenium Complexes

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The reaction of $[RuCl_2(PPh_3)_3]$ and $[NMe_4][7,8\text{-}(SPh)_2\text{-}7,8\text{-}C_2B_9H_{10}]$ in ethanol yields $[RuCl(7,8\text{-}(SPh)_2\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]\cdot CH_2Cl_2$ (**1**). The structure of **1** has been determined by crystallographic studies. The crystal contains the two isomers **1a** and **1b** in a ratio of ca. 3:1. In both isomers the metal has an octahedral geometry and the carborane ligand tricoordinates the Ru(II) center by means of S−Ru, B(11)−H−Ru, and B(2)−H−Ru bonds. Two PPh_3 groups and a chloride ligand fulfill the coordination sphere of the metal. The two isomers arise from two different dispositions of the $[RuCl(PPh_3)_2]^+$ fragment with regard to the carborane cluster. The preference for two agostic B−H−Ru bonds rather than a second S−Ru bond appears to be due to steric factors. The reaction of $[RuCl_2(PPh_3)_3]$ and the cesium or tetramethylammonium salts of $[7\text{-}(SPh)\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = Me, Ph) yields $[RuCl(7\text{-}SPh\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (**2**, R = Me; **3**, R = Ph). NMR spectroscopic analyses of **2** and **3** also indicate the presence of isomers analogous to those observed for **1**. Unlike the S-alkyl-substituted (monothiocarborane)ruthenium complexes reported earlier, complexes **1**−**3** do not undergo B(5) elimination to form an *arachno* cluster. Complex **2** catalyzes the hydrogenation of 1-hexene, exhibiting a TON of 115 ([1-hexene] = 3.9 M, [**2**] = 5.21×10^{-4} M, 66 °C, P = 45 bar, 1 h).

Introduction

Unlike organic thioethers, which are usually considered to be fairly poor ligands,[1] mono- and dithioether derivatives of the 7,8-dicarba-*nido*-undecaborate anion have been shown to possess a high ligand capacity for a wide variety of transition metals.[2] In these complexes, metal−thioether coordination is dominant over metal−halogen coordination, as opposed to the case for normal dithioethers,[3] and some of them have been obtained by the displacement of PPh_3 ligands, which is very uncommon in thioether chemistry. The exaltation of the ligand capacity has to be attributed to the anionic carborane cage directly connected to the sulfur coordinating elements.

The study of the chemistry of dithioether derivatives of *nido*-$[7,8\text{-}C_2B_9H_{12}]^-$ has been restricted exclusively to S-alkyl derivatives. Nevertheless, it is known that the substitution of S-alkyl by S-aryl groups can markedly affect the physical and geometrical properties of the resulting complexes.[4] Since no bis(S-aryl)carborane metal complex has ever been reported in the literature, it seemed interesting to explore the effect of incorporating S-aryl thioether groups in the "$[7,8\text{-}C_2B_9H_{10}]^-$" fragment. In this paper the synthesis and characterization of the first ruthenium complex of $[7,8\text{-}(SPh)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ is described and its coordination features are discussed in reference to those of its S-alkyl counterparts.

Results and Discussion

The reaction of $[RuCl_2(PPh_3)_3]$ and $[NMe_4][7,8\text{-}(SPh)_2\text{-}7,8\text{-}C_2B_9H_{10}]$ in ethanol at reflux for 2 h yielded a red-orange solid (**1**). The $^{31}P\{^1H\}$ NMR spectrum of **1** displayed two sets of resonances which indicated the presence of two compounds. A broad signal at 45.9 ppm and a doublet at 39.7 ppm ($^2J(P, P)$ = 31 Hz) having the same intensity can be associated with one species (**1a**) and two doublets at 52.8 ($^2J(P,P)$ = 32 Hz) and 43.1 ppm ($^2J(P,P)$ = 32 Hz) with a second species (**1b**). The integration of the ^{31}P NMR spectrum revealed a **1a**:**1b**

