Synthesis and Characterization of the Hypoelectronic Ruthenaborane {(η^5-C$_5$Me$_5$)Ru}$_2${η^6-C$_6$H$_6$)Ru}B$_7$H$_7$}

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*Summary: The thermal conversion of commo-{1-(Cp*Ru)-(μ-H)B$_4$H$_9$}$_2$Ru, **1**, into {(η^5-C$_5$Me$_5$)Ru}$_2${η^6-C$_6$H$_6$)Ru}-B$_7$H$_7$}, **2**, is described. Compound **2** is a single cage, hypoelectronic triruthenaborane in which the C$_6$H$_6$ ligand is derived from the reaction solvent. As an (n − 1) skeletal electron pair (sep) closed, deltahedral cluster, **2** constitutes a structural link between 10 fragment metallaboranes with (n + 1) and (n) sep as well as with one with (n − 2) sep. This series establishes a connection between decreasing average coordination number of the cluster boron atoms with decreasing sep thereby providing a useful ^{11}B NMR chemical shift correlation.*

Introduction

Recently, we reported the isolation and characterization of the interesting vertex-fused ruthenaborane, commo-{1-(Cp*Ru)(μ-H)B$_4$H$_9$}$_2$Ru, **1**, shown in Chart 1 (Cp* = η^5-C$_5$Me$_5$).[1] Formed in low yield as a byproduct of the reaction of Co$_2$(CO)$_8$ with (Cp*RuH)$_2$B$_3$H$_7$, it is a trimetallic analogue of 2,2′−M(B$_5$H$_8$)$_2$, M = Be, Fe.[2−4] To date, we have been unable to unravel its origin in this reaction and, therefore, have been unable to improve its yield. However, the unique ruthenium atom of **1** is at the center of a near-octahedron of hydrogen atoms, and we have shown that hydrogen-rich metallaboranes tend to eliminate H$_2$ to form highly condensed clusters.[5,6] Hence, we have examined the pyrolysis of **1** and report the formation and characterization of an unusual ruthenaborane.

Results and Discussion

Examination of a solution of **1** in C$_6$D$_6$ by ^{11}B NMR showed the disappearance of signals corresponding to **1** and the generation of new boron signals on heating at 95 °C. One major product exhibiting three B−H fragment environments in a ratio of 4:2:1 was observed plus a minor product (δ 130, 141 in a ratio of 1:1). Small signals from (Cp*RuH)$_2$B$_3$H$_7$ along with unreacted **1** were also observed.[6] No new bridging hydrogen reso-

Chart 1
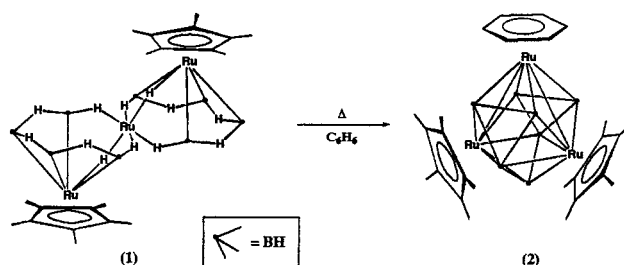
nances were observed in the ^{1}H NMR spectrum. A solid-state structure analysis (Figure 1) of a crystal isolated from the C$_6$D$_6$ reaction mixture reveals a molecule with crystallographic C_{2v} symmetry. The seven B−H groups can be divided into three sets of equivalent boron atoms, four B (1), two B (2), and one B (3), consistent with the ^{11}B and ^{1}H NMR spectra. There are three Ru atoms. Consistent with the ^{1}H NMR, two are equivalent and each is coordinated to a Cp* group whereas the third is unexpectedly associated with a η^6-C$_6$D$_6$ ligand derived from the solvent. Mass spectrometry confirmed the presence of a C$_6$D$_6$ moiety. Heating a solution of **1** in C$_6$H$_6$ generated a fully protonated sample and the ^{1}H NMR corroborated the coordination of benzene in the formation of **2**. Presumably, loss of 5 H$_2$ and BH$_3$ from **1** result in the collapse of the two fused nido clusters into a single closed cage, thereby exposing the unique Ru to the solvent benzene.

