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Insertion of B−X (X = Cl, SMe_2) Moieties into Ruthenaborane Frameworks: Synthesis and Characterization of $(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_mCl_n$, ($m$, n = 4, 3; 5, 2; 7, 2), *closo*-1-(SMe_2)-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu_3\text{-}H)B_5HCl_3$, and *closo*-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2B_6H_3Cl_3$

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The reaction of *nido*-1,2-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)_2B_3H_7$ (**1**) with the dichloroborane $BHCl_2{\cdot}SMe_2$ results in the formation of three sets of B−Cl inserted metallaborane products: *nido*-1,2-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_7Cl_2$ (**2**), *pileo*-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_5Cl_2$ (three geometric isomers, **3**−**5**), and *pileo*-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_4Cl_3$ (a pair of geometric isomers, **6** and **7**). When the same reaction was carried out under more forcing conditions, three new metallaborane compounds, *closo*-1-(SMe_2)-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu_3\text{-}H)B_5HCl_3$ (a pair of geometric isomers, **8** and **9**) and *closo*-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2B_6H_3Cl_3$ (**10**), were isolated in low yield in addition to **2**−**7**. Compounds **8** and **9** exhibit a capped-octahedral geometry, and **10** exhibits a seven-sep (skeletal electron pair) bicapped-octahedral geometry. Reaction of *nido*-2,4-$(\eta^5\text{-}C_5Me_5Ru)_2B_6H_{12}$ and *nido*-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2B_8H_{12}$ with $BHCl_2{\cdot}SMe_2$ results in substitution of terminal H by Cl, producing *nido*-2,4-$(\eta^5\text{-}C_5Me_5Ru)_2B_6H_{10}Cl_2$ (**11**) and *nido*-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2B_8H_{11}Cl$ (**12**) in 82% and 75% yields, respectively.

Introduction

Some of the earliest information on the reactivity of the polyhedral boranes originated in studies of the electrophilic substitution of cage B−H terminal bonds.[1] The halogenation of boron cage compounds is well-known.[2−5] Studies of peralkylation,[6] perhydroxylation,[7] and perhalogenation[2a,8] continue to be of significant interest, because persubstituted borane clusters of all types have potential applications as hydrophobic space-filling pharmacophores,[9] weekly coordinating anions,[10] components of radioimaging reagents,[11] and targets for boron neutron capture therapy.[12] The recent demonstration by Hawthorne's group[6b,c,7,13] of the strong dependence of cluster properties on exo-cluster substituents has led us to explore the development of routes to B-functionalized[14−16] metallaborane species. Methods of halogenation are of particular interest, since halogenated species are important in the synthesis of extended polymetallic clusters[16] and B−B linked systems.[15d,17,18]

The properties of metallaboranes are considerably different from those of pure boranes and carboranes, and

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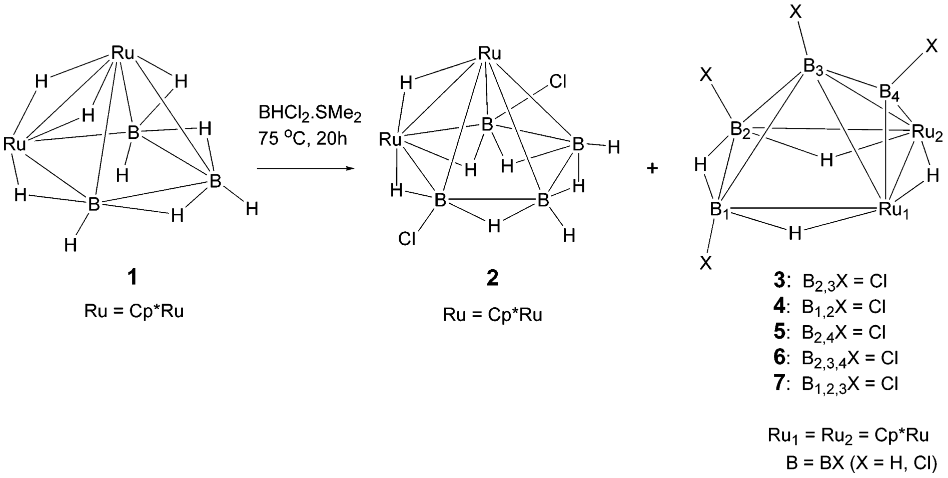
Scheme 1



it is not clear yet what factors will dominate the substitution chemistry. Very little information is known for metallaboranes, although we have previously reported a few reactions that resulted in the chlorination of boron on metallaboranes.[19−22] Chloromonoboranes were used in the cluster building process to access products not found with $BH_3\cdot THF$,[19a] and chlorinated products were produced either by direct incorporation of a chloroborane fragment or by H/Cl exchange.[19,23,24] Although these products increased the complexity of the problem, they also provided an interesting alternative to conventional methods of boron framework halogenation and B−Cl fragment incorporation.

The present work was initiated to explore more thoroughly the reactivity of the ruthenaborane *nido*-1,2-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)_2B_3H_7$[25] (**1**) in terms of the distribution of chlorinated metallaboranes generated from $BHCl_2\cdot SMe_2$. Although the objective of selective halogenation was not fully achieved, interesting chlorine-substituted metallaborane derivatives are found, as well as some which incorporate a three-electron $B{-}SMe_2$ fragment.