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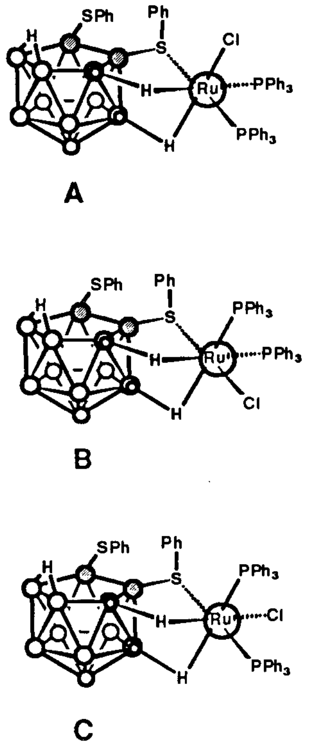

Figure 1. Isomers compatible with the formulation [RuCl-(7,8-(SPh)$_2$-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$].

ratio of 3:1. The lower field resonance of each set was significantly broader than that situated at upper field, suggesting a trans disposition to a B−H group. Besides, the P−P coupling constants indicated cis disposition of the PPh$_3$ ligands for both species. The ^{1}H NMR spectrum was also in accord with the presence of two isomers: the negative zone of the spectrum showed two tetraplets at −2.09 ppm (^1J(B,H) = ca. 114 Hz, B−H−Ru) and −2.22 ppm (^1J(B,H) = ca. 113 Hz, B−H−Ru) and broad resonances at −3.17 (B−H−B), −13.71 (B−H−Ru), and −14.74 (B−H−Ru). The tetraplets collapsed to broad singlets in the ^{1}H{^{11}B} NMR spectrum and the broad resonances sharpened considerably. The integration of the spectrum allowed us to associate the resonances at −2.09, −3.17, and −14.74 with **1a** species and the rest of the resonances (−2.22, −3.17, −13.71) with **1b**, the B−H−B resonance being coincident.

Therefore, the ^{1}H and ^{31}P NMR spectra of **1** indicate the presence of two species in solution whose structure appears to be similar: a [RuCl(PPh$_3$)$_2$]$^+$ fragment bonded to the carborane cage through a S−Ru bond and two B−H−Ru bonds. Three isomers are compatible with the [RuCl(7,8-(SPh)$_2$-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] stoichiometry, which are depicted in Figure 1. The broadness of the lower field ^{31}P{^{1}H} NMR signals corresponding to **1a** and **1b** suggest that only one B−H group trans to a PPh$_3$ ligand exists in both species. This would exclude structure B in Figure 1. An X-ray diffraction study was undertaken to fully characterize complex **1**. Both isomers of the complex crystallized in the same crystal and the percent composition was found to be very close to that found in solution. Simplified drawings of the complex units are found in Figure 2.

The asymmetric unit of [RuCl(7,8-(SPh)$_2$-C$_2$B$_9$H$_{10}$)-(PPh$_3$)$_2$]·CH$_2$Cl$_2$ contains the two diastereomers (**1a** and **1b**) in the ratio 0.763(2):0.237(2) and a dichloromethane molecule, which is divided equally into two positions. In parts a and b of Figure 2 are shown simplified drawings of the two complex units corresponding to the isomers A and C in Figure 1. In both units, the *nido* cage is tricoordinated to the metal and the rest of the coordination positions are filled by a chloride ion and two phosphorus atoms of two PPh$_3$ groups. The three bonds from the cage to Ru(II) are formed by the sulfur atom bonded to C(7) and the hydrogen atoms bonded to B(2) and B(11). As the cage exhibits two orientations with B(3) occupying two positions, only the labeling of complex unit **1a** is in accord with the nomenclature, but not that for **1b**. The coordinated hydrogen atom at the open face is H(11), and that at the second belt is H(2) in **1a**. For **1b** the hydrogen atom at the open face is now H(2) and that of the second belt H(11). The S(2) atom has two quite close positions (S(2a)···S(2b) = 0.610(7) Å), but orientations of the phenyl groups connected to S(2a) and S(2b) are quite different with respect to the [RuCl(PPh$_3$)$_2$]$^+$ fragment, as can also be noticed from parts a and b of Figure 2, and the torsion angle values for C(7)−C(8)−S(2a)−C(19a) (−86.4(4)°) and C(7)−C(8)−S(2b)−C(19b) (92.1(7)°).

