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Articles

Syntheses and Structural Characterizations of *hypho*- and *arachno*-Metalladithiaborane Clusters

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The *hypho*-$S_2B_6H_9^-$ anion has been employed to generate a series of new *arachno*- and *hypho*-metalladithiaborane clusters. Depending upon the conditions, the reaction of *hypho*-$S_2B_6H_9^-$ with $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ yields either *hypho*-1,2,5-$(\eta^6\text{-}C_6Me_6)RuClS_2B_6H_9$ (I) or *arachno*-7,6,8-$(\eta^6\text{-}C_6Me_6)RuS_2B_6H_8$ (II). II may also be produced directly from I by reaction of I with proton sponge. Single-crystal X-ray studies of I and II have confirmed that these nine-vertex clusters adopt structures consistent with their respective 26- and 24-skeletal-electron counts in which the ruthenium atom is bound to the dithiaborane cage in either an η^2- or η^4-fashion. The ruthenadithiaborane cage framework observed for I can be derived from an icosahedron by removal of three vertices, while that of II is based on an octadecahedron missing two vertices. Reactions of *hypho*-$S_2B_6H_9^-$ with *CpCo(CO)I_2 or CpCo(CO)I_2 gave the complexes *hypho*-1,2,5-*CpCo(I)$S_2B_6H_9$ (III), *arachno*-7,6,8-*CpCo$S_2B_6H_8$ (IV), and *arachno*-7,6,8-CpCo$S_2B_6H_8$ (V). Reaction of the anion with (dppe)$NiCl_2$ gave the complex *arachno*-7,6,8-(dppe)Ni$S_2B_6H_8$ (VI), the structure of which was shown to be similar to that of II by means of a single-crystal X-ray determination. The complex *arachno*-7,6,8-$(PMe_3)_2Rh(H)S_2B_6H_8$ (VII) was obtained by the reaction of the anion with $(PMe_3)_2$-Rh(CO)Cl and is proposed to form by a process involving an oxidative addition of a cage-bridging hydrogen to the rhodium followed by insertion of the resulting $(PMe_3)_2Rh(H)$ fragment into the dithiaborane cage framework.

Introduction

We recently reported[1] that the reaction of the *arachno*-$S_2B_7H_8^-$ anion with acetone results in a degradation reaction to give good yields of the *hypho*-$S_2B_6H_9^-$ anion.

$$arachno\text{-}6,8\text{-}S_2B_7H_8^- \xrightarrow{Me_2CO/H_2O} hypho\text{-}S_2B_6H_9^- \quad (1)$$

This dithiaborane anion is a rare example of a $2n + 8$ cluster system (24 skeletal electrons, 8 cage atoms) and according to simple skeletal-electron counting theory[2] should adopt a hypho cage geometry based on an octadecahedron missing three vertices,[3] such as shown in Figure 1.

Subsequent reaction of *hypho*-$S_2B_6H_9^-$ with methyl iodide or methylene iodide gave the *hypho*-2,3-$(CH_3)_2S_2B_6H_8$ and *hypho*-1,2,5-$(CH_2)S_2B_6H_8$ derivatives, respectively. Single-crystal X-ray structural determinations of the latter two compounds confirmed the cage geometry proposed for *hypho*-$S_2B_6H_9^-$.[1]

$$hypho\text{-}S_2B_6H_9^- + 2MeI \rightarrow hypho\text{-}2,3\text{-}(CH_3)_2S_2B_6H_8 + NaI + HI \quad (2)$$

$$hypho\text{-}S_2B_6H_9^- + 2CH_2I_2 \rightarrow hypho\text{-}1\text{-}(CH_2)\text{-}2,5\text{-}S_2B_6H_8 + NaI + HI \quad (3)$$

We also noted that this reactivity is similar to that which has been observed for dithiometal clusters, such as $Fe_2(CO)_6S_2^{2-}$. For example, $Fe_2(CO)_6(SH)_2$ reactions analogous to those in eqs 2 and 3 have been found to yield $Fe_2(CO)_6S_2Me_2$ and $Fe_2(CO)_6S_2CH_2$ products.[4] These results suggested that the *hypho*-$S_2B_6H_9^-$ anion might serve, like $Fe_2(CO)_6(\mu\text{-}S)_2$,[4,5] as a starting material for the synthesis of a variety of new hybrid transition-metal clusters and complexes, in which the metal could exhibit either exopolyhedral or cluster-framework bonding modes. In this paper we report the syntheses and structural characterizations of the first examples of such clusters, including both *hypho*- and *arachno*-metalladithiaborane complexes.

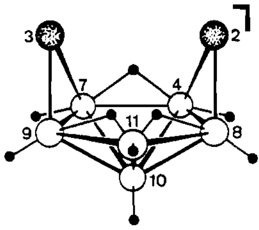

Figure 1. Proposed structure of *hypho*-$S_2B_6H_9^-$.

Experimental Section

Materials. The compounds (dppe)$NiCl_2$, CpCo$(CO)_2$, $[RhCl(CO)_2]_2$, Me_3P, 1,2,3,4,5-pentamethylcyclopentadiene, and [1,8-bis(dimethylamino)naphthalene] (proton sponge) were obtained from Aldrich. $Co_2(CO)_8$ was purchased from Strem Chemicals. $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$,[6] CpCo(CO)$I_2$,[7] *CpCo(CO)$I_2$,[7] *CpCo$(CO)_2$,[8] $Rh(PMe_3)_2(CO)Cl$,[9] and

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Table I. NMR Data

compd	^{11}B NMR δ, ppm (J_{BH}, Hz) B9	B1	B8	B10,11	B12
hypho-1-BH_2-2,5-$S_2B_6H_9$[1]	2.6 (160)	−11.5 (130)	−23.1 (175)	−22.2 (145)	−54.6 (155)
hypho-1,2,5-(η-C_6Me_6)RuCl$S_2B_6H_9$ (I)[a]	−1.8 (160)		−18.5	−20.3 (142)	−52.6 (148)
hypho-1,2,5-*CpCoI$S_2B_6H_9$ (IV)[b]	−0.2 (155)		−18.0	−19.1 (113)	−52.8 (147)

compd	^{11}B NMR δ, ppm (J_{BH}, Hz) B5,9	B7	B2,3	B4	B1
arachno-6,8-$S_2B_7H_9$	2.8	−4.4	−22.5	−37.6	−48.8
arachno-7,6,8-(η-C_6Me_6)Ru$S_2B_6H_8$ (II)[a]	3.1 (151)		−13.1 (163)	−35.5 (145)	−43.1 (145)
arachno-7,6,8-CpCo$S_2B_6H_8$ (III)[10]	4.8 (156)		−9.8 (166)	−33.7 (153)	−40.2 (143)
arachno-7,6,8-*CpCo$S_2B_6H_8$ (V)[9]	5.1 (145)		−8.0 (175)	−34.6 (145)	−39.6 (160)
arachno-7,6,8-(dppe)Ni$S_2B_6H_8$ (VI)[a]	8.7		−6.8	−33.2	−39.4 (143)
arachno-7,6,8-$(PMe_3)_2$Rh(H)$S_2B_6H_8$ (VII)[b]	8.0 (145) 5.7 (167)		−8.0 (146) −12.7 (172)	−32.0 (137)	−44.2 (140)

compd	^{1}H NMR {^{11}B} δ, ppm (mult, assign)
hypho-1,2,5-(η-C_6Me_6)RuCl$S_2B_6H_9$ (I)[a]	2.89 (s, BH), 2.36 (s, BH), 2.04 (s, CH_3), −0.51 (t, J_{HH} = 11 Hz), −1.18 (s, H_{br})
arachno-7,6,8-(η-C_6Me_6)Ru$S_2B_6H_8$ (II)[a]	3.58 (s, BH), 2.11 (s, CH_3), 1.63 (s, BH), −1.54 (s, H_{br})
hypho-1,2,5-*CpCo(I)$S_2B_6H_9$ (IV)[b]	3.94 (s, BH), 3.21 (s, BH), 2.62 (s, BH), 1.11 (s, CH_3), −1.31 (H_{br}), −1.42 (H_{br})
arachno-7,6,8-(dppe)Ni$S_2B_6H_8$ (VI)[a]	7.52 (m, Ph), 3.66 (br, BH), 2.41 (m, CH_2), −0.80 (H_{br})
arachno-7,6,8-$(PMe_3)_2$Rh(H)$S_2B_6H_8$ (VII)[a]	3.83 (s, BH), 2.19 (s, BH), 1.67 (d, CH_3, J_{HPa} = 10 Hz), 1.59 (d, CH_3, J_{HPb} = 11 Hz), −0.94 (s, H_{br}), −1.11 (s, H_{br}), −13.07 (m, Rh–H, $^1J_{HRh}$ = 18 Hz, $^2J_{HPa}$ = 18.5 Hz, $^2J_{HPb}$, = 23.9 Hz, $^3J_{HH(B3H)}$ = 5 Hz)

compd	^{31}P NMR δ, ppm	compd	^{31}P NMR δ, ppm ($^1J_{PRh}$, Hz)
arachno-7,6,8-(dppe)Ni$S_2B_6H_8$ (VI)[a]	+66.4, +54.0	*arachno*-7,6,8-$(PMe_3)_2$Rh(H)$S_2B_6H_8$ (VII)[b]	+7.7 (130), −1.2 (115)

arachno-$S_2B_7H_9$[10] were prepared by literature methods. Methylene chloride was distilled from P_2O_5. Ethyl ether and THF were distilled from sodium benzophenone. Hexane and pentane were dried over molecular sieves. Acetone was used as received.