Results and Discussion

Formation of $M_2B_4H_nCl_2$ and $M_2B_4H_5Cl_3$ ($M = \eta^5\text{-}C_5Me_5Ru$; $n = 6, 8$). When the reaction of *nido*-1,2-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)_2B_3H_7$ (**1**) with $BHCl_2\cdot SMe_2$ in toluene is carried out at 75 °C, three sets of B−Cl inserted metallaborane products were isolated, $(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_7Cl_2$ (**2**), $(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_5Cl_2$ (three geometric isomers, **3**−**5**), and $(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_4Cl_3$ (a pair of geometric isomers, **6** and **7**), which are discussed separately (Scheme 1).

Compound **2** was characterized by spectroscopy and with an X-ray structure. The ^{11}B NMR spectrum shows one type of BH plus one type of BCl environment in a 1:1 ratio. From the mass spectral analysis combined with the ^{11}B NMR spectrum, **2** is formulated as $(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_7Cl_2$. Furthermore, the ^1H NMR spectrum shows two equivalent Cp* ligands, two distinct B−H−B groups (2:1), two Ru−H−B protons, and one Ru−H−Ru proton. Consistent with the spectroscopic data, the molecular structure of **2**, shown in Figure 1, exhibits a pentagonal-pyramidal framework similar to that observed for *nido*-1,2-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_9$.[25]

A second set of products, **3**−**5**, has been isolated in yields of 8%, 55%, and 4%, respectively. The spectroscopic data show that compounds **3**−**5** are geometrical isomers differing in the position of the Cl and H groups relative to the Ru−Ru edge of the cluster. The X-ray structure of one of the compounds, shown in Figure 2, illustrates the capped-square-pyramidal geometry of all three. The spectroscopic data for **3** in solution are consistent with the solid-state structure. The ^1H NMR data of **3** and **5** reveal the presence of two kinds of Cp* signals, two kinds of Ru−H−B, one B−H−B, and one Ru−H−Ru proton. On the other hand, **4** shows only one kind of Cp* signal, two kinds of Ru−H−B signals, one

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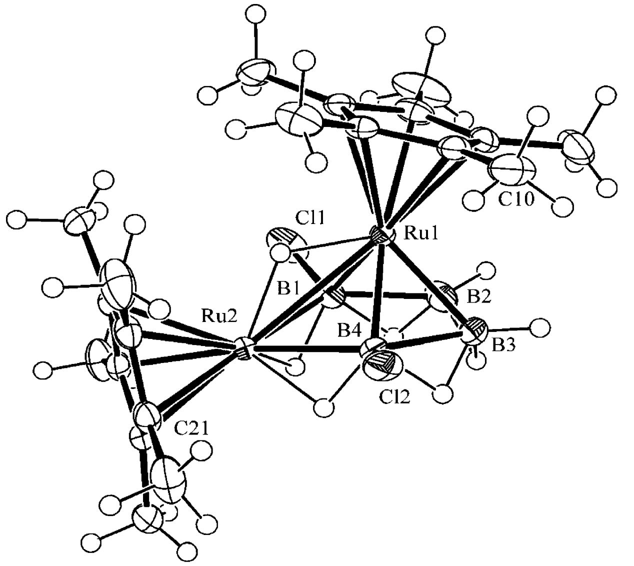

Figure 1. Molecular structure of *nido*-1,2-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_7Cl_2$ (**2**). Selected bond distances (Å) and angles (deg): Ru(1)−B(2) = 2.128(2), Ru(1)−Ru(2) = 2.8644(2), B(1)−B(2) = 1.806(4), B(1)−Ru(2) = 2.278(2), B(3)−B(4) = 1.818(4); B(2)−Ru(1)−B(3) = 50.67(12), B(2)−Ru(1)−B(4) = 87.21(11), B(3)−Ru(1)−B(4) = 50.37(10), B(3)−Ru(1)−Ru(2) = 89.63(7), B(4)−Ru(1)−Ru(2) = 51.62(6), B(2)−B(1)−Ru(2) = 120.77(16), Cl(1)−B(1)−Ru(2) = 122.09(13), B(1)−Ru(2)−Ru(1) = 47.64(6).

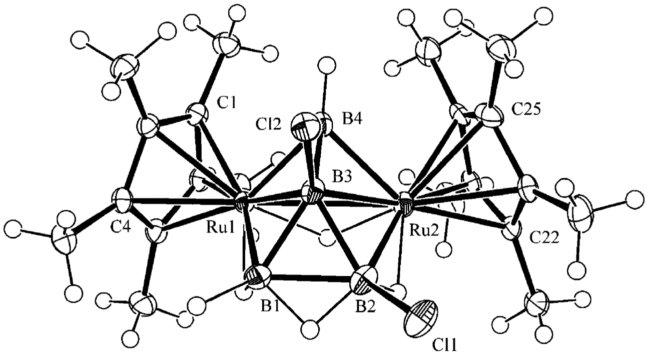

Figure 2. Molecular structure of *pileo*-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_5Cl_2$ (**3**). Selected bond distances (Å) and angles (deg): Ru(1)−B(4) = 2.030(2), Ru(1)−B(1) = 2.226(2), Ru(1)−Ru(2) = 2.8690(2), Ru(2)−B(4) = 2.047(2), Ru(2)−B(2) = 2.214(2), B(3)−B(4) = 1.800(3), B(4)−Ru(1)−B(1) = 95.61(8); B(1)−Ru(1)−B(3) = 46.07(8), B(4)−Ru(1)−C(1) = 85.30(8), B(1)−Ru(1)−Ru(2) = 76.74(6), B(3)−Ru(1)−Ru(2) = 50.12(5), B(3)−B(1)−B(2) = 58.86(12), B(2)−B(1)−Ru(1) = 102.55(12), B(4)−Ru(2)−B(2) = 95.32(8).

