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Study of the Synergy in Electron-Rich Element/Carborane Compounds. Antipodal Boron Atom Labilization by Electron-Rich Elements. Conversion of $\{7\text{-SR-8-Me-7,8-}C_2B_9H_{10}\}^-$ into $\{7\text{-SR-8-Me-7,8-(5)-}C_2B_8H_{11}\}^-$

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The reaction of *nido*-$[NMe_4]\{7\text{-SMe-8-Me-7,8-}C_2B_9H_{10}\}$ with $[RuCl_2(PPh_3)_3]$ leads to the formation of $[RuCl\{7\text{-SMe-8-Me-7,8-(5)-}C_2B_8H_{11}\}(PPh_3)_2]$. The new C_2B_8 carborane ligand has a peculiar *arachno* structure that results from eliminating B(5) in the former $C_2B_9H_{12}^-$ *nido* precursor. The geometry is basketlike with a B–B handle. The reaction takes place for other $\{7\text{-SR-8-Me-7,8-}C_2B_9H_{10}\}^-$ ligands, R = Me, Et, iPr, nBu, and benzyl. The complex was characterized (R = Me) by an X-ray diffraction study. Dark red crystals were monoclinic, space group *Pn* (No. 7), with $Z = 2$, $a = 10.751(2)$ Å, $b = 14.369(3)$ Å, $c = 16.073(3)$ Å, $\beta = 95.83(1)°$, $V = 2470(1)$ Å^3, and $R_w(F_o) = 0.063$ for 3957 reflections having $I \geq 2.5\sigma(I)$.

The existence of two electron-rich elements directly connected to the carborane cage has permitted the finding of new chemical features, e.g., the easy partial degradation of *closo*-carborane derivatives by transition-metal complexes,[1] the finding of a B(3)–Rh σ interaction in $[NMe_4][RhCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_9\}]$[2] or the B(3)–H→Ru interaction in $[RuCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}\}(PPh_3)_2]$.[3] The chelating nature of the $S\text{-}C_c\text{-}C_c\text{-}S$ moiety, common in all these ligands, could induce the reader to believe that the properties of these dithiocarborane derivative ligands were solely due to this effect. To further explore this electron-rich element/carborane synergy we are studying the reactivity of monothiocarborane derivatives with square-planar and octahedral transition-metal ions. A great enhancement of the B–H hydride character was achieved with Pd(II), and $[PdCl\{7\text{-SMe-8-Me-11-}PPh_2\text{-7,8-}C_2B_9H_{10}\}(PPh_3)]$[4] was obtained. We have extended further these studies to Ru(II), and new results have been obtained which contribute to the better understanding of these electron-rich element/carborane containing ligands.

In this paper we report the synthesis of 1-mercapto-2-methyl-*o*-carborane and S-alkylated derivatives and the reactivity of these monothiocarborane derivatives toward Ru(II) complexes, the labilization and removal of B(5) by the antipodal electron-rich C–S fragment to produce 7,8-(5)-$C_2B_8H_{14}$ derivatives, and the molecular structure of $[RuCl\{7\text{-SMe-8-Me-7,8-(5)-}C_2B_8H_{11}\}(PPh_3)_2]$, in the text named $[RuCl(L_{Me8})(PPh_3)_2]$.

Results and Discussion

In order to study the monothio/carborane synergy, 1-mercapto-2-methyl-*o*-carborane and its S-alkylated derivatives have been produced. Scheme 1 illustrates the synthesis of these compounds. The ligands studied and the abbreviations used are schematically indicated in Table 1. The reaction of the *nido* ligands L_{R9} (R = Me, Et, iPr, nBu, and benzyl)[5] with $[RuCl_2(PPh_3)_2]$ in degassed ethanol results in the formation of yellow-red solids with the stoichiometry $[RuCl(L_{R8})(PPh_3)_2]$. See equation 1.

$$[NMe_4]\{L_{R9}\} + [RuCl_2(PPh_3)_2] \xrightarrow[EtOH/N_2]{} [RuCl(L_{R8})(PPh_3)_2] \quad (1)$$

These $[RuCl(L_{R8})(PPh_3)_2]$ complexes present as a general characteristic ^{11}B NMR resonances with a pattern 1:1:1:1:1:1:1:1 (some overlap is common), over a range of resonances between −11 and −38 ppm. As an example the $^{11}B\{^1H\}$ NMR spectrum of $[RuCl(L_{Et8})(PPh_3)_2]$ displays 8 peaks at (ppm) −37.2(1), −28.9(1), −22.6(1), {−20.6, −20}(2), −15.9(1), and {−13.0, −11.1}(2), which relates to a structure with 8 boron cluster atoms. The ^{31}P NMR spectrum shows two split resonances at 40.3 ($^2J_{P-P} = 24$ Hz) and 45.5 (broad) ppm in a 1:1 ratio, which suggests a cis disposition of the two P atoms. The ^1H NMR spectrum displays one resonance per group of equivalent atoms in the organic region, and broad absorptions are observed at −2.45 (quartet), −3.20, −14.7, and −15.2 ppm, which are assigned to B–H–B (−2.45 and −3.20) and B–H→Ru (−14.7 and −15.2 ppm). These data are in agreement with an octahedral Ru(II) ion bonded to a carborane moiety through two inequivalent B–H→Ru agostic bonds, and one sulfur atom. The L_{R8} ligand has to be tridentate in a facial manner by the sulfur atom and two BH groups, forming two B–H→Ru agostic bonds. This restricts the

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(5) L_{Me9} stands for $\{7\text{-SMe-8-Me-7,8-}C_2B_9H_{10}\}^-$ and emphasizes 9 boron atoms in the cluster and a methyl on the sulfur; L_{Me8} symbolizes 8 boron atoms and a methyl on the sulfur; L_{Et9} nine boron atoms and an ethyl on the sulfur, etc.