Physical Measurements. Boron-11 NMR spectra at 64.5 MHz, proton NMR spectra at 200 MHz, and phosphorus-31 NMR spectra at 81 MHz were obtained on a Bruker WP 200 SP spectrometer. Boron-11 NMR spectra at 160.5 MHz and proton NMR spectra at 500 MHz were obtained on a Bruker AM 500 spectrometer. All boron chemical shifts are referenced to $BF_3 \cdot O(C_2H_5)_2$ (0.0 ppm), with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to internal residual protons from the lock solvent. The NMR data are presented in Table I.

High- and low-resolution mass spectra were obtained on VG-ZAB-E or VG Micromass 7070-H mass spectrometers. IR spectra were obtained on a Perkin-Elmer 1430 spectrophotometer. Except where indicated, all yields are calculated on the basis of starting *arachno*-6,8-$S_2B_7H_9$.

***hypho*-2,3-$S_2B_6H_9^-$.** *hypho*-2,3-$S_2B_6H_9^-$ was prepared by a modified procedure of the previously published method.[1] In a typical reaction, a solution of *arachno*-6,8-$Na^+S_2B_7H_8^-$ was prepared by reaction in vacuo of excess sodium hydride with *arachno*-6,8-$S_2B_7H_9$ (0.30 g, 2.02 mmol) in 20 mL of diethyl ether. After H_2 evolution had ceased (1 h), the resulting yellow solution was filtered. The solvent was removed and acetone was cannulated onto the $Na^+S_2B_7H_8^-$ salt. The solution was stirred at 40–50 °C until the yellow solution became colorless (2 h). Acetone was removed by vacuum distillation, 25 mL of ether was added, and the ether solution was filtered.

***hypho*-1,2,5-(η^6-C_6Me_6)RuCl$S_2B_6H_9$ (I).** An ether solution of *hypho*-2,3-$S_2B_6H_9^-$, made from 0.35 g (2.36 mmol) of *arachno*-6,8-$S_2B_7H_9$, was added dropwise to a 0.92 g (1.38 mmol) suspension of [(η^6-C_6Me_6)RuCl_2]$_2$ in methylene chloride. After overnight stirring, the solvents were vacuum-evaporated and the residue was extracted with toluene. Recrystallization from methylene chloride/hexane gave 0.40 g (0.92 mmol, 39% yield) of I: yellow solid; mp 168–172 °C dec; exact mass calc for $RuClS_2C_{12}B_6H_{27}$ 438.0845, found 438.0823; IR (cm^{-1}) 2960 (w), 2910 (w), 2540 (vs), 2510 (vs), 2050 (w), 1445 (w), 1375 (s), 1260 (m), 1195 (m), 1105 (w), 1065 (m), 1015 (w), 1000 (s), 980 (s), 875 (m), 830 (w), 730 (m), 680 (w), 670 (w), 640 (w), 540 (w).

***arachno*-7,6,8-(η^6-C_6Me_6)Ru$S_2B_6H_8$ II.** An ether solution of *hypho*-2,3-$S_2B_6H_9^-$, made from 0.45 g (3.03 mmol) of *arachno*-6,8-$S_2B_7H_9$, was added dropwise to a suspension of 1.06 g (1.59 mmol) of [(η^6-C_6Me_6)RuCl_2]$_2$ in methylene chloride containing an equimolar amount of proton sponge (0.68 g). After stirring overnight, the solution was concentrated and chromatographed on a silica gel column. The mixture was eluted with hexane, followed by solvent mixtures containing increasing amounts of methylene chloride. A yellow band was collected. After evaporation of the solvents, 0.46 g (1.15 mmol, 36% yield) of solid II was obtained: orange; mp 183 °C dec; exact mass calc for $RuS_2C_{12}B_6H_{26}$ 402.1078, found 402.1171; IR (cm^{-1}) 2910 (w), 2550 (s), 2520 (vs), 2480 (s), 1380 (s), 1260 (w), 1060 (w), 1000 (vs), 960 (w), 900 (w), 875 (m), 800 (m), 735 (m), 580 (m), 525 (w).

Alternatively, *arachno*-7,6,8-(η^6-C_6Me_6)Ru$S_2B_6H_8$ was produced directly from I: A methylene chloride solution containing 65 mg (0.15 mmol) of I and an excess of proton sponge was stirred overnight at room temperature. The solvent was then vacuum-evaporated, and the contents of the flask were extracted with benzene. Recrystallization from methylene chloride/hexane gave 47 mg (0.12 mmol) of pure product corresponding to an 80% yield from I.

***hypho*-1,2,6-*CpCo(I)$S_2B_6H_9$ (III).** An ether solution of *hypho*-2,3-$S_2B_6H_9^-$, made from 0.45 g (3.03 mmol) of *arachno*-6,8-$S_2B_7H_9$, was added to a methylene chloride solution containing 1.40 g (2.94 mmol) of *CpCo(CO)I_2. After stirring for 30 min, the solvents were vacuum-evaporated and the residue was extracted with ether. The ether was evaporated, and the remaining solid was then washed with a minimum amount of pentane (5 mL) to give 0.48 g (1.05 mmol, 34% yield) of III: dark green; mp >300 °C; exact mass calc for $ICoS_2C_{10}B_6H_{24}$ 460.0255, found 460.0203; IR (KBr, cm^{-1}) 2950 (m), 2900 (w), 2520 (vs), 2030 (s), 1460 (m), 1425 (w), 1370 (s), 1260 (s), 1200 (w), 1160 (w), 1100 (w), 1000 (s), 870 (w), 800 (s), 550 (m).

***arachno*-7,6,8-*CpCo$S_2B_6H_8$ (IV).** An ether solution of *hypho*-$S_2B_6H_9^-$, made from 0.45 g (3.03 mmol) of *arachno*-$S_2B_7H_9$, was cannulated onto a methylene chloride solution of 1.40 g (2.94 mmol) of *CpCo(CO)I_2 containing an equimolar amount of proton sponge (0.64 g). After stirring overnight at room temperature, the solvents were vacuum-evaporated and the residue was continuously extracted with hexane until the washings were clear. Evaporation of the hexane left 0.64 g (1.94 mmol, 64%

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Table II. Data Collection and Structure Refinement Information

	I	II	VI
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	8.007 (1)	8.525 (2)	11.404 (1)
b, Å	13.889 (3)	9.541 (2)	24.693 (5)
c, Å	17.210 (2)	11.876 (2)	11.593 (1)
α, deg		104.93 (2)	
β, deg	100.68 (1)	88.96 (2)	100.52 (1)
γ, deg		109.68 (2)	
V, Å^3	1880.7 (9)	876.3 (8)	3210 (1)
Z	4	2	4
D_{cal}, g cm^{-3}	1.543	1.517	1.319
$F(000)$	888	408	1332
mol formula	$RuS_2C_{12}B_6H_{27}Cl$	$RuS_2C_{12}H_{26}B_6$	$NiS_2P_2C_{26}H_{32}B_6\cdot{}^1/_2C_6H_{14}$
mol wt	436.87	400.41	637.29
cryst size, mm	0.02, 0.08, 0.20	0.03, 0.05, 0.20	0.15, 0.25, 0.40
λ, Å	Cu Kα, 1.541 84	Cu Kα, 1.541 84	Mo Kα, 0.710 73
μ, cm^{-1}	101.86	94.63	8.49
tran (min, max)	37.6, 99.8	80.7, 99.5	94.4, 99.9
θ range, deg	2.0–65.0	2.0–65.0	2.0–27.5
scan mode	ω–2θ	ω–2θ	ω–2θ
$\pm h,\pm k,\pm l$, colled	±9,+16,+20	±10,±11,±13	+14,–32,±15
no. of measd intensities	3468	3166	7879
no. of unique intensities	3196	2967	7336
no. with $F_o^2 > 3\sigma(F_o^2)$	1301	2536	3668
no. of variables	199	190	385
R	0.063	0.050	0.043
R_w	0.064	0.067	0.056
GOF	1.416	1.888	1.518

yield) of solid. The compound was identified by comparison of its ^{11}B and ^1H NMR spectra with those of the literature.[11]