B−H−B signal, and one Ru−H−Ru proton. Hence, the substitution positions are assigned as shown in Scheme 1.

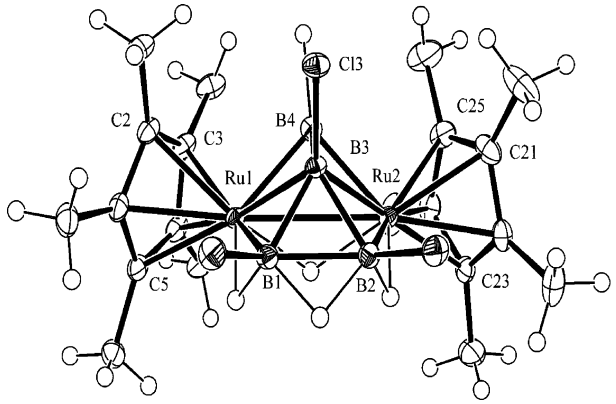

Figure 3. Molecular structure of *pileo*-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_4Cl_3$ (**7**). Selected bond distances (Å) and angles (deg): Ru(1)−B(4) = 2.046(2), Ru(1)−B(3) = 2.225(2), Ru(1)−Ru(2) = 2.8846(2), B(1)−B(2) = 1.814(3), Ru(2)−B(4) = 2.043(2), Cl(3)−B(3) = 1.848(2), B(3)−B(4) = 1.782(3); B(4)−Ru(1)−B(1) = 95.13(8), C(2)−Ru(1)−B(1) = 119.15(8), B(1)−Ru(1)−B(3) = 46.30(8), B(4)−Ru(1)−Ru(2) = 45.09(6), B(1)−Ru(1)−Ru(2) = 75.99(6), B(4)−Ru(2)−B(3) = 49.08(8), B(2)−Ru(2)−C(24) = 163.21(8).

The third set of products, **6** and **7**, has been isolated in 10% yield as a mixture of two compounds roughly in a ratio of 4:6. The mass spectrum of the mixture showed a single parent ion envelope, suggesting the presence of two geometric isomers containing three Cl atoms. By selection of a crystal, a solid-state structure determination of one of the isomers, **7**, shown in Figure 3, was obtained. It possesses the same capped-square-pyramidal Ru_2B_4 framework of **3**−**5**. Attempts to separate these isomers by TLC failed; however, the ^{11}B and ^1H NMR signals of these isomers could be unambiguously assigned from the NMR spectrum of the mixture. The ^{11}B NMR spectrum shows two sets of boron resonances; one set contains three kinds of boron resonances, and the other set contains four kinds of boron resonances. Similarly, the ^1H NMR spectrum shows two sets of Cp* signals; one set contains one kind of Cp* protons, and the other contains two kinds of Cp* protons. As the structure determination of **7** reveals a plane of symmetry, it has been assigned to *pileo*-2,3-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_4Cl_3$ with Cl substitution in the boron 1-, 2-, and 3-positions, while **6** must have the 1-, 3-, and 4-positions substituted by Cl (Scheme 1).

The spectroscopic data of **3**−**5** showed that **2** had lost two hydrogen atoms with heating, suggesting a six-atom, seven-sep cluster product. However, these data are not accommodated by a closo cluster structure, and a solid-state structure determination revealed the clusters to be *pileo*-$(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_5Cl_2$, (**3**−**5**), similar to that observed for $(\eta^5\text{-}C_5Me_5Ru)_2(\mu\text{-}H)B_4H_7$.[25] The square-pyramidal framework of **3**−**7** is also similar to that observed for *nido*-2,3-$(\eta^5\text{-}C_5Me_5Rh)_2B_3H_7$,[25] but with an added B−X (X = H, Cl) fragment which caps the Ru_2B face.

The overall conversion of **1** into product mixture **2**−**7** is slow. The reaction of **1** with $BHCl_2{\cdot}SMe_2$ initially may lead to $(\eta^5\text{-}C_5Me_5Ru)_2B_4H_6Cl_2$, which may then further undergo a Cl-substitution reaction to form $(\eta^5\text{-}C_5Me_5Ru)_2B_4H_5Cl_3$. On thermolysis at 75 °C for 5 days, isomer **4** survives, whereas the other two isomers decompose under these conditions without isomer interconversion. A similar result is observed for isomers **6** and **7**, where isomer **7** is more stable. The above results show that stability relative to decomposition correlates with the position of substitution of the Cl atoms. For example, a Cl atom in the basal position imparts more stability than a Cl atom in the apical or capping position. For **3**−**5** and **6** and **7** stability toward thermal degradation has been established as **4** > **3** > **5** and **7** > **6**.