A 10-fragment closed cluster should exhibit a bicapped square antiprismatic structure with 10 skeletal electron pairs (sep).[7,8] Closed metallaboranes with a total of 10 cluster fragments have been of renewed interest lately in that [(η^6-C$_6$Me$_6$)RuB$_9$H$_9$]$^{2-}$, which exhibits a normal bicapped square antiprismatic shape (Chart 2a), can be reversibly oxidized to (η^6-C$_6$Me$_6$)-RuB$_9$H$_9$ which also exhibits a closed cluster shape (Chart 2b).[9,10] The difference between the two structures is shown in Chart 2, where (η^6-C$_6$Me$_6$)RuB$_9$H$_9$ is seen to be derived from the dianion via a diamond-square-diamond (dsd) rearrangement. In the dsd rearrangement, one 4-connect and one 6-connect vertex are generated from two 5-connect vertexes. Compounds of this type are known and have been variously called

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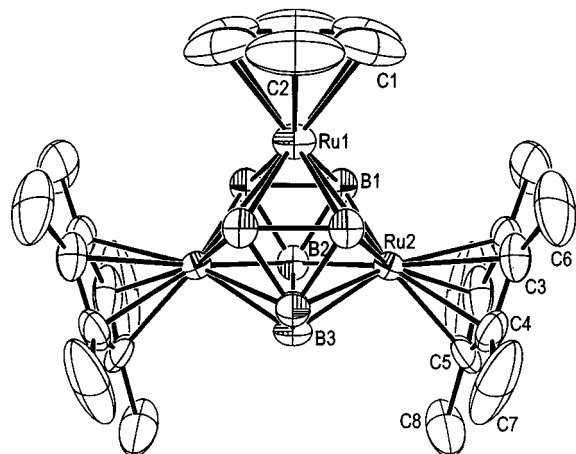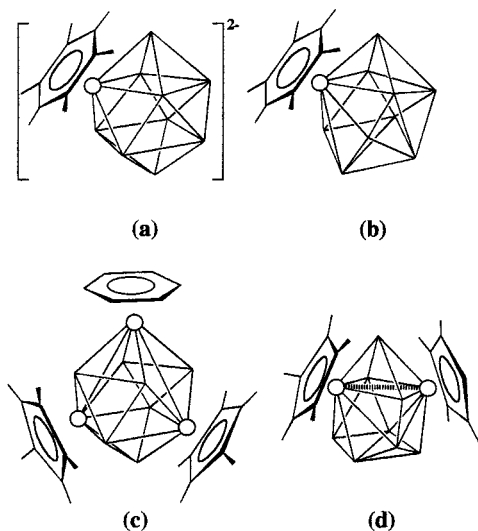
Figure 1. Molecular structure of $\{(\eta^5\text{-}C_5Me_5)Ru\}_2\{\eta^6\text{-}C_6H_6)Ru\}B_7H_7\}$, **2**. Selected bond distances (Å): Ru(1)−B(1) 2.172(10), Ru(1)−Ru(2) 2.8489(18), Ru(2)−B(3) 2.113-(13), Ru(2)−B(1) 2.118(10), Ru(2)−B(2) 2.274(10), B(1)−B(2) 1.724(17), B(2)−B(3) 1.721(19), B(2)−B(1)#3 1.724(17).

Chart 2

isocloso or hypercloso reflecting different perspectives on the origin of the difference.[11−13] Formally, **2** possesses 9 skeletal electron pairs (sep); hence, it constitutes an unprecedented example of a $(n - 1)$ sep closed cluster $((Cp^*Ru)_3Co(CO)_3B_3H_3$ is also a $(n - 1)$ cluster; however, it is adequately described as a tricapped tetrahedron.[14]). As seen in Chart 2c, it is the next member of the series in that two dsd rearrangements converts a bicapped square antiprism into the cluster shape displayed by **2**. Finally, **2** is also connected to $(Cp^*Re)_2B_8H_8$ (Chart 2d), a compound with $(n - 2)$ sep.[15] Its structure can be generated from a bicapped square antiprism by 2 dsd rearrangements and the addition of a cross-cluster M−M bond.