Alternatively, *arachno*-7,6,8-*$CpCoS_2B_6H_8$ (IV) was produced directly from III: A THF solution containing 0.38 g (0.80 mmol) of III and an excess (~2 mmol) of proton sponge, was stirred for 1 h. HCl (5 M) was then added to precipitate any unreacted proton sponge. The solution was filtered, the solvent was evaporated, and the residue was extracted with hexane until the washings were clear. Evaporation of the hexane left 0.19 g (0.57 mmol, 71% yield) of IV.

***arachno*-7,6,8-$CpCoS_2B_6H_8$ (V).** An ether solution of *hypho*-2,3-$S_2B_6H_9^-$, made from 0.30 g (2.02 mmol) of *arachno*-6,8-$S_2B_7H_9$, was cannulated onto a methylene chloride solution containing 0.82 g (2.02 mmol) of $CpCo(CO)I_2$. After stirring overnight at room temperature, the solvents were vacuum-evaporated and the residue was chromatographed on silica gel. Elution with hexane gave a purple band containing 0.19 g (0.73 mmol, 36% yield) of V. The product was identified by comparison of its ^{11}B and ^1H NMR spectra with those of the literature.[12]

***arachno*-7,6,8-(dppe)$NiS_2B_6H_8$ (VI).** A freshly prepared solution of *hypho*-2,3-$S_2B_6H_9^-$, made from 0.40 g (2.69 mmol) of *arachno*-6,8-$S_2B_7H_9$, was added dropwise to a methylene chloride solution containing 1.42 g (2.69 mmol) of [1,2-bis(diphenylphosphino)ethane]nickel(II) chloride at –78 °C. There was an instantaneous change of color from brown to deep blue. The solution was brought to room temperature and stirred overnight. The solvents were removed in vacuo, and the residue was dissolved in ether and filtered. The filtrate was concentrated, and the product was precipitated by addition of pentane. Filtration gave 0.49 g (0.83 mmol, 31% yield) of VI: dark blue; mp >300 °C; exact mass calc (P-1) $NiP_2S_2C_{26}B_6H_{32}$ 593.1254, found 593.1203; IR (KBr, cm^{-1}) 3150 (w), 2560 (s), 2510 (vs), 1480 (m), 1430 (vs), 1305 (w), 1260 (w), 1190 (m), 1100 (s), 1010 (s), 980 (w), 920 (w), 875 (s), 840 (w), 805 (s), 745 (vs), 690 (vs), 675 (w), 645 (w), 555 (m), 515 (vs), 495 (w), 480 (w), 435 (m), 395 (m), 350 (m).

***arachno*-7,6,8-$(PMe_3)_2Rh(H)S_2B_6H_8$ (VII).** An ether solution of *hypho*-2,3-$S_2B_6H_9^-$, made from 0.39 g (2.62 mmol) of *arachno*-6,8-$S_2B_7H_9$, was added dropwise at 0 °C to a methylene chloride solution containing 0.75 g (2.36 mmol) of $(PMe_3)_2Rh(CO)Cl$. After stirring overnight at room temperature, the solvents were removed, benzene was added, and the solution was filtered. Vacuum evaporation of the benzene gave 0.63 g of crude material. Recrystallization from methylene chloride/hexane gave 0.26 g (0.66 mmol, 25%) of pure VII: light-brown; mp 115 °C dec; exact mass calc for $RhS_2P_2C_6B_6H_{27}$ (P-2) 392.0486, found 392.046; IR (KBr, cm^{-1}) 2980 (w), 2920 (w), 2520 (vs), 2060 (m), 1790 (w), 1425 (s), 1305 (w), 1295 (m), 1205 (w), 1150 (w), 1070 (w), 1020 (m), 955 (vs), 870 (m), 805 (w), 740 (m), 690 (m), 650 (w).

Crystallographic Data for I, II, and VI. Single crystals were grown by slow evaporation under nitrogen (I) or air (II, VI) of methylene chloride/hexane solutions. Suitably sized crystals were mounted and transferred to the diffractometer. Refined cell dimensions and their standard deviations were obtained from least-squares refinement of 25 accurately centered reflections.

Collection and Reduction of the Data. Diffraction data were collected at 295 K on an Enraf-Nonius four-circle CAD-4 diffractometer employing radiation from a highly oriented graphite-crystal monochromator. The intensities of three standard reflections measured at regular intervals showed no systematic change during data collection. The raw intensities were corrected for Lorentz and polarization effects.

Solution and Refinement of the Structure. All calculations were performed on a VAX 11/750 computer using the Enraf-Nonius structure package. The full-matrix least-squares refinement was phased on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights (w) were taken as $4F_o^2/(\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The neutral-atom scattering factors and complex anomalous dispersion corrections are those stored in the SDP package. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum(|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$.

Three-dimensional Patterson syntheses gave the coordinates of the metal atoms in all compounds. Subsequent Fourier maps led to the locations of all other non-hydrogen atoms. Anisotropic refinements followed by difference Fourier syntheses resulted in the location of all cage hydrogens. The positions of the remaining hydrogens were then calculated. Calculated hydrogen positions were not refined, but included as constant contributions to the structure factors. The final refinements included either numerical or empirical absorption corrections along with anisotropic thermal parameters for non-hydrogen atoms and fixed isotropic thermal parameters for the hydrogen atoms (6 Å^2). Final difference Fouriers were featureless. Crystal and refinement data are given in Table II. Final positional parameters are given in Tables III, V, and VII. Selected intramolecular bond distances are presented in Tables IV, VI, and VIII.

Results and Discussion

Depending upon the conditions, the reaction of $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ with *hypho*-$Na^+S_2B_6H_9^-$ gave two different ruthenadithiaborane complexes. Thus, when a 2:1 ratio of the anion and $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ was reacted, *hypho*-1,2,5-$(\eta^6\text{-}C_6Me_6)RuClS_2B_6H_9$ (I) was produced, but when proton sponge was added to the reaction mixture *arachno*-7,6,8-$(\eta^6\text{-}C_6Me_6)RuS_2B_6H_8$ (II) was obtained. It was subsequently

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Table III. Refined Positional Parameters for *hypho*-1,2,5-(η^6-C_6Me_6)$RuClS_2B_6H_9$ (I)

atom	x	y	z	B_{eq},[a] Å^2
Ru1	0.1575 (2)	0.1148 (1)	0.28357 (7)	3.31 (2)
S2	0.3411 (5)	0.2281 (4)	0.3641 (3)	4.7 (1)
S5	−0.0189 (5)	0.1057 (4)	0.3820 (2)	4.9 (1)
Cl	−0.0140 (6)	0.2450 (4)	0.2193 (2)	5.6 (1)
B7	0.229 (3)	0.327 (2)	0.412 (1)	5.0 (6)
B8	0.006 (2)	0.338 (2)	0.407 (1)	5.5 (6)
B9	−0.066 (2)	0.226 (2)	0.423 (1)	5.7 (6)
B10	0.117 (3)	0.146 (2)	0.482 (1)	5.5 (6)
B11	0.305 (2)	0.210 (2)	0.472 (1)	4.8 (5)
B12	0.119 (2)	0.273 (2)	0.484 (1)	4.6 (5)
C1	0.222 (2)	−0.037 (1)	0.3069 (8)	4.0 (4)
C2	0.076 (2)	−0.033 (1)	0.2471 (9)	3.7 (4)
C3	0.077 (2)	0.025 (1)	0.1801 (8)	4.6 (4)
C4	0.229 (2)	0.073 (1)	0.1698 (8)	4.8 (4)
C5	0.377 (2)	0.068 (1)	0.2290 (8)	3.8 (4)
C6	0.374 (2)	0.010 (1)	0.2990 (9)	4.5 (4)
C7	0.221 (2)	−0.097 (1)	0.381 (1)	5.5 (5)
C8	−0.080 (2)	−0.089 (1)	0.256 (1)	5.2 (5)
C9	−0.079 (2)	0.028 (1)	0.1145 (9)	5.6 (5)
C10	0.233 (2)	0.129 (1)	0.0946 (8)	6.2 (5)
C11	0.535 (2)	0.118 (2)	0.2199 (9)	6.3 (5)
C12	0.528 (2)	0.008 (2)	0.365 (1)	6.1 (5)