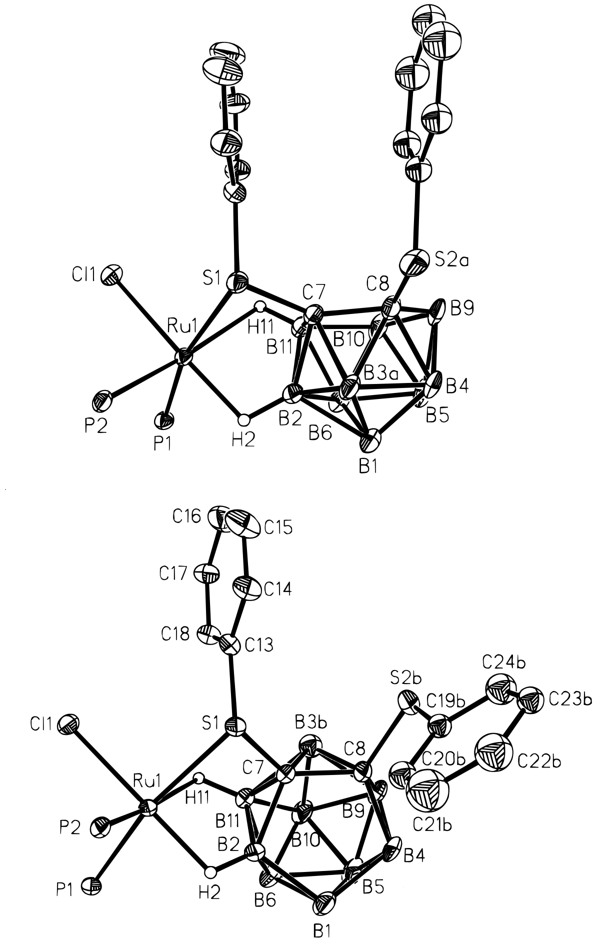

Figure 2. Crystal structures of (a, top) **1a** and (b, bottom) **1b**.

The isomers found in **1** can be compared to Ru complexes containing PR$_2$/(BH)$_2$ tricoordinating *nido* carborane cages.[5] The following are observed: (i) owing

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to the trans influence the Ru−P bonds are dissimilar, with P(2) trans to H(11) forming a shorter bond to the metal than P(1) trans to S(1), and (ii) tridentate coordination of the stiff carborane cage produces considerable differences between the individual angles around the coordinated S(1) atom and the C(7) atom of the carborane cage. Accordingly, the Ru(1)−P(1) bond is ca. 0.04 Å longer than the Ru(1)−P(2) bond, and the angles around S(1) and C(7) vary from 81.7(1) to 115.2(1)° and from 105.4(3) to 126.4(3)°, respectively. The lowest angle value around S(1) is for Ru(1)−S(1)−C(7) and that around C(7) is for S(1)−C(7)−B(2).

The coordination sphere of Ru(II) is not regular octahedral. The P−Ru−P angle of 101.20(4)° is considerably opened compared to the ideal angle (90°) of an octahedral coordination geometry, and the Ru(1)−S(1) bond of 2.489(1) Å is rather long. The opening of the P−Ru−P angle can be explained in terms of mutual steric crowding of bulky PPh_3 groups, and it is probably supported by the small size of the coordinated hydrogen atoms. Long Ru−S bonds have also been reported for the strained S_2/(BH) tricoordinated carborane complex $[RuCl(7,8\text{-}\mu\text{-}(SCS)\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$.[6] Because other bond lengths are very similar in these two complexes, it seems that the lengthening of the Ru−S bond at least partly originate from the strained tricoordination of the carborane cage.