B−X and B−SMe₂ Fragment Incorporation. In an effort to achieve perchlorination of the 2,3-$(\eta^5\text{-}C_5Me_5Ru)_2B_4H_8$ framework, we investigated the reaction of **1** with $BHCl_2{\cdot}SMe_2$ under more forcing conditions for

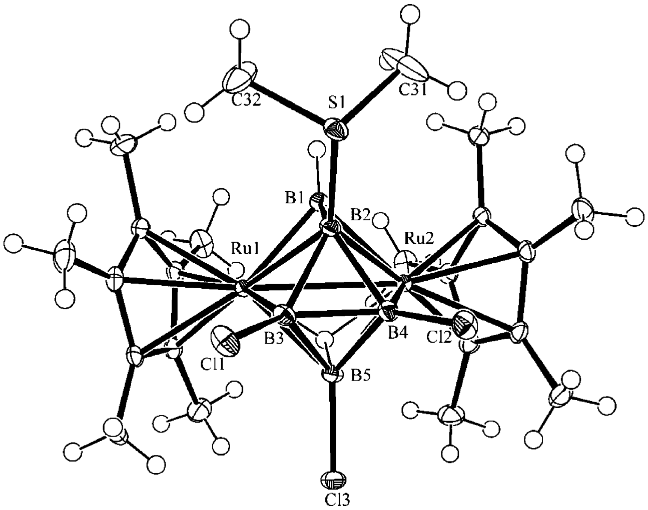

Figure 4. Molecular structure of *closo*-1-(SMe$_2$)-2,3-(η^5-C$_5$Me$_5$Ru)$_2$(μ_3-H)B$_5$HCl$_3$ (**9**). Selected bond distances (Å) and angles (deg): Ru(1)−B(1) = 2.0408(18), Ru(1)−B(5) = 2.2443(18), Ru(1)−Ru(2) = 2.7890(2), S(1)−B(2) = 1.9091(18), B(1)−B(2) = 1.816(3); B(1)−Ru(1)−B(2) = 50.19(7), B(3)−Ru(1)−B(2) = 47.69(7), B(1)−Ru(1)−B(5) = 96.66(7), B(3)−Ru(1)−B(5) = 46.23(7), B(1)−Ru(1)−Ru(2) = 47.23(5), B(3)−Ru(1)−Ru(2) = 75.03(5), B(3)−B(2)−B(1) = 121.66(13), B(4)−B(2)−S(1) = 116.92(11).

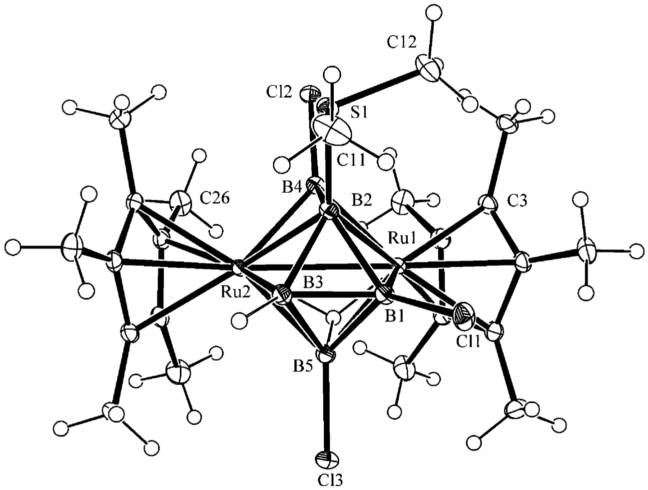

Figure 5. Molecular structure of *closo*-1-(SMe$_2$)-2,3-(η^5-C$_5$Me$_5$Ru)$_2$(μ_3-H)B$_5$HCl$_3$ (**8**). Selected bond distances (Å) and angles (deg): Ru(1)−B(4) = 2.036(3), Ru(1)−B(1) = 2.144(3), Ru(1)−B(5) = 2.267(3), Ru(1)−Ru(2) = 2.7933(4), S(1)−B(2) = 1.913(3), B(2)−B(4) = 1.823(5); B(4)−Ru(1)−B(1) = 96.45(13), B(4)−Ru(1)−C(2) = 132.95(12), B(4)−Ru(1)−B(2) = 50.30(12), B(1)−Ru(1)−B(2) = 46.80(12), B(1)−Ru(1)−Ru(2) = 74.73(9), B(4)−Ru(2)−B(2) = 50.59(13), B(3)−B(2)−B(4) = 122.2(2), B(1)−B(2)−B(4) = 122.1(2), B(3)−B(2)−S(1) = 119.8(2).

longer times. Treatment of **1** with BHCl$_2$·SMe$_2$ in toluene at 95 °C for 30 h gave the three new metallaboranes **8**−**10** along with the formation of **3**−**7**. The mass spectrometric data for metallaboranes **8** and **9** show a molecular ion peak at *m/z* 697 with a fragment loss of *m/z* 60. The ^{11}B NMR spectra of **8** and **9** display five and four resonances, respectively, with intensity ratios of 1:1:1:1:1 and 1:2:1:1. Thus, on the basis of the mass spectral analysis combined with ^{11}B NMR spectra, these metallaboranes have been formulated as (η^5-C$_5$Me$_5$Ru)$_2$B$_5$H$_2$Cl$_3$(SMe$_2$) (**8** and **9**), thereby requiring the incorporation of a BSMe$_2$ fragment. The ^{11}B NMR spectrum of **10**, on the other hand, shows six different boron signals with equal intensities, indicating the incorporation of two boron cluster fragments. Compounds, **8**−**10** have all been characterized by X-ray diffraction studies.

The ^{1}H NMR spectrum of **9** shows a single Cp* resonance at δ 1.89 ppm, and **8** shows two Cp* resonances at δ 1.92 and 1.91 ppm. In addition to this, both molecules show the presence of a resonance for the BH$_t$ proton and one Ru−H(B)−Ru proton. The ^{1}H{^{11}B} experiment confirms the presence of a triply bridged proton via observed coupling of the Ru−H−Ru proton with the axial boron (B−Cl). The ^{11}B NMR spectrum of **9** shows four different boron atoms in the ratio of 1:2:1:1, one of which is a doublet, while all the others are singlets. The most upfield resonance at δ −12.3 ppm has been assigned to a boron atom attached to a SMe$_2$ ligand, and the most downfield resonance at δ 130.3 ppm has been assigned to the capping boron atom. The ^{11}B NMR data of **8** immediately suggest a similarity to **9**, albeit with a BCl rather than BH face-capping fragment. As this lowers the symmetry, the exchange must involve the one of the two equivalent BCl groups in **9**.