[a] $B_{eq} = {}^4/_3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha]$.

determined that I can, in fact, be directly converted to II by reaction of I with proton sponge.

$$2\ hypho\text{-}Na^+S_2B_6H_9^- + [(\eta^6\text{-}C_6Me_6)RuCl_2]_2 \rightarrow 2\ hypho\text{-}1,2,5\text{-}(\eta^6\text{-}C_6Me_6)RuClS_2B_6H_9\ (I) + 2NaCl \quad (4)$$

$$2\ hypho\text{-}Na^+S_2B_6H_9^- + [(\eta^6\text{-}C_6Me_6)RuCl_2]_2 + 2\ \text{proton sponge} \rightarrow 2\ arachno\text{-}7,6,8\text{-}(\eta^6\text{-}C_6Me_6)RuS_2B_6H_8\ (II) + 2NaCl + 2HCl \quad (5)$$

$$hypho\text{-}1,2,5\text{-}(\eta^6\text{-}C_6Me_6)RuClS_2B_6H_9\ (I) + \text{proton sponge} \rightarrow arachno\text{-}7,6,8\text{-}(\eta^6\text{-}C_6Me_6)RuS_2B_6H_8\ (II) + HCl \quad (6)$$

The ^{11}B NMR spectra (Figure 2) of I and III (discussed below) and *hypho*-$S_2B_7H_{11}$ (i.e. *hypho*-1-BH_2-2,5-$S_2B_6H_9$) are quite similar and are highly characteristic of their cage frameworks. For example, as we previously noted, compounds, such as *hypho*-$S_2B_6H_9^-$ and *hypho*-1-BH_2-2,5-$S_2B_6H_9$, that contain a dithiahexaborane fragment with three boron–boron bridging hydrogens, have spectra in which the B8 resonance appears near −25 ppm and the apical B12 resonance near −55 ppm.[1] Similar spectra were observed for I and III consistent with such bridged-dithiahexaborane frameworks. A single-crystal X-ray study confirmed these features, as shown in Figure 3.

The observed cage structure has one puckered six-membered Ru–S2–B7–B8–B9–S5 open face and one five-membered Ru–S2–B11–B10–S5 open face. The five-membered face is also nonplanar, with the Ru atom lying 0.67 Å out of the S2–B11–B10–S5 plane. Bridging hydrogens are present on both faces, at the B7–B8, B8–B9, and B10–B11 edges, respectively.

There are at least two different ways in which the structure of I may be viewed. If the compound is considered a nine-vertex cluster, composed of six boron, two sulfur, and one ruthenium atoms, then according to skeletal-electron counting procedures,[2] the compound would contain 26 skeletal electrons and fall into the hypho electronic class. I would therefore be isoelectronic in a cluster sense with *hypho*-1-(CH_2)-2,5-$S_2B_6H_8$ and should adopt a similar structure derived from an icosahedron by removing three vertices. The observed cage geometry of I can indeed be derived in this manner, as shown in Figure 4.

Table IV. Bond Distances (Å) in *hypho*-1,2,5-(η^6-C_6Me_6)$RuClS_2B_6H_9$ (I)

Ru1–S2	2.409 (4)	S5–B10	1.943 (19)	C1–C7	1.514 (23)
Ru1–S5	2.402 (4)	B7–B8	1.779 (28)	C2–C3	1.410 (22)
Ru1–Cl	2.412 (5)	B7–B11	1.964 (30)	C2–C8	1.496 (22)
Ru1–C1	2.195 (16)	B7–B12	1.819 (29)	C3–C4	1.424 (23)
Ru1–C2	2.213 (15)	B8–B9	1.690 (34)	C3–C9	1.522 (19)
Ru1–C3	2.172 (15)	B8–B12	1.714 (27)	C4–C5	1.415 (19)
Ru1–C4	2.218 (16)	B9–B12	1.772 (26)	C4–C10	1.516 (22)
Ru1–C5	2.240 (15)	B10–B11	1.783 (30)	C5–C6	1.455 (22)
Ru1–C6	2.240 (16)	B10–B12	1.767 (32)	C5–C11	1.477 (22)
S2–B7	1.905 (23)	B11–B12	1.776 (29)	C6–C12	1.514 (19)
S2–B11	1.943 (20)	C1–C2	1.412 (18)		
S5–B9	1.887 (25)	C1–C6	1.411 (21)		

Table V. Refined Positional Parameters for *arachno*-7,6,8-(η^6-C_6Me_6)$RuS_2B_6H_8$ (II)

atom	x	y	z	B_{eq},[a] Å^2
Ru7	0.21675 (6)	0.33541 (5)	0.23796 (4)	2.511 (9)
S6	0.5002 (2)	0.4047 (2)	0.3037 (2)	4.35 (5)
S8	0.1543 (2)	0.5358 (2)	0.3736 (2)	4.59 (5)
B1	0.485 (1)	0.714 (1)	0.2908 (8)	4.1 (2)
B2	0.447 (1)	0.515 (1)	0.2043 (8)	4.1 (2)
B3	0.274 (1)	0.5838 (9)	0.2401 (8)	3.8 (2)
B4	0.546 (1)	0.765 (1)	0.4386 (9)	4.9 (2)
B5	0.609 (1)	0.620 (1)	0.338 (1)	4.8 (2)
B9	0.335 (1)	0.725 (1)	0.3963 (9)	5.0 (2)
C1	0.2145 (8)	0.1490 (7)	0.0805 (6)	3.0 (1)
C2	0.1088 (8)	0.2291 (7)	0.0581 (6)	3.1 (1)
C3	−0.0246 (8)	0.2396 (7)	0.1309 (6)	3.3 (2)
C4	−0.0480 (7)	0.1791 (7)	0.2289 (6)	3.0 (1)
C5	0.0596 (8)	0.0984 (7)	0.2537 (6)	3.2 (2)
C6	0.1907 (8)	0.0852 (7)	0.1788 (6)	3.2 (1)
C7	0.355 (1)	0.1375 (9)	0.0038 (8)	4.6 (2)
C8	0.135 (1)	0.2968 (9)	−0.0457 (7)	4.6 (2)
C9	−0.137 (1)	0.3242 (9)	0.1076 (8)	5.0 (2)
C10	−0.182 (1)	0.192 (1)	0.3087 (8)	5.0 (2)
C11	0.030 (1)	0.0274 (9)	0.3552 (7)	4.8 (2)
C12	0.3082 (9)	0.0088 (8)	0.2091 (8)	4.6 (2)

[a] $B_{eq} = {}^4/_3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha]$.

Alternatively, I may be regarded as an exopolyhedrally substituted *hypho*-$S_2B_6H_9^-$ cluster. The (η^6-C_6Me_6)RuCl fragment, or the CH_2 fragment in *hypho*-1-(CH_2)-2,5-$S_2B_6H_8$, could then be considered as an exopolyhedral bridging unit having localized two-center, 2-electron bonding interactions with the two sulfur cage atoms. The observed ruthenium–sulfur distances Ru–S2 2.409 (4) Å and Ru–S5 2.402 (4) Å are, in fact, at the high end of the range observed for normal ruthenium–sulfur bonds.[13] Likewise, the bond angles at the metal center, S2–Ru–S5 90.3 (2)°, S2–Ru–Cl 90.5 (2)°, S5–Ru–Cl 90.2 (2)° are consistent with a six-coordinate ruthenium. Thus, I could be considered a hybrid molecule that is composed of a "nonclassical" dithiaborane cluster substituted by a "classical" arene–ruthenium fragment. In this view, the dithiaborane anion would be an analogue of η^2-dithiolene or bis(mercapto) ligands.