We have reported earlier[6] that dithioether carborane anions of formula $[7,8\text{-}\mu\text{-}(SRS)\text{-}7,8\text{-}C_2B_9H_{10}]^-$ react with $[RuCl_2(PPh_3)_3]$ to yield $[RuCl(7,8\text{-}\mu\text{-}(SRS)\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ complexes, in which the carborane cage is bonded to the $[RuCl(PPh_3)_2]^+$ fragment through two S−Ru bonds and a B(3)−H−Ru bond. This B(3)−H−Ru interaction can be modulated by modifying the length of the R chain connected to the sulfur atoms. Hence, the shorter the R chain, the smaller the B(3)−Ru distance produced. Accordingly, when long R chains or nonconnected S,S′ strings are used, the B(3)−H−Ru interaction is no longer observed. For instance, the reaction of the ligand $[NMe_4][7,8\text{-}(SMe)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ with $[RuCl_2(PMePh_2)_4]$ yields the complex $[NMe_4][RuCl_2(7,8\text{-}(SMe)_2\text{-}7,8\text{-}C_2B_9H_{10})(PMePh_2)_2]$, in which the carborane cage is bonded to the metal through two S−Ru bonds and no B−H−Ru interactions are observed. Since the ligand $[7,8\text{-}(SPh)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ is a dithioether carborane anion whose sulfur atoms are not connected by a chain, a complex similar to that obtained with $[7,8\text{-}(SMe)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ would be expected. However, no traces of such a complex have been detected. In this regard, complexes **1a** and **1b** are striking, since the formation of two B−H−Ru bonds is preferred to a stronger S−Ru bond. A careful inspection using molecular models[7] of all the possible isomers in which ligand $[7,8\text{-}(SPh)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ is linked to the $[RuCl(PPh_3)_2]^+$ fragment through both sulfur atoms suggests that dithio coordination is hampered due to steric congestion between the SPh groups and the bulky PPh_3 groups. Thus, although electronic factors arising from the substitution of S-alkyl by S-aryl groups cannot be excluded here, the molecule seems to prefer a less crowded structure by forming two B−H−Ru bonds.

Since the ligand $[7,8\text{-}(SPh)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ behaves as a monothiocarborane ligand, it is not surprising that the structure of **1a** and **1b** is similar to that of the complex $[RuCl(7\text{-}SMe\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_8H_{10})(PPh_3)_2]$ reported earlier.[8] Besides, two isomers analogous to **1a** and **1b** were observed when S-alkyl-substituted monothiocarboranes were reacted with $[RuCl_2(PPh_3)_3]$, though the resulting complexes were observed to eliminate boron atom B(5) to yield an *arachno* 7,8-C_2B_8 cluster. No such elimination has been observed for **1a** or **1b**. To study whether this behavior was extensible to other S-aryl-substituted monothiocarboranes, the ligands $[7\text{-}Me\text{-}8\text{-}(SPh)\text{-}7,8\text{-}C_2B_9H_{10}]^-$ and $[7\text{-}Ph\text{-}8\text{-}(SPh)\text{-}7,8\text{-}C_2B_9H_{10}]^-$ were reacted with $[RuCl_2(PPh_3)_3]$. The use of the tetramethylammonium salt in ethanol at reflux or, alternatively, the cesium salt in toluene:ethanol (8:1) at room temperature led to the isolation of the respective complexes $[RuCl(7\text{-}Me\text{-}8\text{-}(SPh)\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (**2**) and $[RuCl(7\text{-}Ph\text{-}8\text{-}(SPh)\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$ (**3**), whose elemental analyses were consistent with retention of the C_2B_9 cluster. Insolubility of **3** in common solvents precluded NMR spectroscopic characterization, and thus, only **2** was studied. The ^1H and $^{31}P\{^1H\}$ NMR spectra presented a pattern analogous to that found for **1**. Hence, two species were observed in the $^{31}P\{^1H\}$ NMR spectrum: a broad doublet at 45.4 ppm and a doublet at 41.1 ppm ($^2J(P,P) = 31$ Hz) (**2a**) and two doublets at 51.3 and 44.1 ppm ($^2J(P,P) = 32$ Hz) (**2b**). The **2a**:**2b** ratio was 4:1. The respective ^1H NMR resonances appeared at 1.24 (C_{cage}−Me), −2.41 (B−H−Ru), −3.23 (B−H−B), and −14.70 ppm (B−H−Ru) (**2a**) and at 1.15 (C_{cage}−Me), −2.54 (B−H−Ru), −3.23 (B−H−B), and −14.0 ppm (B−H−Ru) (**2b**). Despite not knowing all the factors governing the B(5) elimination process in these complexes, the results reported here indicate that this process is sensitive to changes of substituents bonded to the sulfur atoms which, in turn, is related to changes in electronic density at sulfur.