The solid-state structures of **8** and **9**, shown in Figures 4 and 5, reveal capped-octahedral clusters. Consistent with the NMR data, the structures of **8** and **9** differ only in the fact that **9** has a plane of symmetry with a BH capping fragment, whereas the BH fragment of **8** is part of the octahedral framework.

Like *closo*-boranes in general, **8** and **9** are relatively unreactive, and isomerization of the 4,5,6-species to 4,6,7 or vice versa could not be achieved by thermal means. A sample of **9** was heated at 95 °C for 5 days, resulting in slight decomposition with no change in the ^{11}B NMR spectrum. On the other hand, when a sample of **8** was heated under the same conditions, complete decomposition occurred. Perhaps this is why **8** is a minor component in the mixture.

Although we do not have any direct evidence of intermediates for the formation of **8** and **9** from **1**, reaction of **1** with BHCl$_2$·SMe$_2$ may lead initially to (η^5-C$_5$Me$_5$Ru)$_2$B$_4$H$_7$SMe$_2$, which may then further undergo BCl incorporation followed by an H−Cl exchange reaction to form isomers **8** and **9**, as shown in Scheme 2. The existence of borane clusters containing SMe$_2$ ligands are known;[26−28] however, to the best of our knowledge this synthesis of dialkyl sulfide derivatives is the first example for metallaboranes.

Another product isolated from the reaction of **1** with BHCl$_2$·SMe$_2$ at 95 °C results from the incorporation of two boron cluster fragments. The composition and structure of **10** are established from mass spectral analysis and X-ray diffraction studies. The exact mass measurement of **10** gives a molecular ion corresponding to C$_{20}$H$_{33}$B$_6$Ru$_2$Cl$_3$. The ^{11}B NMR spectrum shows six types of boron atoms with equal intensity, three of which

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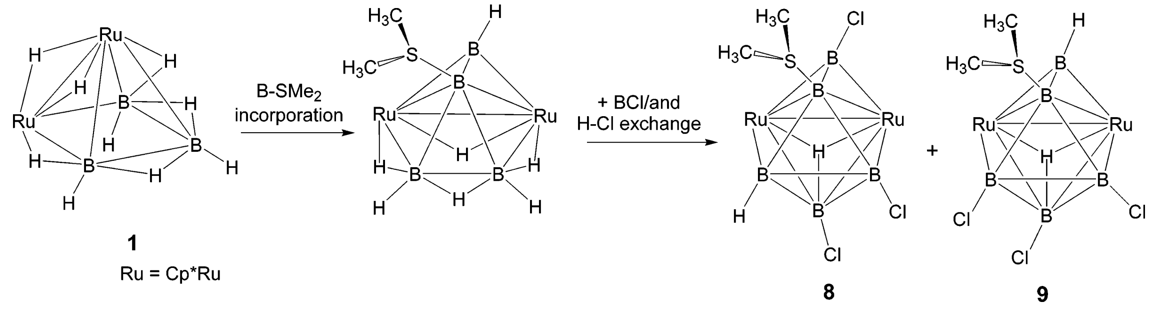
(27) Miller, H. C.; Miller, N. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1963**, *85*, 3885.

(28) Miller, H. C.; Miller, N. E.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1456.

Scheme 2



are singlets in the $^1H\{^{11}B\}$ NMR. The ^1H NMR spectra reveal that **10** has two types of Cp* and three types of B−H protons.

The single-crystal X-ray diffraction structure of *closo*-2,3-(η^5-$C_5Me_5Ru)_2B_6H_3Cl_3$ (**10**) in Figure 6 shows a bicapped-octahedral cluster geometry. If the Cp*Ru fragment is reasonably treated as a one-electron ligand, then **10** also possesses the seven skeletal electron pairs appropriate for its structure. The core cluster of **10** is the same as that found for the seven-sep *closo*-(η^5-$C_5Me_5W)_2B_6H_{10}$ observed in the reaction of $\{\eta^5$-$C_5Me_5W\}$-B_4H_8 with excess BH_3·THF.[29]

The pathway for the formation of **10** from **1** is of interest, but we were unable to obtain any direct information. One possible pathway is the addition of two BH fragments to isomers **3**−**5**/or **6** and **7** followed by an H/Cl exchange reaction. However, the reaction of **8** and **9** with $BHCl_2$·SMe_2 does not produce **10**.

Substitution of H on [(η^5-$C_5Me_5Ru)_2B_nH_{12}$] (n = 6, 8) by Cl. Testing for further cluster buildup of [(η^5-$C_5Me_5Ru)_2B_nH_{12}$][30] (n = 6, 8) with $BHCl_2$·SMe_2 leads to substitution of terminal H by Cl. Thermolysis of yellow (η^5-$C_5Me_5Ru)_2B_6H_{12}$ and red (η^5-$C_5Me_5Ru)_2B_8H_{12}$ with an excess of $BHCl_2$·SMe_2 at 85 °C yielded **11** and **12** in 82% and 75% yields, respectively. Mass spectrometric data were obtained for both **11** and **12**, suggesting the molecular formulas (η^5-$C_5Me_5Ru)_2B_6H_{10}Cl_2$ and (η^5-$C_5Me_5Ru)_2B_8H_{11}Cl$, respectively.