The boron–boron and boron–sulfur cage distances in I are similar to those found[1] in *hypho*-2,3-$(CH_3)_2S_2B_6H_8$ and *hypho*-1-(CH_2)-2,5-$S_2B_6H_8$ with the exception that the B10–B11 distance, 1.783 (30) Å, in I is longer (compared to 1.64 (1) and

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(13) See, for example: (a) Brunner, H.; Janietz, N.; Wachter, J. *J. Organomet. Chem.* **1988**, *356*, 85–91. (b) Cordes, A. W. *Acta Crystallogr.* **1988**, *C44*, 363–364. (c) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1988**, *352*, 199–204. (d) Killops, S. D.; Knox, S. A. R.; Riding, G. H.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1978**, 486–488. (e) Torres, M. R.; Perales, A.; Ros, J. *Organometallics* **1988**, *7*, 1223–1224. (f) Dev, S.; Imagawa, K.; Mizobe, Y.; Cheng, G.; Wakatsuki, Y.; Yamazaki, H.; Hidai, M. *Organometallics* **1989**, *8*, 1232–1237. (g) Amarasekern, J.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 2017–2018. (h) Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 5733–5738. (i) Clearfield, A.; Epstein, E. F.; Bernal, I. *J. Coord. Chem.* **1977**, *6*, 227–240. (j) Sellmann, D.; Binker, G.; Knoch, F. *Z. Naturforsch.* **1987**, *42B*, 1298–1306.

Table VI. Bond Distances (Å) in *arachno*-7,6,8-(η^6-C_6Me_6)$RuS_2B_6H_8$ (II)

Ru7–S6	2.369 (2)	S8–B3	1.939 (9)	C1–C2	1.429 (11)
Ru7–S8	2.367 (2)	S8–B9	1.899 (9)	C1–C6	1.431 (11)
Ru7–B2	2.235 (8)	B1–B2	1.835 (12)	C1–C7	1.505 (11)
Ru7–B3	2.246 (9)	B1–B3	1.813 (12)	C2–C3	1.431 (10)
Ru7–C1	2.219 (6)	B1–B4	1.735 (14)	C2–C8	1.513 (11)
Ru7–C2	2.182 (6)	B1–B5	1.781 (17)	C3–C4	1.410 (11)
Ru7–C3	2.217 (7)	B1–B9	1.779 (15)	C3–C9	1.514 (13)
Ru7–C4	2.233 (5)	B2–B3	1.811 (15)	C4–C5	1.458 (11)
Ru7–C5	2.261 (6)	B2–B5	1.939 (13)	C4–C10	1.490 (11)
Ru7–C6	2.242 (6)	B3–B9	1.951 (12)	C5–C6	1.434 (10)
S6–B2	1.920 (11)	B4–B5	1.807 (15)	C5–C11	1.507 (12)
S6–B5	1.880 (10)	B4–B9	1.759 (16)	C6–C12	1.518 (12)

Table VII. Refined Positional Parameters for *arachno*-7,6,8-(dppe)$NiS_2B_6H_8$ (VI)

atom	x	y	z	B_{eq},[a] Å^2
Ni7	0.07482 (5)	0.15195 (2)	0.31997 (5)	2.89 (1)
P1	0.2518 (1)	0.14731 (5)	0.4251 (1)	3.20 (2)
P2	0.0190 (1)	0.19867 (5)	0.4596 (1)	3.40 (3)
S6	0.0898 (1)	0.20839 (6)	0.1643 (1)	4.55 (3)
S8	0.0530 (1)	0.06476 (5)	0.2671 (1)	3.96 (3)
B1	–0.1064 (5)	0.1275 (3)	0.0727 (5)	4.3 (1)
B2	–0.0595 (5)	0.1800 (2)	0.1806 (5)	3.6 (1)
B3	–0.0802 (5)	0.1118 (2)	0.2260 (5)	3.7 (1)
B4	–0.0039 (7)	0.1053 (3)	–0.0105 (6)	5.5 (2)
B5	–0.0027 (6)	0.1750 (3)	0.0328 (5)	4.8 (2)
B9	–0.0331 (6)	0.0640 (2)	0.1106 (6)	4.5 (1)
C1	0.3791 (4)	0.1521 (2)	0.3516 (4)	3.6 (1)
C2	0.3684 (5)	0.1358 (2)	0.2367 (5)	5.0 (1)
C3	0.4642 (5)	0.1368 (3)	0.1790 (5)	6.4 (2)
C4	0.5715 (5)	0.1539 (3)	0.2380 (6)	7.4 (2)
C5	0.5862 (5)	0.1716 (3)	0.3520 (7)	7.5 (2)
C6	0.4889 (5)	0.1706 (2)	0.4090 (6)	5.8 (2)
C7	0.2805 (4)	0.0868 (2)	0.5178 (4)	3.6 (1)
C8	0.1876 (5)	0.0649 (2)	0.5642 (5)	4.8 (1)
C9	0.2078 (5)	0.0201 (2)	0.6366 (5)	5.4 (1)
C10	0.3183 (6)	–0.0027 (2)	0.6637 (5)	5.7 (1)
C11	0.4095 (5)	0.0181 (2)	0.6189 (5)	5.9 (2)
C12	0.3921 (5)	0.0628 (2)	0.5454 (5)	4.7 (1)
C13	0.2672 (4)	0.2037 (2)	0.5294 (5)	4.1 (1)
C14	0.1528 (5)	0.2098 (2)	0.5745 (4)	4.4 (1)
C15	–0.0383 (4)	0.2661 (2)	0.4175 (4)	3.5 (1)
C16	–0.1584 (5)	0.2791 (2)	0.4024 (5)	4.7 (1)
C17	–0.1995 (5)	0.3290 (2)	0.3628 (5)	5.2 (1)
C18	–0.1234 (6)	0.3673 (2)	0.3374 (5)	5.9 (2)
C19	–0.0037 (6)	0.3557 (2)	0.3528 (6)	6.6 (2)
C20	0.0397 (5)	0.3058 (2)	0.3932 (5)	5.3 (1)
C21	–0.0866 (4)	0.1711 (2)	0.5454 (4)	3.9 (1)
C22	–0.1200 (5)	0.2014 (2)	0.6349 (5)	5.3 (1)
C23	–0.1944 (6)	0.1783 (3)	0.7023 (5)	6.8 (2)
C24	–0.2344 (6)	0.1265 (3)	0.6821 (6)	7.4 (2)
C25	–0.2008 (6)	0.0961 (3)	0.5951 (5)	6.1 (2)
C26	–0.1267 (5)	0.1185 (2)	0.5250 (4)	4.4 (1)
C27	0.4358 (7)	–0.0038 (4)	0.0008 (7)	9.9 (3)
C28	0.4200 (5)	–0.0023 (3)	0.1129 (5)	6.3 (2)
C29	0.3041 (8)	–0.0027 (3)	0.1291 (8)	10.4 (3)
HB1	–0.195 (4)	0.129 (2)	0.033 (4)	6.0*
HB2	–0.130 (4)	0.209 (2)	0.197 (4)	6.0*
HB3	–0.156 (4)	0.104 (2)	0.268 (4)	6.0*
HB4	–0.034 (4)	0.093 (2)	–0.094 (4)	6.0*
HB5	–0.036 (4)	0.200 (2)	–0.042 (4)	6.0*
HB9	–0.094 (4)	0.023 (2)	0.075 (4)	6.0*
HB45	0.078 (4)	0.139 (2)	–0.004 (4)	6.0*
HB49	0.045 (4)	0.070 (2)	0.044 (4)	6.0*

[a] Starred values refer to atoms whose thermal parameters were not refined. $B_{eq} = {}^4/_3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha]$.