Finally, considering the key role that B−H−M bonds play in some catalytic systems,[9] the activity of complex **2** in catalytic hydrogenation reactions was briefly investigated. We have recently reported the synthesis of the (monothiocarborane)rhodium complex $[Rh(7\text{-}Me\text{-}8\text{-}(SPh)\text{-}7,8\text{-}C_2B_9H_{10})(PPh_3)_2]$, which exhibits high catalytic activity in the hydrogenation of 1-hexene.[10] However, complex **2** showed a much lower activity and the use of relatively high pressures was needed in order to achieve moderate turnover numbers ([1-hexene] = 3.9 M, [**2**] = 5.21×10^{-4} M, 66 °C, P = 45 bar, 1 h, TON = 115). The presence of a base such as NEt_3, which in some ruthenium catalytic systems has been shown to favor the heterolytic activation of H_2,[11] did not result in an increase in activity.

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In summary, we have reported the first example of an *exo-nido*-dithiocarborane complex in which a coordinating S/(BH)$_2$ moiety is favored versus an S$_2$/(BH) surrounding. Relief of steric congestion appears to be the cause of this unusual behavior. This result expands the known ways in which modification of carborane clusters can be used to modify their coordinating properties. On the other hand, unlike their S-alkyl-substituted counterparts, S-aryl-substituted *exo-nido*-thioruthenacarborane complexes do not undergo B(5) elimination but retain the initial C_2B_9 structure.

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. NMR spectra were recorded using a Bruker ARX 300 instrument. Catalytic hydrogenations were conducted in a 35-mL autoclave. The autoclave was equipped with a water jacket, a rupture disk, a manometer, and sample and gas inlets. GC analyses were performed with a Shimadzu GC-15A instrument using an SPB-1 capillary column (Supelco; 30 m length, 0.25 mm inner diameter, and 1 mm thick stationary phase).

Materials. All manipulations were carried out under a dinitrogen atmosphere using standard vacuum line techniques. Toluene used in the synthesis was distilled from sodium benzophenone prior to use. The rest of the solvents were of reagent grade quality and were used without further purification. Deuterated solvents for NMR (Fluorochem) were freeze−pump−thawed three times under N$_2$ and transferred to the NMR tube using standard vacuum line techniques. 1-Hexene (Aldrich) was freshly distilled from CaH$_2$ prior to use. Salts of thiocarborane anions[12] [7,8-(SPh)$_2$-7,8-$C_2B_9H_{10}$]$^-$, [7-Me-8-(SPh)-7,8-$C_2B_9H_{10}$]$^-$, [7-Ph-8-(SPh)-7,8-$C_2B_9H_{10}$]$^-$, and [RuCl$_2$(PPh$_3$)$_3$][13] were prepared according to the literature methods.