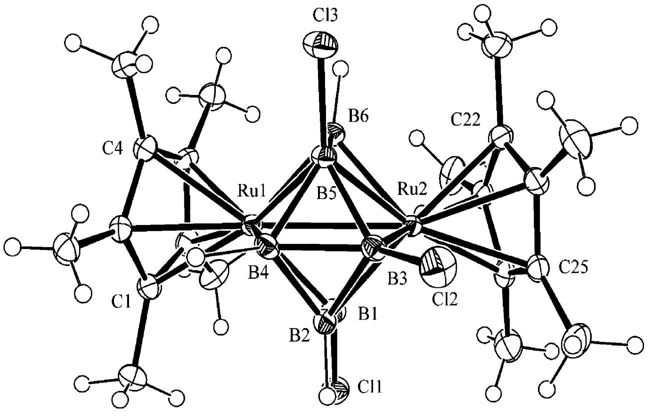


Figure 6. Molecular structure of *closo*-2,3-(η^5-$C_5Me_5Ru)_2B_6H_3Cl_3$ (**10**). Selected bond distances (Å) and angles (deg): Ru(1)−B(6) = 2.021(5), Ru(1)−B(4) = 2.132(5), Ru(1)−B(5) = 2.248(5), Ru(1)−Ru(2) = 2.7155(5), B(1)−Ru(2) = 2.076(5), Ru(2)−B(2) = 2.293(5), B(2)−B(4) = 1.742(7), B(5)−B(6) = 1.865(7); B(6)−Ru(1)−B(1) = 89.59(19), B(1)−Ru(1)−B(4) = 94.93(19), B(1)−Ru(1)−B(5) = 98.59(18), B(4)−Ru(1)−B(5) = 46.40(17), B(4)−Ru(1)−Ru(2) = 76.92(13), Ru(1)−B(1)−Ru(2) = 81.92(17), B(1)−Ru(2)−B(5) = 97.92(18).

The ^{11}B NMR spectrum of **11** exhibits two signals at δ 38.1 and 11.2 ppm with 4:2 area ratios. The $^1H\{^{11}B\}$ decoupled spectrum suggests the presence of one kind of terminal H atom and two kinds of bridging H atoms, at δ 6.88, −0.32, and −13.7 ppm, respectively. One of the resonances assigned to bridging hydrogens is at high field, consistent with a proton associated with a metal atom. The ^{11}B NMR spectrum of **11** is similar to that of *nido*-(η^5-$C_5Me_5Ru)_2B_6H_{12}$, except that one of the resonances is shifted downfield by about 10 ppm. By comparison to the boron resonances of its parent molecule, *nido*-(η^5-$C_5Me_5Ru)_2B_6H_{12}$, this boron signal has been assigned to a boron which is attached to Cl. The ^{11}B and ^1H NMR spectra of **12** are similar to those of its parent compound *nido*-(η^5-$C_5Me_5Ru)_2B_8H_{12}$.

The molecular structures of **11** and **12** shown in Figures 7 and 8 are consistent with the analysis of the observed spectroscopic data and reveal core geometries that are the same as those observed for *nido*-(η^5-$C_5Me_5Ru)_2B_6H_{12}$ and *nido*-(η^5-$C_5Me_5Ru)_2B_8H_{12}$, respectively. The 8-vertex ruthenaborane **11** and 10-vertex **12** have structures analogous to those of B_8H_{12} and $B_{10}H_{14}$, respectively.[30,31] When the {Cp*Ru} fragment is considered to be a three-orbital, one-electron fragment, the formal electron counts are 10 sep for **11** and 11 sep for **12**; the structure of **11** follows the borane analogy, but **12** is formally one pair short.[30] The 10-vertex ruthenaborane **12** has a structure similar to that of *nido*-$B_{10}H_{14}$ but with a diamond−square−diamond rearrangement[30] and can be considered to be an isonido compound.[32]

Curiously, the reactions of *nido*-(η^5-$C_5Me_5Ru)_2B_6H_{12}$ and *nido*-(η^5-$C_5Me_5Ru)_2B_8H_{12}$ with $BHCl_2$·SMe_2 lead to the formation of **11** and **12**, respectively, in essentially quantitative yield, whereas **1** yields five different kinds of products (**2**−**10**). One possible explanation is that **11** and **12** possess more stable core structures and are not readily subject to multiple substitutions or boron cluster fragment addition. This is consistent with the fact that *nido*-(η^5-$C_5Me_5Ru)_2B_nH_{12}$ (n = 6, 8) clusters do not react further with BH_3·THF or BH_3·SMe_2, eliminating that pathway.

Conclusion

An alternative route to the chlorination of boron on ruthenaboranes has been developed on the basis of the

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[29] Ghosh, S.; Noll, B. C.; Halet, J.-F.; Fehlner, T. P. To be submitted for publication in *Organometallics*.

[30] Ghosh, S.; Beatty, A. M.; Fehlner, T. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 4678.