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Scheme 1

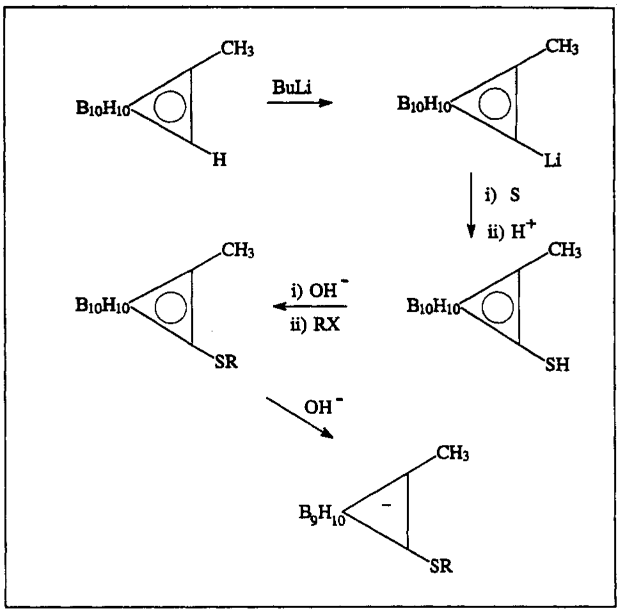

Table 1. *nido*-Carborane Ligands with Their Abbreviations and the Complexes Obtained

L_{H10}	$\{1\text{-SH-2-Me-1,2-}C_2B_{10}H_{10}\}$
L_{Me10}	$\{1\text{-SMe-2-Me-1,2-}C_2B_{10}H_{10}\}$
L_{Me9}	$\{7\text{-SMe-8-Me-7,8-}C_2B_9H_{10}\}^-$
L_{Et9}	$\{7\text{-SEt-8-Me-7,8-}C_2B_9H_{10}\}^-$
L_{iPr9}	$\{7\text{-S}(^i\text{Pr})\text{-8-Me-7,8-}C_2B_9H_{10}\}^-$
L_{Bu9}	$\{7\text{-S(nBu)-8-Me-7,8-}C_2B_9H_{10}\}^-$
L_{Bz9}	$\{7\text{-SBz-8-Me-7,8-}C_2B_9H_{10}\}^-$
L_{Me8}	$\{7\text{-SMe-8-Me-7,8-(5)-}C_2B_8H_{11}\}^-$
L_{Et8}	$\{7\text{-SEt-8-Me-7,8-(5)-}C_2B_8H_{11}\}^-$
L_{iPr8}	$\{7\text{-S}(^i\text{Pr})\text{-8-Me-7,8-(5)-}C_2B_8H_{11}\}^-$
L_{Bu8}	$\{7\text{-S(nBu)-8-Me-7,8-(5)-}C_2B_8H_{11}\}^-$
L_{Bz8}	$\{7\text{-SBz-8-Me-7,8-(5)-}C_2B_8H_{11}\}^-$

$[RuCl(L_{Me8})(PPh_3)_2]$
$[RuCl(L_{Et8})(PPh_3)_2]$
$[RuCl(L_{iPr8})(PPh_3)_2]$
$[RuCl(L_{Bu8})(PPh_3)_2]$
$[RuCl(L_{Bz8})(PPh_3)_2]$

phosphorus atom disposition in the complex to only a cis manner, as has been found by the ^{31}P NMR spectrum. The sixth position will be occupied by the counterion (Cl). This scheme should lead to three possible geometrical isomers. Figure 1 graphically shows the three possible isomers. According to the NMR data, only one of these isomers has been obtained in $[RuCl(L_{Et8})(PPh_3)_2]$, however the ^1H NMR spectra of the other $[RuCl(L_{R8})(PPh_3)_2]$ complexes indicate the coexistence of different species in solution. As an example, in the case of $[RuCl(L_{Me8})(PPh_3)_2]$, the ^1H NMR spectrum shows three peaks attributable to BC–CH$_3$ and two attributable to S–CH$_3$ while the ratio Ar–H:BC–CH$_3$:S–CH$_3$ remains constant at 30:3:3, as expected for a stoichiometrically pure compound. High field resonances at −2.45, −3.25, −14.2, and −15.25 ppm, which are indicative of B–H–B and B–H→M bonds[6] are found as in the $[RuCl(L_{Me8})(PPh_3)_2]$ example. The ^{31}P NMR spectrum is also in agreement with more than one species in solution and two sets of signals, two in each set, have been found. The coupling constants are of the order of 30 Hz, characteristic of a cis disposition of the phosphine ligands.[7] As suggested earlier, the different species found by ^1H and ^{31}P NMR were attributed to the different isomers generated by geometrical arrangements of the PPh$_3$ and Cl with regard to the coordinating sulfur atom and B–H groups of the carborane fragment.

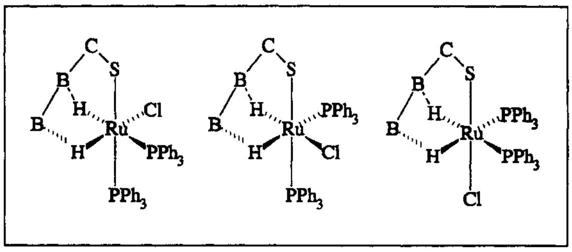

Figure 1. Schematic representation of the three possible isomers found in $[RuCl(L_{R8})(PPh_3)_2]$. The carborane moiety has been schematically represented as B–B–C–S, to provide an asymmetric view.

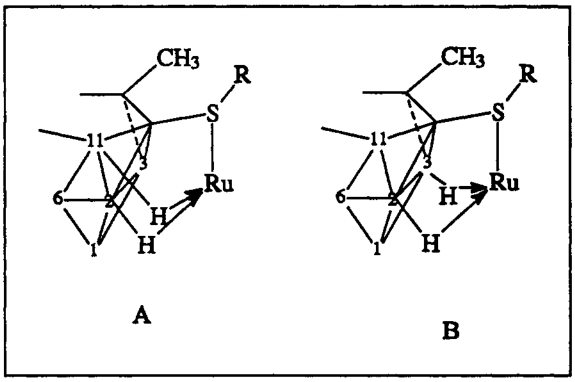

Figure 2. Proposed coordination motif of the carborane ligand to Ru. In (A), the B–H→Ru agostic interactions involve B(11) and B(2); in (B) boron atoms B(2) and B(3) are involved. Only a fragment of the cluster is represented in this figure.

These reactions have been extended to other L_{R9} ligands to get identical results (R = iPr, nBu, and benzyl).