We have chosen to call compounds of this type hypoelectronic—a term originated by Corbett to describe
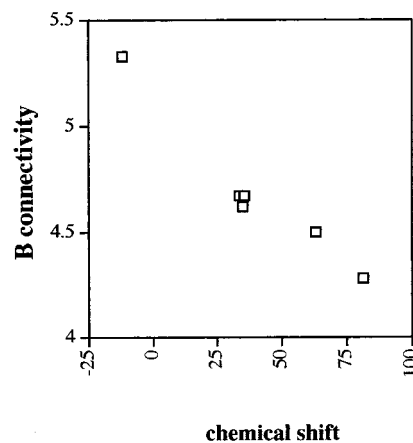
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Figure 2. Correlation between the average connectivity of the cluster vertexes occupied by BH fragments and the weighted average ^{11}B NMR chemical shift observed for each compound. From left to right the points correspond to: $[(\eta^6\text{-}C_6Me_6)RuB_9H_9]^{2-}$; $(\eta^6\text{-}C_6Me_6)RuB_9H_9$, $(pcym)RuB_9H_9$, and $(pcymRu)_2B_8H_8$; $(Cp^*Re)_2B_8H_8$; and **2**.

clusters that display distortions from the canonical shapes in order to accommodate a smaller number of sep.[16,17] A general attribute of the compounds discussed here is that as the number of sep decreases the cluster shape distorts to produce a greater number of lower and higher connectivity vertexes without changing the overall number of polyhedral edges. The metal atoms occupy the higher connectivity vertexes and the boron atoms the lower. The net result is that the average connectivity per boron decreases, and this is reflected in the weighted ^{11}B chemical shifts. In fact, there is a good correlation between these two numbers (Figure 2) where the inclusion of $(\eta^6\text{-}pcym)RuB_9H_9$ and $(\eta^6\text{-}pcymRu)_2B_8H_8$, pcym = 1-Me-4-^{i}Pr-$C_6H_4$,[18] suggests the correlation is not strongly affected by the number of metal atoms in the metallaborane or the substituents on the arene ring.

Experimental Section

General Procedures. Operations were conducted under argon atmosphere, and solvents were purified using standard techniques.[19] $\{(\eta^5\text{-}C_5Me_5)RuB_4H_{10}\}_2Ru$, **1**, was prepared as described earlier.[1] NMR spectra were recorded on a 300 or 500 MHz Varian FT-NMR spectrometer. Residual protons of solvent were used as reference (δ, ppm, benzene, 7.15), and a sealed tube containing $[(Me_4N)(B_3H_8)]$ in acetone-d_6 (δ_B, ppm, −29.7) was used as the external reference for the ^{11}B NMR. Infrared spectra were obtained on a Nicolet 205 FT-IR spectrometer. Mass spectra were obtained on Finnigan MAT Model 8400 mass spectrometer using the EI ionization mode.

Synthesis of $\{(\eta^5\text{-}C_5Me_5)Ru\}_2\{\eta^6\text{-}C_6H_6)Ru\}B_7H_7\}$, **2.** Five milligrams of $\{(\eta^5\text{-}C_5Me_5)RuB_4H_{10}\}_2Ru$, **1**, was loaded into a 5 mm NMR tube and 0.7 mL of C_6H_6 was added. The solution was put in a 95 °C oil bath for 6 h. Slow evaporation of the resulting orange solution gave red orange crystals. The yield is ∼60%.