Synthesis of [RuCl(7,8-(SPh)$_2$-7,8-$C_2B_9H_{10}$)(PPh$_3$)$_2$] (1). A suspension of [NMe$_4$][7,8-(SPh)$_2$-7,8-$C_2B_9H_{10}$] (55 mg, 0.13 mmol) and [RuCl$_2$(PPh$_3$)$_3$] (113 mg, 0.12 mmol) in ethanol (20 mL) was refluxed for 2 h. During this time an orange-red precipitate formed, which was filtered while hot. The solid was washed with hot ethanol (3 × 5 mL) and ether (3 × 5 mL) and vacuum-dried. Yield: 95 mg (80%). IR (KBr): ν (cm^{-1}) 2556, 2532 (B−H). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C, TMS): δ 7.13−6.52 (m, 40, H$_{aryl}$), −2.09 (tetrap, ^1J(B,H) = ca. 114 Hz, 0.76, B−H−Ru, **1a**), −2.22 (tetrap, ^1J(B,H) = ca. 113 Hz, 0.23, B−H−Ru, **1b**), −3.17 (br, 1, B−H−B, **1a**,**b**), −13.71 (br, 0.23, B−H−Ru, **1b**), −14.74 (br, 0.76, B−H−Ru, **1a**). ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$, 25 °C, H$_3$PO$_4$, 85%): δ 52.8 (br d, ^2J(P,P) = 32 Hz, 1, **1b**), 45.9 (br, 3, **1a**), 43.1 (d, ^2J(P, P) = 32 Hz, 1, **1b**), 39.7 (d, ^2J(P,P) = 31 Hz, 3, **1a**). Anal. Calcd for $C_{50}H_{50}B_9ClP_2S_2Ru\cdot CH_2Cl_2$: C, 56.39; H, 4.70; S, 5.78. Found: C, 56.18; H, 4.76; S, 5.43.

Synthesis of [RuCl(7-Me-8-(SPh)-7,8-$C_2B_9H_{10}$) (PPh$_3$)$_2$] (2). Method a. The procedure used was as for **1**. Conditions and reagents: [NMe$_4$][7-Me-8-(SPh)-7,8-$C_2B_9H_{10}$] (100 mg, 0.30 mmol), [RuCl$_2$(PPh$_3$)$_3$] (280 mg, 0.29 mmol), ethanol (20 mL), 2 h. Yield: 240 mg (90%).

Method b. A suspension of Cs[7-Me-8-(SPh)-7,8-$C_2B_9H_{10}$] (66 mg, 0.16 mmol) and [RuCl$_2$(PPh$_3$)$_3$] (148 mg, 0.15 mmol) in toluene/ethanol (8/1) was stirred at room temperature for 4 h. The white precipitate of CsCl formed was filtered through Celite, the orange filtrate was concentrated under vacuum to 2 mL, and ethanol (18 mL) was added with stirring. The resulting orange solid was isolated by filtration, washed with ethanol (2 × 3 mL) and ether (2 × 3 mL), and dried under vacuum. Yield: 114 mg (81%). IR (KBr): ν (cm^{-1}) 2565, 2539, 2517 (B−H). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$, 25 °C, TMS): δ 7.33−7.13 (m, 35, aryl), 1.24 (s, 2.40, CH$_3$, **2a**), 1.15 (s, 0.60, CH$_3$, **2b**), −2.41 (tetrap, ^1J(B,H) = ca. 110 Hz, 0.80, B−H−Ru, **2a**), −2.54 (tetrap, ^1J(B,H) = ca. 107 Hz, 0.20, B−H−Ru, **2b**), −3.23 (br, 1, B−H−B, **2a**, **2b**), −14.0 (br, 0.20, B−H−Ru, **2b**), −14.7 (br, 0.80, B−H−Ru, **2a**). ^{31}P{^{1}H} NMR (121.5 MHz, CD$_2$Cl$_2$, 25 °C, H$_3$PO$_4$, 85%): δ 51.3 (br d, ^2J(P,P) = 33 Hz, 1, **2b**), 45.4 (br d, ^2J(P,P) = 31 Hz, 4, **2a**), 44.1 (d, ^2J(P,P) = 33 Hz, 1, **2b**), 41.1 (d, ^2J(P,P) = 31 Hz, 4, **2a**). Anal. Calcd for $C_{45}H_{48}B_9ClP_2SRu$: C, 58.96; H, 5.28; S, 3.50. Found: C, 58.97; H, 5.31; S, 2.96.