Three main points arise from this discussion: (i) additional partial degradation has taken place in the 7,8-C$_2$B$_9$ *nido* cluster to get a 7,8-(*x*)-C$_2$B$_8$ *arachno* cluster, where (*x*) means the vacant position as a result of removing one boron atom from the initial *nido* cluster; (ii) the formation of two agostic B–H→Ru bonds occurs; (iii) there exist two types of B–H–B interactions. Point i is proven by the existence of eight resonances in the $^{11}B\{^1H\}$ NMR spectrum, all of intensity one. With regard to point ii concerning the formation of two B–H→Ru agostic bonds, it is proposed that either the pairs B(11)–H and B(2)–H or B(2)–H and B(3)–H interactions could be involved. However it is known[8] that in *exo-nido* species there is always present a B–H→M from an open face (C$_2$B$_3$) boron atom. As a result, the moieties B(11)–H and B(2)–H (form A in Figure 2) should be preferred to B(2)–H and B(3)–H (form B in Figure 2). Point iii deals with the existence of two types of B–**H**–B shown by the ^1H NMR spectrum. A detail of the negative side of the spectrum in the case of $[RuCl(L_{iPr8})(PPh_3)_2]$ is shown in Figure 3. The apparent quartet of doublets at −2.75 ppm is attributed to two new B–H–B bonds, in addition to the typical apical hydrogen

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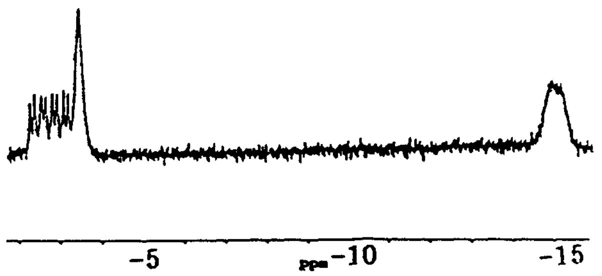

Figure 3. Detail of the negative side of the ^{1}H NMR spectrum of $[RuCl(L_{iPr8})(PPh_3)_2]$.

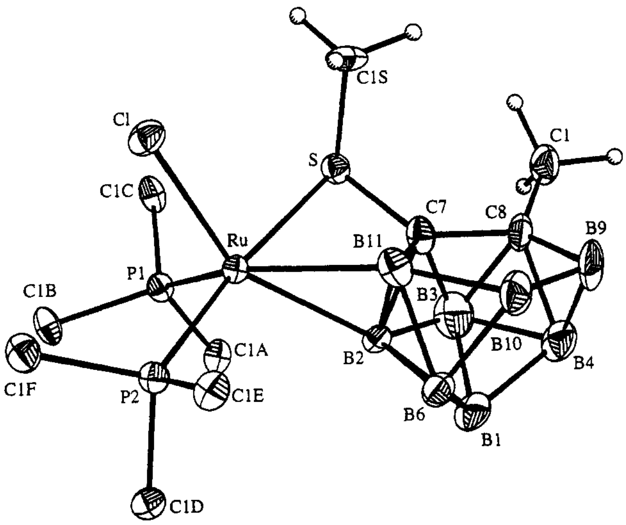

Figure 4. Molecular structure of $[RuCl(L_{Me8})(PPh_3)_2]$ (hydrogens omitted).

in the C_2B_3 open face of C_2B_9 *nido* derivatives which is assigned at -3.48 ppm. The fine structure observed in the ^{1}H NMR spectrum at -2.75 ppm has its counterpart in the ^{11}B NMR spectrum where fine structure is also found at -19.91, -20.65, and -36.58 ppm, tentatively assigned to B(6), B(4), and B(1), respectively. These boron atoms were initially surrounding B(5) in the initial C_2B_9 *nido* cluster.

To fully characterize the nature of the carborane moiety, which was expected to be a C_2B_8 cluster, and to know precisely which boron atom had been removed, an X-ray analysis of $[RuCl(L_{Me8})(PPh_3)_2]$ was undertaken. Figure 4 illustrates the molecular structure. Listings of atomic positional parameters, bond lengths, and bond angles appear in Tables 2-4. The analysis clearly establishes the *arachno* nature of the carborane fragment, which presents a geometry reminiscent of the initial *nido* cluster C_2B_9. The eliminated boron atom is the former B(5) in the initial *nido* cluster C_2B_9. On this basis we can describe this *arachno* compound as the initial *nido* cluster, C_2B_9, with B(5) removed, and it is written as 7,8-(5)-C_2B_8. Remarkably, B(5) is the boron atom "antipodal" to the $C_{cluster}$–S which shows the importance of this "antipodal" effect found in the ^{11}B NMR[9] spectra. Figure 5 shows a simplified view of the new basket-shaped carborane with the handle provided by the B(9)–B(10) link. This is relevant since an isomer of this carborane with a C–C handle was reported several years ago, as a dimetallacarborane.[10] In that case, both open faces were occupied by cobalt atoms, yielding, in total, a 12 atom cluster.

Table 2. Refined Atomic Coordinates (×10^4) with Esd's in Parentheses and Equivalent Isotropic Thermal Parameters (Å^2) for $[RuCl(L_{Me8})(PPh_3)_2]$

atom	*x/a*	*y/b*	*z/c*	B_{eq}
Ru	5825(0)	2198(0)	7644(0)	2.1
S	3625(2)	2649(2)	7633(2)	2.7
Cl	5520(2)	835(2)	8451(2)	3.4
P1	5383(2)	1558(2)	6334(2)	2.4
P2	8003(2)	1983(2)	7878(2)	2.4
C1	2201(10)	4638(8)	7906(9)	4.4
C2	2989(12)	2218(8)	8548(10)	4.6
B1	5833(13)	5031(8)	7358(10)	4.4
B2	5650(8)	3817(7)	7540(8)	2.5
B3	4366(19)	4516(14)	7178(12)	6.2
B4	4465(15)	5536(10)	7693(10)	4.5
B6	6621(11)	4475(8)	8278(8)	3.3
C7	4318(9)	3729(7)	7974(6)	2.9
C8	3582(10)	4656(7)	8040(8)	3.7
B9	4371(14)	5304(10)	8780(10)	4.9
B10	5759(14)	4647(9)	9171(10)	4.2
B11	5627(11)	3575(9)	8593(8)	3.3
C1A	5198(7)	2467(5)	5509(5)	3.1
C2A	4141(7)	3034(5)	5485(5)	6.4
C3A	3967(7)	3747(5)	4896(5)	7.3
C4A	4851(7)	3894(5)	4331(5)	6.4
C5A	5908(7)	3328(5)	4356(5)	8.0
C6A	6082(7)	2615(5)	4945(5)	5.8
C1B	6406(5)	675(4)	5928(5)	3.1
C2B	7609(5)	919(4)	5754(5)	3.7
C3B	8412(5)	241(4)	5492(5)	5.1
C4B	8013(5)	–681(4)	5405(5)	5.2
C5B	6811(5)	–925(4)	5579(5)	5.3
C6B	6007(5)	–247(4)	5840(5)	4.1
C1C	3887(5)	968(5)	6144(4)	3.3
C2C	3304(5)	546(5)	6783(4)	3.8
C3C	2248(5)	–8(5)	6590(4)	4.6
C4C	1776(5)	–140(5)	5758(4)	6.1
C5C	2359(5)	281(5)	5119(4)	5.5
C6C	3414(5)	835(5)	5312(4)	5.1
C1D	8675(6)	810(4)	8059(5)	3.3
C2D	9852(6)	712(4)	8503(5)	3.7
C3D	10412(6)	–164(4)	8585(5)	4.2
C4D	9795(6)	–941(4)	8224(5)	5.7
C5D	8618(6)	–843(4)	7781(5)	5.2
C6D	8058(6)	32(4)	7698(5)	3.9
C1E	8975(5)	2498(5)	7108(4)	2.7
C2E	8656(5)	3371(5)	6772(4)	4.1
C3E	9358(5)	3765(5)	6179(4)	4.8
C4E	10380(5)	3286(5)	5922(4)	4.0
C5E	10700(5)	2412(5)	6257(4)	4.6
C6E	9997(5)	2018(5)	6850(4)	3.5
C1F	8634(6)	2517(5)	8865(3)	2.9
C2F	8143(6)	2214(5)	9589(3)	3.6
C3F	8627(6)	2556(5)	10368(3)	4.9
C4F	9602(6)	3201(5)	10422(3)	5.8
C5F	10093(6)	3503(5)	9699(3)	5.3
C6F	9609(6)	3161(5)	8920(3)	3.6
C20	9294(50)	–3154(43)	6246(37)	14.1
C21	9005(48)	–3663(38)	7085(34)	14.1
C22	132(53)	–2356(41)	5787(36)	14.1
O23	8431(30)	–3355(25)	5598(21)	14.1
O1	5024(19)	–1689(15)	7551(13)	14.6