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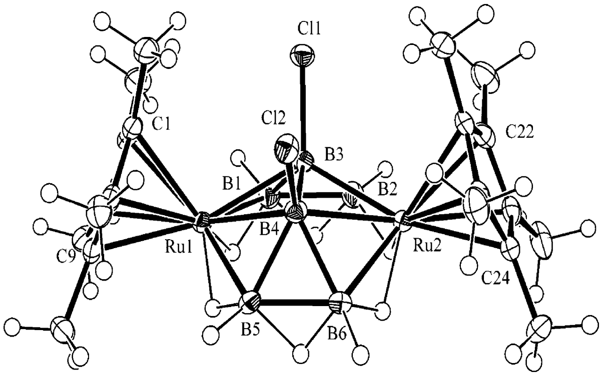

Figure 7. Molecular structure of *nido*-2,4-(η^5-$C_5Me_5Ru)_2B_6H_{10}Cl_2$ (**11**). Selected bond distances (Å) and angles (deg): Ru(1)–B(5) = 2.209(4), Ru(1)–B(4) = 2.310(4), B(1)–B(2) = 1.743(6), Ru(2)–B(3) = 2.312(4), B(3)–B(4) = 1.775(6), B(4)–B(6) = 1.787(6), B(5)–B(6) = 1.740(6); B(5)–Ru(1)–B(1) = 111.81(17), B(1)–Ru(1)–B(4) = 86.96(16), B(3)–Ru(1)–B(4) = 45.26(15), B(2)–B(1)–B(3) = 60.7(2), B(2)–B(1)–Ru(1) = 120.7(3), B(3)–B(1)–Ru(1) = 69.5(2), B(6)–Ru(2)–B(2) = 111.73(17).

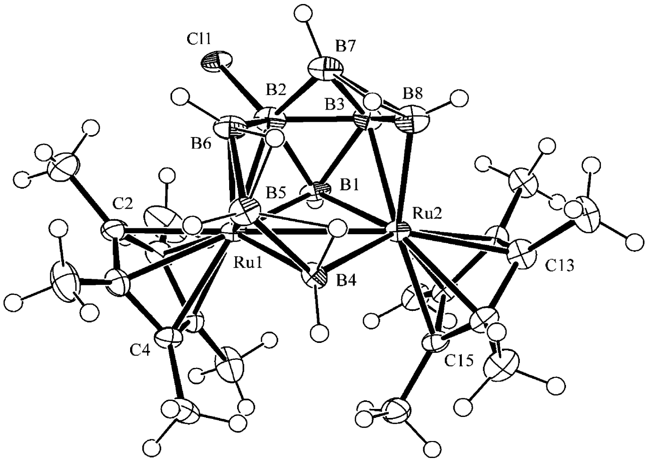

Figure 8. Molecular structure of *nido*-2,3-(η^5-$C_5Me_5Ru)_2B_8H_{11}Cl$ (**12**). Selected bond distances (Å) and angles (deg): Ru(1)–Ru(2) = 2.9012(10), Ru(1)–B(6) = 2.179(6), Cl(1)–B(2) = 1.830(8), Ru(1)–B(2) = 2.241(7), Ru(2)–B(3) = 2.274(7), B(1)–B(3) = 1.776(9), Cl(1)–B(2) = 1.830(8); B(4)–Ru(1)–B(6) = 88.8(3), B(1)–Ru(1)–B(6) = 91.2(3), B(4)–Ru(1)–B(5) = 49.3(2), B(4)–Ru(1)–B(2) = 106.9(3), B(6)–Ru(1)–Ru(2) = 89.9(2), B(4)–Ru(2)–B(8) = 97.9(3), B(7)–B(2)–Cl(1) = 110.8(4).

reaction of *nido*-1,2-(η^5-$C_5Me_5Ru)_2(\mu$-$H)_2B_3H_7$ and *nido*-(η^5-$C_5Me_5Ru)_2B_nH_{12}$ (n = 6, 8) clusters with $BHCl_2 \cdot SMe_2$. For the cluster containing three boron atoms, the reaction at lower temperature yielded chlorinated products either by direct incorporation of a chloroborane fragment, B–Cl, or by H/Cl exchange; however, at higher temperatures more complex chemistry is observed. Not only are interesting metallaborane derivatives obtained by novel insertion of B–Cl moieties into *nido*-1,2-(η^5-$C_5Me_5Ru)_2(\mu$-$H)_2B_3H_7$ but also a three-electron B–SMe_2 fragment is incorporated into the cluster. The direct incorporation of a three-electron B–SMe_2 fragment into metallaborane may be useful for the preparation of other functionalized metallaborane clusters. In contrast, the cluster substitution reactions at B–H on the (η^5-$C_5Me_5Ru)_2B_nH_{12}$ (n = 6, 8) cluster cleanly yields the dichloro species (η^5-$C_5Me_5Ru)_2B_6H_{10}Cl_2$ and monochloro species (η^5-$C_5Me_5Ru)_2B_8H_{11}Cl$ with the same cluster structures as the starting material. Although, the objective, controlled chlorination reaction of metallaborane was only achieved for the larger clusters, the route constitutes an alternative to conventional methods, provided the cluster framework is relatively inert toward framework expansion and fragment exchange reactions.

Experimental Section

General Procedures. All the operations were conducted under an Ar/N_2 atmosphere using standard Schlenk techniques. Solvent were distilled prior to use under N_2. $BH_3 \cdot THF$, $BHCl_2 \cdot SMe_2$, and $LiBH_4$ in THF (Aldrich) were used as received. (η^5-$C_5Me_5Ru)_2(\mu$-$H)_2B_3H_7$ (**1**)[25] and (η^5-$C_5Me_5Ru)_2B_nH_{12}$[30] (n = 6, 8) were prepared as described previously. Chromatography was carried out on 3 cm of silica gel in a 2.5 cm diameter column. Thin-layer chromatography was carried out on 250 mm diameter alumina-supported silica gel TLC plates. NMR spectra were recorded on a 300 MHz Varian or 400 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ (ppm) benzene, 7.15), while a sealed tube containing $[Me_4N(B_3H_8)]$ in acetone-d_6 (δ(B) (ppm), −29.7) was used as an external reference for the ^{11}B NMR. Infrared spectra were obtained on a Nicolet 205 FT-IR spectrometer. Mass spectra were obtained on a JEOL JMS-AX505HA mass spectrometer with perfluorokerosene as standard. Crystal data were collected and integrated using a Bruker Apex system, with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation at 100 K. The structure was solved by heavy-atom methods using SHELXS-97 and refined using SHELXL-97 (G. M. Sheldrick, University of Göttingen).