Table 1. Crystallographic Data for [RuCl(7,8-(SPh)$_2$-$C_2B_9H_{10}$)(PPh$_3$)$_2$]·CH$_2$Cl$_2$ (1)

chem formula	$C_{51}H_{52}B_9Cl_3P_2RuS_2$
fw	1095.70
T (°C)	21
λ (Å)	0.710 69
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a (Å)	14.176(2)
b (Å)	16.019(2)
c (Å)	12.384(1)
α (deg)	91.66(1)
β (deg)	109.100(8)
γ (deg)	77.75(1)
V (Å^3)	2594.4(6)
Z	2
d_{calcd} (g cm^{-3})	1.403
μ (cm^{-1})	6.3
F(000)	1120
R[a]	0.043
R_w[b]	0.046

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

Synthesis of [RuCl(7-Ph-8-(SPh)-7,8-$C_2B_9H_{10}$)(PPh$_3$)$_2$] (3). The procedure used was as for **2** (method b). Conditions and reagents: Cs[7-Ph-8-(SPh)-7,8-$C_2B_9H_{10}$] (53 mg, 0.12 mmol), [RuCl$_2$(PPh$_3$)$_3$] (106 mg, 0.11 mmol), toluene/ethanol (8/1, 9 mL), 4 h. Yield: 74 mg (59.8%). IR (KBr): ν (cm^{-1}) 2574, 2533 (B−H). Anal. Calcd for $C_{50}H_{50}B_9ClP_2SRu\cdot 0.25\ OP(C_6H_5)_3$: C, 62.46; H, 5.13; S, 3.06. Found: C, 62.39; H, 5.28; S, 2.75.

Catalytic Hydrogenation of 1-Hexene. Toluene and 1-hexene were previously freeze−pump−thawed three times under N$_2$. To a Schlenck flask was added **2** (4.8 mg, 5.21 × 10^{-3} mmol), a magnetic stirring bar and the system was evacuated and filled with N$_2$ three times. Toluene (5 mL) was added and the system was stirred until dissolution of the solid. Meanwhile the autoclave had been evacuated and filled with H$_2$, fitted with hoses supplying water maintained at 66 °C from the constant-temperature bath and the gas inlet had been connected to the H$_2$ line. Then 1-hexene (5 mL) was added to the Schlenck flask, the solution was transferred to the autoclave through the sample inlet via syringe, the gas inlet was opened, the system was pressurized to 45 at of H$_2$ and the magnetic stirring was started. After 1 h, the autoclave was vented and dismantled, and the composition of the solution was analyzed by capillary GC.

X-ray Structure Determination of [RuCl(7,8-(SPh)$_2$-$C_2B_9H_{10}$)(PPh$_3$)$_2$]·CH$_2$Cl$_2$. Single-crystal data collection was performed at ambient temperature on a Rigaku AFC5S diffractometer using graphite-monochromatized Mo Kα radiation. The unit cell parameters were determined by least-squares refinement of 25 carefully centered reflections. The data obtained were corrected for Lorentz and polarization effects, dispersion, and absorption (*y* scan). A total of 9533 reflections giving 9129 unique reflections ($R_{int} = 0.030$) were collected by $\omega/2\theta$ scan mode ($2\theta_{max} = 50°$). Of those, 6572 were considered as observed according to the criterion $F > 4\sigma(F)$. Crystallographic data are presented in Table 1.