In $[RuCl(L_{Me8})(PPh_3)_2]$ the new open face is defined by the boron atoms B(1), B(4), B(9), B(10), and B(6). This B_5 face is best described as having two hydrogen bridges connecting B(9)–B(4) and B(6)–B(10), keeping the face

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Table 3. Selected Interatomic Distances (Å) with Esd's in Parentheses for $[RuCl(L_{Me8})(PPh_3)_2]$

S–Ru	2.450(2)	B3–B2	1.76(2)
Cl–Ru	2.391(2)	B6–B2	1.77(1)
P1–Ru	2.303(2)	B11–B2	1.73(2)
P2–Ru	2.354(2)	B4–B3	1.68(2)
B2–Ru	2.34(1)	B9–B4	1.79(2)
B11–Ru	2.52(1)	B10–B6	1.80(2)
C2–S	1.79(1)	B11–B6	1.78(2)
C7–S	1.78(1)	B2–C7	1.66(1)
C1A–P1	1.859(6)	B3–C7	1.71(2)
C1B–P1	1.841(5)	B11–C7	1.65(1)
C1C–P1	1.817(5)	C1–C8	1.48(1)
C1D–P2	1.846(5)	C7–C8	1.56(1)
C1E–P2	1.853(5)	B3–C8	1.71(2)
C1F–P2	1.829(5)	B4–C8	1.71(2)
B2–B1	1.78(1)	B9–C8	1.67(2)
B3–B1	1.74(2)	B10–B9	1.82(2)
B4–B1	1.77(2)	B11–B10	1.80(2)
B6–B1	1.81(2)		

neutral, which explains the ^1H NMR signal at −2.45 ppm. The distances and angles within the cluster are similar to other values found in the literature for *closo* and *nido* carboranes.[11]

The Ru atom is octahedrally coordinated by the thioether group, two triphenylphosphine ligands, one chlorine atom, and two hydrogen atoms from the B–H groups, which correspond to B(11)–H and B(2)–H, as had been discussed earlier. These last hydrogen atoms could not be located by X-ray diffraction, but the B–Ru distances (2.34, 2.52 Å) agree well with agostic bonds.[12] The carborane is a facially tricoordinating ligand and, consequently, the other three ligands have to occupy an opposite face. The chlorine is cis with regard to the thioether group.

This structure is in agreement with the spectroscopic studies, and with the existence of other geometrical arrangements of the PPh_3 and Cl, as indicated before.

As a conclusion three C_2B_8 *arachno* structures are known: The expected[13] "one open face" found in $[PPh_3AgC_2B_8H_{11}]_2$[14] and the two "basketlike" types with a C–C handle in $[(C_2B_9H_{11})Co(C_2B_8H_{10})Co(C_2B_9H_{11})]$[10] and B–B handle in $[RuCl(L_{Me8})(PPh_3)_2]$ presented in this article. In addition, B(11)–H→Ru and B(2)–H→Ru have been found for the first time in C_2B_9 derivatives, even though in the present case it is the *arachno* derivative.

Experimental Section

Instrumentation. Elemental analyses were performed in our analytical laboratory using a Perkin-Elmer 240-B microanalyzer. IR spectra were obtained with KBr pellets on a Nicolet 710-FT spectrophotometer. The ^1H NMR and ^{11}B NMR spectra were obtained on a Bruker AM 400WB or AC 400 instrument.

Materials. Before use, 1-methyl-*o*-carborane (Dexsil Chemical Corp.) was sublimed under high vacuum. A 1.6 M solution of *n*-butyllithium in hexane from Fluka was used as purchased. $[RuCl_2(PPh_3)_3]$ was prepared following literature procedures.[15]

Table 4. Selected Angles (deg) with Esd's in Parentheses for $[RuCl(L_{Me8})(PPh_3)_2]$