Table VIII. Bond Distances (Å) in *arachno*-7,6,8-(dppe)$NiS_2B_6H_8$ (VI)

Ni7–P1	2.162 (1)	B1–HB1	1.028 (44)	C7–C8	1.382 (8)
Ni7–P2	2.176 (1)	B2–B3	1.792 (8)	C7–C12	1.388 (7)
Ni7–S6	2.311 (2)	B2–B5	1.943 (9)	C8–C9	1.383 (8)
Ni7–S8	2.240 (1)	B2–HB2	1.125 (50)	C9–C10	1.362 (9)
Ni7–B2	2.129 (5)	B3–B9	1.933 (9)	C10–C11	1.346 (9)
Ni7–B3	2.143 (5)	B3–HB3	1.088 (51)	C11–C12	1.387 (8)
P1–C1	1.817 (5)	B4–B5	1.791 (10)	C13–C14	1.499 (8)
P1–C7	1.835 (5)	B4–B9	1.816 (10)	C15–C16	1.386 (7)
P1–C13	1.831 (5)	B4–HB4	1.013 (44)	C15–C20	1.387 (7)
P2–C14	1.854 (5)	B4–HB45	1.246 (47)	C16–C17	1.369 (7)
P2–C15	1.822 (5)	B4–HB49	1.150 (46)	C17–C18	1.352 (9)
P2–C21	1.827 (5)	B5–HB5	1.071 (45)	C18–C19	1.374 (10)
S6–B2	1.883 (6)	B5–HB45	1.388 (48)	C19–C20	1.377 (8)
S6–B5	1.879 (6)	B9–HB9	1.250 (45)	C21–C22	1.387 (8)
S8–B3	1.903 (5)	B9–HB49	1.288 (52)	C21–C26	1.383 (7)
S8–B9	1.898 (6)	C1–C2	1.375 (7)	C22–C23	1.377 (9)
B1–B2	1.813 (8)	C1–C6	1.384 (7)	C23–C24	1.363 (10)
B1–B3	1.790 (8)	C2–C3	1.381 (9)	C24–C25	1.367 (9)
B1–B4	1.733 (11)	C3–C4	1.356 (8)	C25–C26	1.389 (9)
B1–B5	1.785 (10)	C4–C5	1.373 (11)	C27–C28	1.346 (11)
B1–B9	1.795 (9)	C5–C6	1.391 (9)	C28–C29	1.368 (12)

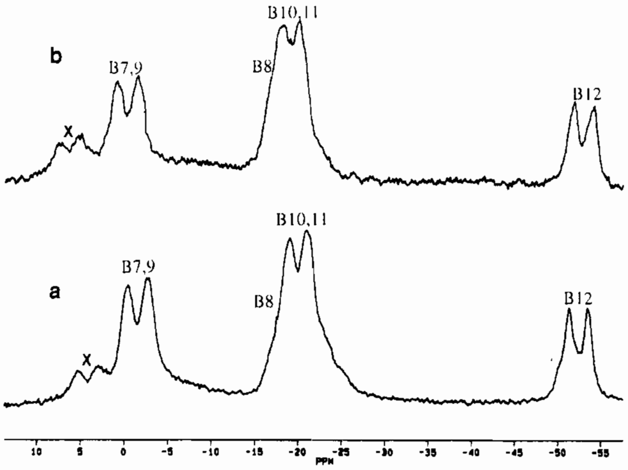

Figure 2. Boron-11 NMR spectra of *hypho*-1,2,5-(η^6-C_6Me_6)$RuClS_2B_6H_9$ (I) and *hypho*-1,2,5-*$CpCoIS_2B_6H_9$ (III).

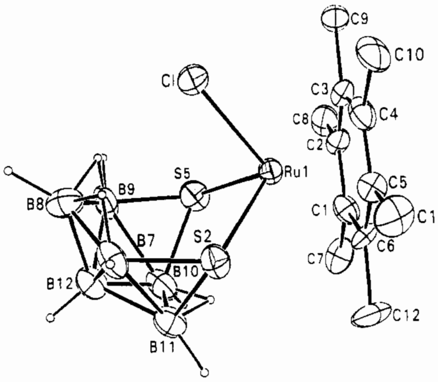

Figure 3. ORTEP drawing of the molecular structure of *hypho*-1,2,5-(η^6-C_6Me_6)$RuClS_2B_6H_9$ (I).

1.660 (6) Å, respectively), consistent with the presence of the bridging hydrogen at this edge. The nonbonded sulfur–sulfur distance 3.410 (9) Å is similar to that in *hypho*-1-(CH_2)-2,5-$S_2B_6H_8$ (3.34 Å). The Ru–(η^6-C_6Me_6) centroid distance (1.696 (1) Å) is normal and in the range observed for other metallaborane–arene compounds.[14] The arene ring is aligned such that the Cl–Ru–B12–B8 plane forms a dihedral angle of 90.7 (8)° with the C2–Ru–C5 plane and thus bisects the C3–C4 and C1–C6 distances.

The loss of HCl from I results in the loss of two skeletal electrons. Therefore, the elimination product II, which was obtained as a product of both the original reaction and of the reaction of I with

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[14] See, for example: (a) Faridoon; McGrath, M.; Spalding, T. R.; Fontaine, X. L. R.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1819–1829. (b) Brown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 925–930. (c) Brown, M.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3039–3049.

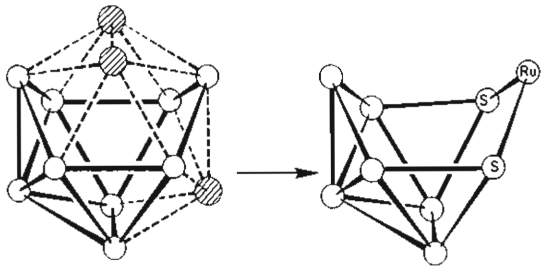

Figure 4. Derivation of nine-vertex hypho structures for I and III from an icosahedron by removal of three vertices.

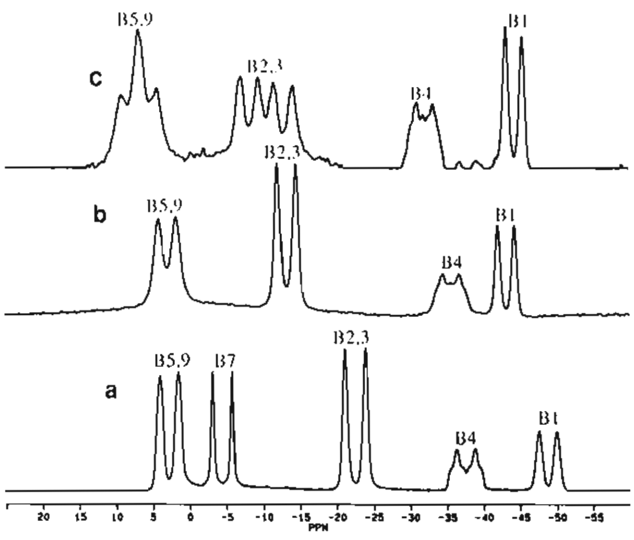

Figure 5. Boron-11 NMR spectra of (a) *arachno*-$S_2B_7H_9$, (b) *arachno*-7,6,8-(η^6-C_6Me_6)$RuS_2B_6H_8$ (II), and (c) *arachno*-7,6,8($(Me_3P)_2(H)RhS_2B_6H_8$ (VII).

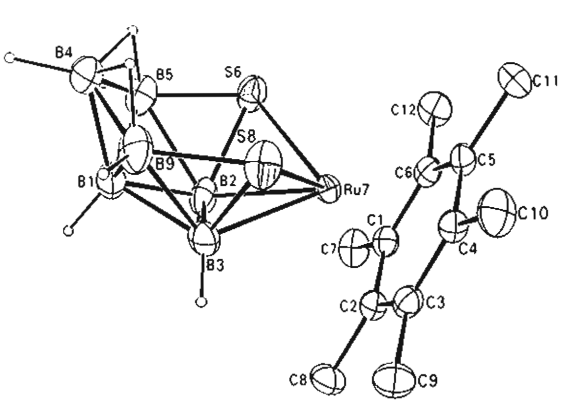

Figure 6. ORTEP drawing of the molecular structure of *arachno*-7,6,8-(η^6-C_6Me_6)$RuS_2B_6H_8$ (II).

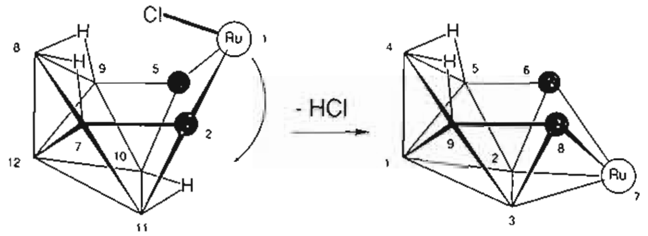

Figure 7. Conversion of *hypho*-1,2,5-(η^6-C_6Me_6)$RuClS_2B_6H_9$ (I) to *arachno*-7,6,8-(η^6-C_6Me_6)$RuS_2B_6H_8$ (II).

proton sponge, should be a nine-vertex 24-skeletal-electron cluster. Such a cluster should exhibit an arachno geometry based on an octadecahedron missing two vertices, as suggested for the isoelectronic cluster *arachno*-6,8-$S_2B_7H_9$.[10] The ^{11}B NMR spectra of II and *arachno*-6,8-$S_2B_7H_9$ are quite similar (Figure 5) and support similar cage geometries. This was confirmed by a single-crystal structural study of II, as shown in Figure 6.