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[13] Hallmam, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) with Esd's in Parentheses for $[\mathrm{RuCl(7,8\text{-}(SPh)_2\text{-}C_2B_9H_{10})(PPh_3)_2]\cdot CH_2Cl_2}$ (1)

Ru(1)−Cl(1)	2.396(1)	S(1)−C(7)	1.789(5)
Ru(1)−S(1)	2.489(1)	S(1)−C(13)	1.787(5)
Ru(1)−P(1)	2.343(1)	S(2A)−C(8)	1.796(5)
Ru(1)−P(2)	2.304(1)	S(2A)−C(19A)	1.766(4)
Ru(1)−B(2)	2.328(4)	S(2B)−C(8)	1.754(7)
Ru(1)−B(11)	2.558(5)	S(2B)−C(19B)	1.76(2)
Ru(1)−H(2)	1.70(3)	C(7)−C(8)	1.564(5)
Ru(1)−H(11)	2.08(5)		

Cl(1)−Ru(1)−S(1)	95.50(4)	Ru(1)−S(1)−C(13)	115.2(1)
Cl(1)−Ru(1)−P(1)	91.70(4)	C(7)−S(1)−C(13)	106.2(2)
Cl(1)−Ru(1)−P(2)	93.16(4)	C(8)−S(2A)−C(19A)	107.1(2)
Cl(1)−Ru(1)−H(2)	176(1)	C(8)−S(2B)−C(19)B	103.1(6)
S(1)−Ru(1)−P(1)	165.86(4)	S(1)−C(7)−B(2)	105.4(3)
S(1)−Ru(1)−P(2)	90.57(4)	S(1)−C(7)−B(3A)	110.2(4)
P(1)−Ru(1)−P(2)	101.20(4)	S(1)−C(7)−B(3)B	25.2(9)
P(2)−Ru(1)−H(11)	169(1)	S(1)−C(7)−C(8)	126.4(3)
Ru(1)−S(1)−C(7)	81.7(1)	S(1)−C(7)−B(11)	113.4(3)

The structure was partly solved by direct methods by using the MITRIL program.[14] Least-squares refinements and all subsequent calculations were performed using the XTAL3.2 program system,[15] which minimized the function $\sum w(\Delta F)^2$ ($1/w = \sigma^2(F_o)$). The asymmetric unit contains two diastereomers with occupancies 0.763(2) (**1a**) and 0.237(2) (**1b**). This has resulted because the sulfur atom S(2), the phenyl group attached to S(2), the carborane cage, and the solvent dichloromethane have two positions or orientations. In the two orientations of the carborane cage B(3) occupies two positions, B(3a) and B(3b). The phenyl group C(19a)−C(24a) bonded to S(2a) of molecule **1a** and the solvent molecule of **1b** are partly superimposed, as well as the solvent of **1a** and the phenyl group C(19b)−C(24b) of **1b**. The phenyl group connected to S(2) for both diastereomers were refined as rigid groups with isotropic displacement parameters. Also B(3b) and the solvent carbon of **1b** were refined with isotropic displacement parameters. The rest of the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of the carborane cage, except that of B(3B) and the bridging hydrogen atom of **1b**, were refined with fixed displacement parameters (U(H) equal to 1.2 × U of carrying atom), but the rest of the hydrogen atoms were placed at their calculated positions. The bridging hydrogen atom of **1b** was not positioned.

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Supporting Information Available: Tables giving experimental details of the X-ray crystallographic analysis, atomic positional and isotropic displacements, atomic anisotropic displacements, and interatomic distances and angles for **1** (28 pages). Ordering information is given on any current masthead page.

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