Cl–Ru–S	92.0(1)	C1F–P2–Ru	111.0(3)
P1–Ru–S	89.4(1)	C1F–P2–C1D	98.1(3)
P1–Ru–Cl	98.1(1)	C1F–P2–C1E	103.2(3)
P2–Ru–S	168.4(1)	B3–B1–B2	59.9(8)
P2–Ru–Cl	89.7(1)	B4–B1–B2	104.0(9)
P2–Ru–P1	101.7(1)	B4–B1–B3	57.2(9)
B2–Ru–S	70.5(2)	B6–B1–B2	59.0(6)
B2–Ru–Cl	147.1(3)	B6–B1–B3	106.8(10)
B2–Ru–P1	109.0(3)	B6–B1–B4	105.5(11)
B2–Ru–P2	102.3(2)	C7–B2–Ru	87.8(5)
B11–Ru–S	69.9(3)	B1–B2–Ru	167.3(8)
B11–Ru–Cl	106.9(3)	B1–B2–C7	104.9(8)
B11–Ru–P1	147.7(3)	B3–B2–Ru	130.3(8)
B11–Ru–P2	98.6(3)	B3–B2–C7	60.0(8)
B11–Ru–B2	41.5(4)	B3–B2–B1	58.9(8)
C2–S–Ru	110.5(5)	B6–B2–Ru	116.5(6)
C7–S–Ru	81.7(3)	B6–B2–C7	103.5(8)
C7–S–C2	103.4(6)	B6–B2–B1	61.3(7)
C1A–P1–Ru	111.6(3)	B6–B2–B3	107.8(9)
C1B–P1–Ru	121.6(2)	B11–B2–Ru	74.9(6)
C1B–P1–C1A	104.8(3)	B11–B2–C7	58.3(6)
C1C–P1–Ru	115.9(2)	B11–B2–B1	111.7(9)
C1C–P1–C1A	100.3(4)	B11–B2–B3	110.5(10)
C1C–P1–C1B	99.8(3)	B11–B2–B6	61.2(7)
C1D–P2–Ru	120.8(2)	C7–B3–C8	54.3(8)
C1E–P2–Ru	117.4(2)	B1–B3–C8	109.2(12)
C1E–P2–C1D	103.4(3)	B1–B3–C7	104.6(11)
		B2–B3–C8	103.6(12)
C7–C8–C1	119.0(9)	B2–B3–C7	57.1(8)
B3–C8–C1	116.8(11)	B2–B3–B1	61.3(8)
B3–C8–C7	63.1(9)	B4–B3–C8	60.6 (9)
B4–C8–C1	123.3(10)	B4–B3–C7	102.3(12)
B4–C8–C7	107.9(8)	B4–B3–B1	62.3(10)
B4–C8–B3	59.1(9)	B4–B3–B2	109.1(12)
B9–C8–C1	122.9(9)	B1–B4–C8	107.5(9)
B9–C8–C7	107.4(8)	B3–B4–C8	60.3(9)
B9–C8–B3	112.8(11)	B3–B4–B1	60.4(10)
B9–C8–B4	64.0(9)	B9–B4–C8	57.0(7)
B4–B9–C8	59.0(8)	B9–B4–B1	110.5(10)
B10–B9–C8	107.2(8)	B9–B4–B3	108.1(11)
B10–B9–B4	107.9(10)	B2–B6–B1	59.6(6)
B9–B10–B6	105.4(10)	B10–B6–B1	110.7(9)
B11–B10–B6	59.4(7)	B10–B6–B2	106.9(8)
B11–B10–B9	104.3(9)	B11–B6–B1	107.8(8)
C7–B11–Ru	81.9(6)	B11–B6–B2	58.2(6)
B2–B11–Ru	63.6(5)	B11–B6–B10	60.1(7)
B2–B11–C7	58.7(6)	C8–C7–S	124.4(7)
B6–B11–Ru	107.9(7)	B2–C7–S	106.8(6)
B6–B11–C7	103.4(8)	B2–C7–C8	115.4(8)
B6–B11–B2	60.6(7)	B3–C7–S	112.8(8)
B10–B11–Ru	168.2(8)	B3–C7–C8	62.6(8)
B10–B11–C7	102.4(8)	B3–C7–B2	62.8(8)
B10–B11–B2	109.0(9)	B11–C7–S	111.9 (7)
B10–B11–B6	60.5(7)	B11–C7–C8	118.7(8)
		B11–C7–B2	62.9(6)
		B11–C7–B3	116.7(10)

Synthesis of 1-Mercapto-2-methyl-*o*-carborane (L_{H10}). To a three-necked round bottom flask (250 mL) fitted with a dinitrogen inlet/outlet, containing deoxygenated dry THF (40 mL), was added 1-methyl-*o*-carborane (2 g, 12.6 mmol). The mixture was cooled (ice–water) during the addition of *n*-butyllithium (8 mL, 12.8 mmol). After stirring for 30 min at the ice–water temperature, the mixture was allowed to stir at room temperature for 12 h and again cooled at 0 °C before adding sulfur (0.4 g, 12.6 mmol) in a period of 2 h. The ice bath was removed, and the mixture was stirred for an additional 4 h at room temperature, before pumping off the THF. Diethyl ether (40 mL) was added, and the system was cooled at 0 °C, then 1 mol L^{-1} HCl (30 mL) was added. Stirring was continued for 10 min, before the two layers were separated. The diethyl ether extract was dried and evaporated under vacuum until 4 mL. This solution was chromatographed on alumina, using hexane as eluent. The evaporation of the solvent yielded an off-white powder (1.7 g, 70%). Anal. Calcd for $C_3H_{14}B_{10}S$: C, 19.5; H, 7.58. Found: C, 19.99; H, 7.70. FTIR (KBr): ν [cm^{-1}] = 2595 (B–H). ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.16 (s, 3, CH_3), 3.61 (s, 1, S–H). ^{11}B NMR (128 MHz, THF, 25 °C,

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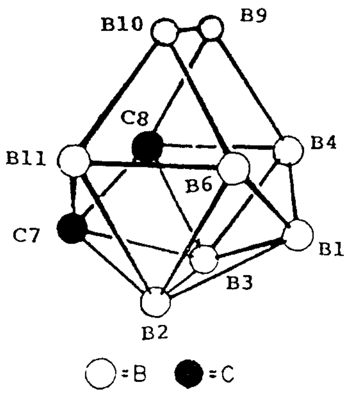

Figure 5. Schematic view of the basketlike *arachno* carborane 7,8-(5)-$C_2B_8H_{13}^-$ (hydrogens omitted). Notice the B–B handle connecting the C_2B_3 and B_5 open faces.

$BF_3{\cdot}Et_2O$): $\delta = -9.96$ (d, ^1J(B,H) = 147.2 Hz, 2B), −9.42 (d, ^1J(B,H) = 177.7 Hz, 4B), −8.06 (d, ^1J(B,H) = 70.7 Hz, 2B), −4.63 (d, ^1J(B,H) = 70.7 Hz, 2B).

Synthesis of 1-(Methylthio)-2-methyl-*o*-carborane (L_{Me10}). To a two-necked round bottom flask (100 mL) fitted with a dinitrogen inlet/outlet, containing deoxygenated ethanol (40 mL), was added KOH (0.1 g, 1.78 mmol). After stirring for 1 h, 1-mercapto-2-methyl-*o*-carborane (0.3 g, 1.57 mmol) and Me_2SO_4 (0.3 g, 2.38 mmol) were added to the solution. The mixture was allowed to be at room temperature for 30 min and at reflux for 2 h. Once the mixture cooled, the solvent was evaporated under vacuum. To the residue were added diethyl ether (30 mL) and aqueous 0.5 mol L^{-1} KOH (20 mL). The organic extract was separated, dried, and evaporated under vacuum. The semisolid residue was sublimed (0.01 Torr) to yield a white solid (0.19 g, 60%). Anal. Calcd for $C_4H_{16}B_{10}S$: C, 23.53; H, 7.58. Found: C, 23.20; H, 8.10. FTIR (KBr): ν [cm^{-1}] = 2591 (B–H). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.13 (s, 3, $\mathrm{C{-}C\mathbf{H}_3}$), 2.45 (s, 3, $\mathrm{S{-}C\mathbf{H}_3}$).