Spectroscopic Data. $\{(\eta^5\text{-}C_5Me_5)Ru\}_2\{\eta^6\text{-}C_6H_6)Ru\}B_7H_7\}$, **2**: MS (EI), P^+= 740, 7B, 3Ru atoms. NMR: ^{11}B(C_6H_6, 22 °C),

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Table 1. Crystal Data and Structure Refinement for {C$_5$Me$_5$Ru}$_2${C$_6$H$_6$Ru)B$_7$H$_7$, 2

emp formula	C$_{26}$H$_{43}$B$_7$Ru$_3$
formula wt	734.48
cryst syst	orthorhombic
space grp	*Cmcm*
unit cell dimens (Å)	$a = 13.8251(14)$
	$b = 10.3360(16)$
	$c = 20.7562(77)$
volume (Å^3)	2965.9(12)
Z	4
density (calcd) (Mg/m^3)	1.643
F(000)	1464
wavelength (Å)	0.71073
absorption coefficient (mm^{-1})	1.521
crystal size (mm)	0.40 × 0.10 × 0.10
T (K)	293(2)
diffractometer	Nonius CAD4
θ range for data collection (deg)	2.46–24.97
index ranges	$0 \le h \le 16$, $0 \le k \le 12$, $-24 \le l \le 24$
scan method	ω/2q
scan rate	1.37–8.24°/min (in ω)
scan width	0.80 + 0.35°tanq (in ω)
total data collected	1603
unique data	1409 [R(int) = 0.0228]
unique obsd data	[$I > 2\sigma(I)$] 1060
decay correction	linear decay (0)
absorption correction	empirical
max and min transmission	1.0000 and 0.7684
refinement method	full-matrix on F^2 (SHELXL-93)
weighting scheme	σ weight
data/restraints/parameters	1409/0/99
goodness-of-fit on F^2	1.055
final R indices [$I > 2\sigma(I)$]	R1 = 0.0593, wR2 = 0.1535
R indices (all data)	R1 = 0.0816, wR2 = 0.1693
largest diff. peak and hole (e·Å^{-3})	2.639 and −1.434

δ 80.2 (d, J_{B-H} = 132 Hz, {^{1}H}, s, 4B), 102.0 (d, J_{B-H} = 154 Hz, {^{1}H}, s, 2B), 126.7.0 (d, J_{B-H} = 156 Hz, {^{1}H}, s, 1B); ^{1}H-({^{11}B, acetone-d_6, 22 °C), δ 11.49 (b, 1H, BH$_t$), 9.06 (b, 2H, BH$_t$), 8.44 (b, 4H, BH$_t$), 6.26 (s, C$_6$H$_6$), 1.60 (s, 30H, C$_5$Me$_5$).

Structure Determination. A red orange platelike crystal of **2** from a C$_6$H$_6$ solution suitable for X-ray diffraction was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.710 73 Å) on a CAD4 computer controlled κ axis diffractometer equipped with a graphite crystal, incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range 24° < 2θ < 28°, measured by the computer controlled diagonal slit method of centering. Crystal data are given in Table 1. Most of the nonhydrogen atoms were located by the direct method; the remaining nonhydrogen atoms were found in succeeding difference Fourier synthesis. Least-squares refinement was carried out on F^2 for all reflections. In the final refinement hydrogen atoms for the pentamethylcyclopentadienyl groups were refined with an idealized riding model that restrained the C–H distance to 0.96 Å, and the isotropic thermal parameter of a hydrogen atom to 1.5 times of the equivalent isotropic thermal parameter of its bonded carbon atom. After all non-hydrogen atoms were refined anisotropically and hydrogen atoms of pentamethylcyclopentadienyl groups refined isotropically, difference Fourier synthesis located the rest of the hydrogen atoms which were refined isotropically with bond length restraints. All reflections, including those with negative intensities, were included in the refinement, and the $I > 2\sigma(I)$ criterion was used only for calculating R1. Parameters of the refinement are given in Table 1.

Supporting Information Available: Tables of atomic coordinates, bond distances and angles, aniostropic thermal parameters and H atom coordinates of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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