In I the chloride is situated over the Ru–S2–B7–B8–B9–S5 face of the dithiaborane framework with a Cl–H78(89) distance of ~2.9 Å, suggesting that HCl elimination should involve either the H78 or H89 protons. However, the H10-11 hydrogen bridges two borons, B10 and B11, that are both directly bonded to a sulfur atom, and the electron-withdrawing effect of these two sulfurs would be expected to significantly enhance the acidity of this hydrogen. Furthermore, the Ru–H10-11 distance is only ~2.6 Å and an elimination process involving an initial addition of H10-11 to the ruthenium, as observed for compound VII discussed below, would be reasonable. Regardless of the detailed elimination mechanism, the conversion of I to II involves the loss of the H10-11 hydrogen, as depicted in the scheme in Figure 7, with the Ru atom then bonding in an η^4-fashion to the B10–B11–S2–S5 face of the dithiaborane cage (Ru to plane centroid 1.514 Å). Accordingly, the B2–B3 distance is greater, 1.881 (2) Å, in II than in I, consistent with the bonding interactions of these two borons with the Ru atom. Likewise, the Ru–B3 2.246 (9) Å and Ru–B2 2.235 (8) Å distances clearly indicate bonding interactions. The Ru–S bonding distances, Ru–S6 2.369 (2) Å and 2.367 (2) Å, in II are slightly shorter (~0.03 Å) than in I, and both the S6–Ru–S8 angle (98.2°) and the nonbonded S6–S8 distance (3.580 (3) Å) are greater. The Ru–(η^6-C_6Me_6) centroid distance remains essentially the same (1.703 (1) Å), but in contrast to I, the ring is aligned such that two of the ring carbons, C5 and C2, lie on the Ru–B1–B4 plane. The S6–B2–B3–S8 and arene planes are parallel.

As observed for the ruthenium compounds, it was found that, depending upon the presence of proton sponge, the reaction of *CpCo(CO)I_2 with an equimolar amount of *hypho*-$Na^+S_2B_6H_9^-$ led to the formation of two different cobaltadithiaborane complexes, *hypho*-1,2,5-*$CpCoIS_2B_6H_9$ (III) or *arachno*-7,6,8-*$CpCoS_2B_6H_8$ (IV). On the other hand, reaction of the parent CpCo(CO)I_2 with *hypho*-$Na^+S_2B_6H_9^-$ even in the absence of proton sponge gave only *arachno*-7,6,8-$CpCoS_2B_6H_8$ (V).

$$\textit{hypho}\text{-}Na^+S_2B_6H_9^- + {}^*CpCo(CO)I_2 \rightarrow \textit{hypho}\text{-}1,2,5\text{-}{}^*CpCoIS_2B_6H_9\ (III) + NaI \quad (7)$$

$$\textit{hypho}\text{-}Na^+S_2B_6H_9^- + {}^*CpCo(CO)I_2 + \text{proton sponge} \rightarrow \textit{arachno}\text{-}7,6,8\text{-}{}^*CpCoS_2B_6H_8\ (IV) + NaI + HI \quad (8)$$

$$\textit{hypho}\text{-}Na^+S_2B_6H_9^- + CpCo(CO)I_2 \rightarrow \textit{arachno}\text{-}7,6,8\text{-}CpCoS_2B_6H_8\ (V) + NaI + HI \quad (9)$$

IV and V were identified by comparison of their spectroscopic data with those from the literature.[11,12] V has previously been structurally characterized and has been shown to have a cage geometry similar to that of its isoelectronic analogues *arachno*-6,8-$S_2B_7H_9$ and II, in which the CpCo unit occupies the seven-vertex cage position.[12] As noted above, the ^{11}B NMR spectrum of III (Figure 2b) is quite similar to that of I and is therefore consistent with the proposed hypho structure shown in Figure 8.

As with CpCo(CO)I_2 (eq 9), only an arachno cage product was obtained in the reaction of (dppe)NiCl_2 with $Na^+S_2B_6H_9^-$.

$$\textit{hypho}\text{-}Na^+S_2B_6H_9^- + (dppe)NiCl_2 \rightarrow \textit{arachno}\text{-}7,6,8\text{-}(dppe)NiS_2B_6H_8\ (VI) + NaCl + HCl \quad (10)$$

An X-ray study (Figure 9) confirmed that VI has a cage structure similar to that of II, IV, and V, with the metal again occupying the seven-vertex cage position. The observed Ni–S8 2.239 (1) Å, Ni–S6 2.312 (2) Å, Ni–B2 2.133 (6) Å, and Ni–B3 2.139 (6) Å bond distances are consistent with an η^4-bonding mode with respect to the dithiaborane cage (nickel to plane centroid, 1.254 (1) Å). Both the S6–Ni–S8 angle (112.7 (1)°) and

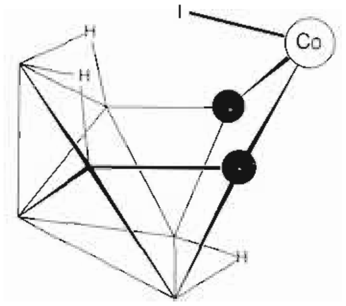

Figure 8. Proposed structure for *hypho*-1,2,5-*CpCo(I)$S_2B_6H_9$ (III).

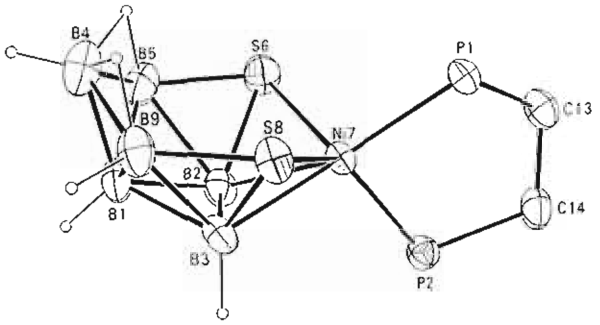

Figure 9. ORTEP drawing of the molecular structure of *arachno*-7,6,8-(dppe)$NiS_2B_6H_8$ (VI). The phenyl rings on the dppe ligand have been omitted in the figure.

the S6–S8 (3.790 (2) Å) nonbonded distance are greater than those in either I or II.

The two phosphorus atoms of the dppe ligand lie on opposite sides of the Ni–B1–B4 plane of the cage, with the Ni–P1–P2 and Ni–B1–B4 planes having a dihedral angle of 12.7°. Likewise, the S6–B2–B3–S8 and Ni–B1–B4 planes have a dihedral angle of 81.87 (8)°. Thus, P1 and P2 are oriented such that P1 is closer to the B3–S8 edge (e.g. P1–S6 3.576 (2) Å and P1–S8 3.336 (2) Å) and P2 is closer to the B2–S6 edge (e.g. P2–B2 3.228 (6) Å and P2–B3 3.478 (6) Å) of the cage. This orientation is consistent with the ^{11}B NMR spectrum of the compound, which shows resonances in the same chemical shift ranges as II and IV, but with the resonances assigned to the B5,9 and B2,3 borons significantly broadened, suggesting that B5 and B9 and B2 and B3 are not equivalent in VI. Likewise, two singlets are observed in the ^{31}P NMR spectrum, indicating that the two phosphorus atoms are oriented differently and do not interconvert on the NMR time scale. The remaining cage distances in VI are similar to those observed in II.

The Ni–dppe bond distances (Ni–P1 2.161 (1) Å and Ni–P2 2.175 (2) Å) and angles (e.g. P1–Ni–P2 angle of 88.1 (1)°) are in the ranges observed for Ni(dppe) complexes.[15] Also, as observed in other dppe complexes,[15,16] the Ni–P1–C13–C14–P2 ring is not planar, with the C13 and C14 atoms out of the Ni–P1–P4 plane bent toward the S6 side of the cage by 0.67 and 0.11 Å, respectively.