Synthesis of [NMe_4]{L_{Me9}}. To a two-necked round bottom flask (100 mL) fitted with a dinitrogen inlet/outlet, containing deoxygenated ethanol (30 mL), was added KOH (0.5 g, 9 mmol). After stirring for 1 h, 1-(methylthio)-2-methyl-*o*-carborane (0.5 g, 2.9 mmol) was added to the solution. The mixture was refluxed for 2 h. Once the mixture cooled, the solvent was evaporated under vacuum. To the residue was added water (20 mL). Turbidity was filtered. While N_2 was bubbled through the solution, an excess of NMe_4Cl in 5 mL of water was added and a solid precipitated. After the suspension stood for 15 min, the solid was collected by filtration, washed twice with water (5 mL) and recrystallized with ethanol/water (1:1), to get white crystals (0.69 g; 98%). Anal. Calcd for $C_8H_{28}B_9NS$: C, 35.93; H, 10.47. Found: C, 36.48; H, 11.07; N, 5.26. FTIR (KBr): ν [cm^{-1}] = 2526 (B–H). ^{1}H NMR (400 MHz, CD_3COCD_3, 25 °C, TMS): δ = −2.16 (b, 1, BHB); 1.5 (s, 3, $\mathrm{C{-}C\mathbf{H}_3}$), 2.11 (s, 3, $\mathrm{S{-}C\mathbf{H}_3}$), 3.40 (s, 12, $\mathrm{N(C\mathbf{H}_3)_4}$). ^{11}B NMR (128 MHz, CH_3COCH_3, 25 °C, $BF_3{\cdot}Et_2O$): δ = −35.54 (d, ^1J(B,H) = 136.9 Hz, 1B), −33.58 (d, ^1J(B,H) = 108.9 Hz, 1B), −18.29 (d, ^1J(B,H) = 144.9 Hz, 2B), −16.22 (d, ^1J(B,H) = 149.1 Hz, 1B), −15.21 (d, ^1J(B,H) = 130.2 Hz, 1B), −10.46 (d, ^1J(B,H) = 161.4 Hz, 1B), −8.08 (d, ^1J(B,H) = 118.6 Hz, 1B), −7.29 (d, ^1J(B,H) = 116.9 Hz, 1B).

Synthesis of [NMe_4]{L_{Et9}}. To a two-necked round bottom flask (100 mL) fitted with a dinitrogen inlet/outlet, containing deoxygenated ethanol (25 mL) was added KOH (0.088 g, 1.56 mmol). After stirring for 1 h, 1-mercapto-2-methyl-*o*-carborane (0.3 g, 1.57 mmol) and ethyl bromide (0.33 g, 2.38 mmol) were added to the solution. The mixture was refluxed for 2 h. Once the mixture cooled, the solvent was evaporated under vacuum. To the residue were added diethyl ether (30 mL) and aqueous 2 mol L^{-1} KOH (20 mL). The organic extract was separated. The aqueous layer was washed twice with ethyl ether (10 mL). The organic layers were assembled, and the solvent was pumped off. The residue was added to a two-necked round bottom flask (100 mL) fitted with a dinitrogen inlet/outlet, containing deoxygenated ethanol (30 mL) and KOH (0.3 g, 5.34 mmol). The mixture was refluxed for 6 h and allowed to cool to room temperature. The solvent was evaporated under vacuum. To the residue was added water (15 mL). Turbidity was filtered. While N_2 was bubbled through the solution, an excess of NMe_4Cl in 5 mL of water was added and a solid precipitated. After the suspension stood for 15 min, the solid was collected by filtration, washed twice with water (5 mL), and recrystallized with ethanol/water (1:1), to get white crystals (0.36 g; 80%). Anal. Calcd for $C_9H_{30}B_9NS$: C, 38.4; H, 10.66; N, 4.97. Found: C, 37.84; H, 10.66; N, 4.91. FTIR (KBr): ν [cm^{-1}] = 2526 (B–H). ^{1}H NMR (400 MHz, CD_3COCD_3, 25 °C, TMS): δ = −2.45 (b, 1, BHB), 1.16 (t, 3, $\mathrm{{-}C\mathbf{H}_3}$), 1.52 (s, 3, $\mathrm{C{-}C\mathbf{H}_3}$), 2.56 (b, 1, $\mathrm{S{-}C\mathbf{H}_2}$), 2.79 (b, 1, $\mathrm{S{-}C\mathbf{H}_2}$), 3.43 (s, 12, $\mathrm{N(C\mathbf{H}_3)_4}$). ^{11}B NMR (128 MHz, CH_3COCH_3, 25 °C, $BF_3{\cdot}Et_2O$): δ = −35.18 (d, ^1J(B,H) = 138.9 Hz, 1B), −33.05 (d, ^1J(B,H) = 123.6 Hz, 1B), −17.01 (d, ^1J(B,H) = 167.9 Hz, 2B), −15.58 (d, ^1J(B,H) = 164.1 Hz, 2B), −10.07 (d, ^1J(B,H) = 160.3 Hz, 1B), −7.41 (d, ^1J(B,H) = 137.6 Hz, 2B).

Synthesis of [NMe_4]{L_{Bu9}}. The synthesis was done as for [NMe_4]{L_{Et9}}. The tosylate $TsO(CH_2)_3CH_3$ was used as the alkylating agent. Yield: 85%. Anal. Calcd for $C_{11}H_{34}B_9NS$: C, 42.69; H, 10.99; N, 4.53. Found: C, 42.29; H, 11.14; N, 4.29. FTIR (KBr): ν [cm^{-1}] = 2516 (B–H). ^{1}H NMR (400 MHz, CD_3COCD_3, 25 °C, TMS): δ = −2.45 (b, 1, BHB), 0.91 (t, 3, $\mathrm{{-}C\mathbf{H}_3}$), 1.39 (m, 2, $\mathrm{{-}C\mathbf{H}_2{-}CH_3}$), 1.50 (m, 2, $\mathrm{{-}C\mathbf{H}_2{-}CH_2}$), 1.53 (s, 3, $\mathrm{C{-}C\mathbf{H}_3}$), 2.59 and 2.78 (m, m, 1, 1, $\mathrm{S{-}C\mathbf{H}_2}$), 3.44 (s, 12, $\mathrm{N(C\mathbf{H}_3)_4}$). ^{11}B NMR (128 MHz, CH_3COCH_3, 25 °C, $BF_3{\cdot}Et_2O$): δ = −35.48 (d, ^1J(B,H) = 139.4 Hz, 1B), −33.45 (d, ^1J(B,H) = 108.4 Hz, 1B), −17.69 (d, ^1J(B,H) = 152.0 Hz, 2B), −15.81 (d, ^1J(B,H) = 139.1 Hz, 2B), −10.47 (d, ^1J(B,H) = 161.0 Hz, 1B), −7.66 (d, ^1J(B,H) = 136.1 Hz, 2B).

Synthesis of [NMe_4]{L_{iPr9}}. The synthesis was done as for [NMe_4]{L_{Et9}}. The tosylate $TsO(CH)(CH_3)_2$ was used as the alkylating agent. Yield: 60%. Anal. Calcd for $C_{10}H_{32}B_9NS{\cdot}H_2O$: C, 38.31; H, 10.85; N, 4.47. Found: C, 37.72; H, 10.51; N, 4.50. FTIR (KBr): ν [cm^{-1}] = 2525 (B–H). ^{1}H NMR (400 MHz, CD_3COCD_3, 25 °C, TMS): δ = −2.4 (b, 1, BHB), 1.12 (d, 3, $\mathrm{{-}C\mathbf{H}_3}$), 1.24 (d, 3, $\mathrm{{-}C\mathbf{H}_3}$), 1.52 (s, 3, $\mathrm{BCC\mathbf{H}_3}$), 3.27 (m, 1, $\mathrm{S{-}C\mathbf{H}{-}}$), 3.43 (s, 12, $\mathrm{N(C\mathbf{H}_3)_4}$).

Synthesis of [NMe_4]{L_{Bz9}}. The synthesis was done as for [NMe_4]{L_{Et9}}. Benzyl bromide was used as the alkylating agent. Yield: 40%. Anal. Calcd for $C_{14}H_{32}B_9NS{\cdot}H_2O$: C, 46.51; H, 9.41; N, 3.87. Found: C, 46.74; H, 9.1; N, 3.50. FTIR (KBr): ν [cm^{-1}] = 2520 (B–H). ^{1}H NMR (400 MHz, CD_3COCD_3, 25 °C, TMS): δ = −2.45 (b, 1, BHB), 1.37 (s, 3, $\mathrm{BC{-}C\mathbf{H}_3}$), 3.44 (s, 12, $\mathrm{N(C\mathbf{H}_3)_4}$), 3.85 (d, 1, $\mathrm{S{-}C\mathbf{H}}$), 3.98 (d, 1, $\mathrm{S{-}C\mathbf{H}}$), 7.17–7.35 (m, 5, $\mathrm{Ar{-}\mathbf{H}}$).

Synthesis of [$RuCl(L_{Me8})(PPh_3)_2$]. To 25 mL of degassed ethanol were added 40 mg (0.149 mmol) of [NMe_4]{L_{Me9}} and 120 mg (0.098 mmol) of [$RuCl_2(PPh_3)_3$]. The mixture was put to reflux, and complete dissolution of the reagents was observed. In approximate 15 min a yellow solid began to separate. The reflux was continued for an additional 2 h, and the solid was filtered warm and washed with cold ethanol (2 mL) and ethyl ether (5 mL). Yield: 70 mg (65%). Dark red crystals were obtained by slow evaporation of the product in a mixture chloroform:acetone (1:1). Anal. Calcd for $C_{40}H_{47}B_8ClP_2RuS{\cdot}H_2O$: C, 55.7; H, 5.68; S, 3.71. Found: C, 55.76; H, 5.70; S, 3.67. FTIR (KBr): ν [cm^{-1}] = 2550 (B–H). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = −15.25, −14.2 (b, b, 1, 1, $\mathrm{B{-}\mathbf{H}{\rightarrow}Ru}$), −3.25 (b, 1, $\mathrm{B{-}\mathbf{H}{-}B}$), −2.45 (m, 2, $\mathrm{B{-}\mathbf{H}{-}B}$), 1.25, 1.44, 1.47 (s, 3, $\mathrm{BC{-}C\mathbf{H}_3}$), 2.11, 2.51 (s, 3, $\mathrm{S{-}C\mathbf{H}_3}$), 7.10–7.58 (m, 30, $\mathrm{Ar{-}\mathbf{H}}$). ^{11}B NMR (128 MHz, CH_3COCH_3, 25 °C, $BF_3{\cdot}Et_2O$): δ = −38.2 (d, ^1J(B,H) = 134.9 Hz, 1B), −28.9 (1B), {−23.4, −22.5, −21} (3B), {−15.6, −13.9} (3B). ^{31}P NMR (162 MHz, CH_2Cl_2, 25 °C, H_3PO_4): δ = 38.44 (d, ^1J(P,H) = 29.15 Hz, relative area = 1), 42.23 (d, ^1J(P,H) = 20.76 Hz, relative area = 0.27), 45.17 (broad, relative area = 1), 51.16 (broad, relative area = 0.27).

Synthesis of [$RuCl(L_{Et8})(PPh_3)_2$]. The synthesis was done as for [$RuCl(L_{Me8})(PPh_3)_2$] starting from [NMe_4]{L_{Et9}}. Yield: 60%. Anal. Calcd for $C_{41}H_{49}B_8ClP_2RuS{\cdot}2H_2O$: C, 55.0; H, 5.71;

Table 5. Crystallographic Data for [RuCl(L_{Me8})(PPh_3)$_2$]

chem formula	$C_{40}H_{47}B_8ClP_2RuS\cdot{}^3/_4(CH_3)_2CO\cdot H_2O$
fw	888.9
a (Å)	10.751(2)
b (Å)	14.369(3)
c (Å)	16.073(3)
β (deg)	95.83(1)
V (Å^3)	2470(1)
Z	2
space group	*Pn* (No. 7)
T (K)	293
λ (Å)	0.71069
ρ_{calcd} (g cm^{-3})	1.19
μ (cm^{-1})	13.3
transm coeff	0.95–1.00
$R(F_o)$	0.06
$R_w(F_o)$	0.063

S, 3.57. Found: C, 54.96; H, 5.93; S, 3.20. FTIR (KBr): ν [cm^{-1}] = 2562 (B–H). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = −15.2, −14.7 (broad, 1, B–**H**→Ru), −3.20 (broad, 1, B–**H**–B), −2.45 (m, 2, B–**H**–B), 1.32 (t, 3, CH_2–C**H**$_3$), 1.49 (s, 3, BC–C**H**$_3$), 2.85, 3.50 (m, m, 1, 1, S–C**H**$_2$–CH_3), 7.20–7.52 (m, 30, Ar–**H**). ^{11}B NMR (128 MHz, CH_3COCH_3, 25 °C, $BF_3\cdot Et_2O$): δ = −37.19 (d, ^1J(B,H) = 143.0 Hz, 1B), −28.9 (1B), −22.6 (d, ^1J(B,H) = 80.8 Hz, 1B), −20.6 (d, ^1J(B,H) = 114.8 Hz, 1B), −19.9 (d, ^1J(B,H) = 108.0 Hz, 1B), −15.9 (1B), −13.0 (1B), −11.2 (1B). ^{31}P NMR (162 MHz, CH_2Cl_2, 25 °C, H_3PO_4): δ = 40.34 (d, ^1J(P,H) = 23.7 Hz, 1), 45.5 (broad, 1).