$(PMe_3)_2Rh(CO)Cl$ reacts with *hypho*-$S_2B_6H_9^-$ to yield a single product, VII. In principle, two types of isomeric complexes, having different metal-bonding modes, could be formed in this reaction. For example, if the rhodium retains its 16-electron square-planar environment in the product, then chloride displacement and carbonyl loss could result in a four-coordinate rhodium(I) complex in which the dithiaborane cage is bound in an η^2 fashion to the metal, eq 11, as observed for I and III, with the bonding to the metal involving one normal covalent and one dative sulfur → metal bond.

$$\textit{hypho}\text{-Na}^+\text{S}_2\text{B}_6\text{H}_9^- + (\text{PMe}_3)_2\text{Rh(CO)Cl} \rightarrow (\text{PMe}_3)_2\text{Rh}(\eta^2\text{-S}_2\text{B}_6\text{H}_9) + \text{CO} + \text{NaCl} \quad (11)$$

The spectroscopic data discussed below, however, clearly establish the presence of a rhodium hydride. Thus, the reaction must have involved (eq 12) an oxidative addition of a bridging

$$\textit{hypho}\text{-Na}^+\text{S}_2\text{B}_6\text{H}_9^- + (\text{PMe}_3)_2\text{Rh(CO)Cl} \rightarrow \textit{arachno}\text{-7,6,8-}(\text{PMe}_3)_2\text{Rh(H)S}_2\text{B}_6\text{H}_8\ (\text{VII}) + \text{NaCl} + \text{CO} \quad (12)$$

proton to the rhodium to produce a rhodium(III) center and insertion of the resulting $(PMe_3)_2RhH$ unit into the cage. The $(PMe_3)_2RhH$ fragment would then be a 2-skeletal-electron donor, and as a result, the cluster would be isoelectronic with II and IV–VI. Similar oxidative additions of bridging hydrogens to metal centers in metallacarboranes,[17] as well as a metallathiaborane,[18] are well-documented.

The ^{11}B NMR spectrum of VII has resonances in the same general region as II and IV–VI, suggesting that it is also structurally similar to *arachno*-$S_2B_7H_9$. However, the spectrum of VII also shows (Figure 5c) that the two resonances assigned to the equivalent B2,3 and B5,9 borons in II, IV, and V are each split into two resonances, suggesting that VII like VI does not have a molecular mirror plane. Likewise, there are two resonances in the ^{31}P NMR spectrum, indicating that the two PMe_3 ligands are not symmetry related and do not interconvert on the NMR time scale. Both phosphorus resonances show doublet structure due to coupling to the Rh, along with multiplet fine structure consistent with J_{PP} and complex J_{PH} (methyl and hydride) couplings.

The ^{1}H NMR spectrum shows two methyl resonances each split into doublets owing to phosphorus-coupling ($^2J_{H\text{-}P_a}$ = 10 Hz, $^2J_{H\text{-}P_b}$ = 11 Hz, respectively), as well as two different bridging-hydrogen resonances. Most significantly, the ^{1}H NMR spectrum also has a multiplet resonance upfield at −13.07 ppm, consistent with the presence of a rhodium hydride. Analysis of the multiplet structure of the hydride resonance (Figure 10), in conjunction with the ^{11}B and ^{31}P NMR data, supports the structure proposed in Figure 11 in which the $Rh(PMe_3)_2H$ is substituted at the seven-vertex cage position but cannot freely rotate with respect to the dithiaborane cage. Thus, as shown in Figure 10b, the hydride resonance appears as a doublet of doublets in the ^{31}P spin-decoupled spectrum, owing to coupling of the hydride to the rhodium (J_{HRh} = 18 Hz) and to one cage hydrogen (J_{HH} = 5 Hz). Selective proton decoupling experiments established that the latter coupling arises from coupling of the hydride to one terminal cage proton. The observed 5-Hz coupling is consistent with $^3J_{HH}$

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(15) See, for example: Kriege-Simondsen, J.; Feltham, R. D. *Inorg. Chim. Acta* **1983**, *71*, 185–194.

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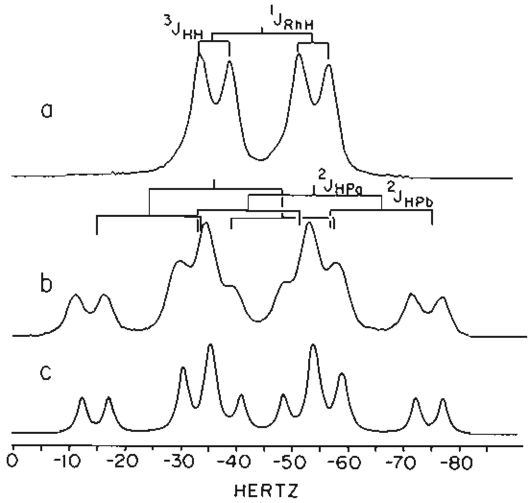

Figure 10. Hydride resonance in the ^{1}H NMR spectra of *arachno*-7,6,8-$(Me_3P)_2(H)RhS_2B_6H_8$ (VII): (a) ^{31}P-decoupled; (b) ^{31}P-coupled; (c) PANIC simulation.

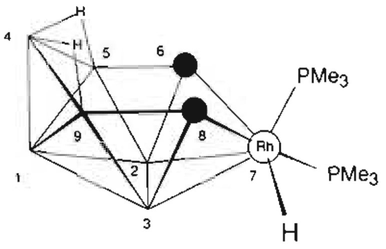

Figure 11. Proposed structure for *arachno*-7,6,8-$(Me_3P)_2(H)RhS_2B_6H_8$ (VII).

couplings observed in other $M(CH_2R)(H)$ hydride complexes[19] and in carborane cages.[20] Therefore, the ruthenium hydride is most likely coupled to the terminal B3 proton. In the ^{31}P-coupled ^{1}H NMR spectrum (Figure 10a) the doublet of doublet resonance is further split by the two different phosphorus atoms as indicated to give the multiplet structure shown. PANIC simulations of this structure gave estimated J_{HP} couplings of $J_{HP_a} = 18.5$ Hz and $J_{HP_b} = 23.9$ Hz. Thus, collectively these NMR data support the proposed structure in which the mirror symmetry of the dithiaborane cage is broken, as was observed in VI by the arrangement of the PMe_3 and hydride ligands relative to the cage.

In summary, as demonstrated by the results discussed above, the *hypho*-$S_2B_6H_9^-$ anion exhibits different types of reactivity, centered at the sulfur and bridge hydrogens, respectively, and may thus exhibit a variety of bonding configurations with respect to transition-metal coordination. As evidenced by its reactions with transition metals and with methyl iodide (eq 2), methylene diiodide (eq 3), and (borane)·THF,[1] the electron density in the anion appears to be primarily located at the sulfur atoms, leading to initial electrophilic attacks at these sites. Such reactions could give η^1-coordinations, but these complexes were not observed. Instead, bridging η^2-complexes were obtained in the case of ruthenium and cobalt (I and III) in which an exopolyhedral lone pair of electrons on the second sulfur atom is apparently sufficiently basic to form a dative sulfur–metal bond. In this configuration the $S_2B_6H_9^-$ anion functions as a 4-electron ligand to the formal Ru^{2+} and Co^{3+} metal centers, giving an 18-electron count for both metals.

Bridging hydrogens on polyhedral boranes are protonic. The *hypho*-$S_2B_6H_9^-$ anion has three bridging hydrogens, with the hydrogen bridging the B10–B11 edge expected to have enhanced acidity owing to its proximity to the cage sulfur atoms. This reactivity results in the ready elimination of any metal-coordinated halogen as HX. This loss changes both the cluster and metal electron counts and requires a change in the coordination geometry to an η^4-configuration in order for the metal to achieve an 18-electron count. Thus, in these η^4-complexes the formal $S_2B_6H_8^{2-}$ dianion functions as a 6-electron donor to the Ru^{2+} (II), Co^{3+} (IV, V), and Ni^{2+} (VI) metal ions. In the absence of a second halogen at the metal, as in the reaction with $(PMe_3)_2Rh(CO)Cl$, an elimination reaction is not possible; however, the acidic nature of the H10–11 proton results in an oxidative addition to the rhodium to yield the hydride complex (VII).

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Supplementary Material Available: Tables of positional parameters, anisotropic temperature factors, bond distances, bond angles, and least-squares planes (25 pages); lists of structure factors (54 pages). Ordering information is given on any current masthead page.

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