Synthesis of [RuCl(L_{iPr8})(PPh_3)$_2$]. The synthesis was done as for [RuCl(L_{Me8})(PPh_3)$_2$] starting from [NMe_4]{L_{iPr9}}. Yield: 68%. Anal. Calcd (of the recrystallized compound from $CHCl_3$: acetone (1:1)) for $C_{42}H_{51}B_8ClP_2RuS\cdot CHCl_3$: C, 52.0; H, 5.24; S, 3.22. Found: C, 52.29; H, 5.5; S, 3.02. FTIR (KBr): ν [cm^{-1}] = 2585, 2554, 2515 (B–H). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = −15.2, −14.9 (b, b, 1, 1, B–**H**→Ru), −3.48 (b, 1, B–**H**–B), −2.75 (m, 2, B–**H**–B), 0.96, 1.13 (d, d, 6, C**H**$_3$), 1.35 (s, 3, BC–C**H**$_3$), 3.76 (m, 1, S–C**H**–), 6.97–7.27 (m, 30, Ar–**H**). ^{11}B NMR (128 MHz, CH_3COCH_3, 25 °C, $BF_3\cdot Et_2O$): δ = −36.6 (d, ^1J(B,H) = 137.4 Hz, 1B), −28.9 (1B), −22.2 (d, ^1J(B,H) = 92.4 Hz, 1B), −20.6 (d, ^1J(B,H) = 116.8 Hz, 1B), −19.9 (d, ^1J(B,H) = 113.0 Hz, 1B), −15.7 (1B), −13.0 (1B), −10.3 (1B). ^{31}P NMR (162 MHz, CH_2Cl_2, 25 °C, H_3PO_4): δ = 40.3 (d, ^1J(P,H) = 24 Hz, 1), 45.4 (broad, 1).

Synthesis of [RuCl(L_{Bu8})(PPh_3)$_2$]. The synthesis was done as for [RuCl(L_{Me8})(PPh_3)$_2$] starting from [NMe_4]{L_{Bu9}}. Yield: 65%. Anal. Calcd for $C_{43}H_{53}B_8ClP_2RuS\cdot H_2O$: C, 57.1; H, 6.08; S, 3.53. Found: C, 56.7; H, 6.01; S, 3.29. FTIR (KBr): ν [cm^{-1}] = 2560, 2546, 2525 (B–H). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = −15.1 (b, 2, B–**H**→Ru), −3.24 (b, 1, B–**H**–B), −2.57 (m, 2, B–**H**–B), 0.94 (t, 3, C**H**$_3$), 1.38 (t, 2, C**H**$_2$–CH_3), 1.48 (s, 3, BC–C**H**$_3$), 1.56 (t, 2, –C**H**$_2$), 2.73, 3.48 (m, m, 1, 1, S–C**H**$_2$–), 7.12–7.47 (m, 30, Ar–**H**). ^{11}B NMR (128 MHz, CH_3COCH_3, 25 °C, $BF_3\cdot Et_2O$): δ = −37.5 (1B), −29.1 (1B), −22.5 (1B), −20.6 (1B), −20.4 (1B), {−15.3, −12.1} (3B). ^{31}P NMR (162 MHz, CH_2Cl_2, 25 °C, H_3PO_4): δ = 38.4 (d, ^1J(P,H) = 30 Hz, relative area = 1), 41.8 (b, relative area = 0.15), 44.6 (b, relative area = 1), 51.96 (b, relative area = 0.15).

Synthesis of [RuCl(L_{Bz8})(PPh_3)$_2$]. The synthesis was done as for [RuCl(L_{Me8})(PPh_3)$_2$] starting from [NMe_4]{L_{Bz9}}. Yield: 55%. Anal. Calcd for $C_{46}H_{51}B_8ClP_2RuS\cdot H_2O$: C, 58.8; H, 5.65; S, 3.41. Found: C, 58.8; H, 5.98; S, 2.83. FTIR (KBr): ν [cm^{-1}] = 2550, 2535, 2518 (B–H). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = −15.2 (b, 2, B–**H**→Ru), −3.28 (b, 1, B–**H**–B), −2.33 (m, 2, B–**H**–B), 0.62 (s, 3, BC–C**H**$_3$), 4.11, 4.49 (d, d, 1, 1, S–C**H**$_2$), 7.08–7.67 (m, 35, Ar–**H**). ^{11}B NMR (128 MHz, CH_3COCH_3, 25 °C, $BF_3\cdot Et_2O$): δ = −38.5 (d, ^1J(B,H) = 126.1 Hz, 1B), −29.7 (1B), {−21.9, −21.5} (3B), { −16.9, −14.1, −12.0} (3B).

X-ray Crystallographic Study of [RuCl(L_{Me8})(PPh_3)$_2$]. $C_{40}H_{47}B_8ClP_2RuS\cdot{}^3/_4(CH_3)_2CO\cdot H_2O$. The unit cell parameters were determined by least-squares refinement from 25 carefully centered reflections (17° < θ < 25°) measured at ambient temperature on an Enraf/Nonius CAD4 diffractometer. The compound crystallizes in the monoclinic crystal system and systematic absences indicated space group *Pn* (No. 7). Crystal data and details of data collection are presented in Table 5. The data were corrected for Lorentz and polarization effects. An absorption correction was applied (program DIFABS).

Intensity variation of three standard reflections was of ≈1.1% during the data collection. A total of 4317 unique reflections with $\theta \leq 25°$ were collected, from which 3957 were observed ($I \geq 2.5\sigma(I)$).

The structure was solved with MULTAN[16] and refined with SHELX-76[17] to $R(F_o)$ = 0.060, $R_w(F_o)$ = 0.063. The hydrogen atoms were placed at geometrically calculated positions, and the phenyl rings were refined as rigid bodies with atomic anisotropic temperature factors (refined in blocks due to the large number of parameters involved). The number of parameters refined was 489. The *S* value was 1.86, and *R* was 6% (*wR* = 6.3%) where $w = 1.00/(\sigma^2(F) + 0.0130F^2)$. The greatest residuals in the final difference Fourier map were $\Delta\rho_{max}$ = 1.01 (e/Å^3), and $\Delta\rho_{min}$ = 0.55 (e/Å^3).

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Supplementary Material Available: Tables of crystal data, bond distances and angles, and thermal parameters (9 pages). Ordering information is given on any current masthead page.

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