Preparation of (η^5-$C_5Me_5Ru)_2(\mu$-$H)B_4H_7Cl_2$ (2) and (η^5-$C_5Me_5Ru)_2(\mu$-$H)B_4H_mCl_n$ (3–7: m, n = 5, 2; 4, 3). In a typical reaction, *nido*-1,2-(η^5-$C_5Me_5Ru)_2(\mu$-$H)_2B_3H_7$ (**1**; 0.2 g, 0.389 mmol) was loaded into a 100 mL dried Schlenk flask with 20 mL of freshly distilled toluene to generate a yellow solution. $BHCl_2 \cdot SMe_2$ (0.28 mL, 2.33 mmol) was added very slowly by syringe, and the reaction mixture was placed into an oil bath having a temperature of 75 °C and was heated for 18 h, converting the yellow solution to a red solution. The reaction mixture was warmed to room temperature, the solvent was evaporated, and the residue was extracted into hexane and the extract filtered through a small neutral alumina column. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with hexane–CH_2Cl_2 (7/3 v/v) yielded five closely spaced bands: the first yellow band has been characterized as $(Cp^*Ru)_2(\mu$-$H)B_4H_7Cl_2$ (**2**; 0.04 g, 18%), the second red band as $(Cp^*Ru)_2(\mu$-$H)B_4H_5Cl_2$ (**5**; 0.009 g, 4%), the third orange band as $(Cp^*Ru)_2(\mu$-$H)B_4H_5Cl_2$ (**4**; 0.12 g, 55%), the fourth orange band as $(Cp^*Ru)_2(\mu$-$H)B_4H_5Cl_2$ (**3**; 0.01 g, 8%), and the fifth orange band as $(Cp^*Ru)_2(\mu$-$H)B_4H_4Cl_3$ (**6** and **7**; 0.02 g, 10%; mixture of two isomers).

Data for 2. MS (FAB; *m/z*): P^+(max) 594 (isotopic pattern for 2Ru, 2Cl, and 4B atoms); mass calcd for $^{12}C_{20}{}^{1}H_{38}{}^{11}B_4{}^{101}Ru_2{}^{37}Cl_2$ 595.0731, obsd 595.0773. ^{11}B NMR (C_6D_6, 22 °C): δ 30.43 (d, J_{B-H} = 51 Hz, 2B), 0.08 (d, J_{B-H} = 75 Hz, 2B). ^1H NMR (C_6D_6, 22 °C): δ 2.47 (partially collapsed quartet (pcq), 2 BH_t), 1.88 (s, 15H, Cp*), 1.87 (s, 15H, Cp*), −1.63 (quartet on ^1H–^{11}B decoupling, 2B–H–B), −3.87 (quintet on ^1H–^{11}B decoupling, 1B–H–B), −12.07 (doublet on ^1H–^{11}B decoupling, 2Ru–H–B), −12.82 (s, 1Ru–H–Ru). IR (hexane, cm^{-1}): 2506 w, 2448 w (B–H_t).

Data for 3. MS (EI; *m/z*): P^+(max) 590 (isotopic pattern for 2Ru, 2Cl, and 4B atoms); mass calcd for $^{12}C_{20}{}^{1}H_{36}{}^{11}B_4{}^{101}Ru_2{}^{37}Cl_2$ 593.2322, obsd 593.2345. ^{11}B NMR (C_6D_6, 22 °C): δ 132.08 (s, br, 1B), 22.96 (s, 1B–Cl), 18.56 (s, br, 1B), −9.3 (s, 1B–Cl). ^1H NMR (C_6D_6, 22 °C): δ 10.75 (partially collapsed quartet (pcq), 1BH$_t$), 5.25 (pcq, 1BH$_t$), 1.69 (s, 15H, Cp*), 1.65 (s, 15H, Cp*), 0.75 (s, br, 1B−H−B), −9.79 (s, br, 1Ru−H−B), −10.87 (s, br, 1Ru−H−B), −15.63 (s, 1Ru−H−Ru). IR (hexane, cm^{-1}): 2498 w, 2456 w (B−H$_t$).

Data for 4. MS (EI; *m/z*): P$^+$(max) 589 (isotopic pattern for 2Ru, 2Cl, and 4B atoms); mass calcd for $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{36}{}^{11}\mathrm{B}_4{}^{101}\mathrm{Ru}_2{}^{37}\mathrm{Cl}_2$ 593.2322, obsd 593.2400. ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 125.14 (s, br, 1B), 23.85 (s, 2B−Cl), −33.28 (d, $J_{\mathrm{B-H}} = 115$ Hz, 1B). ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 10.12 (partially collapsed quartet (pcq), 1BH$_t$), 1.68 (s, 30H, Cp*), −0.89 (s, br, 1B−H−B), −1.86 (pcq, 1BH$_t$), −10.90 (pcq, 2Ru−H−B), −15.83 (s, 1Ru−H−Ru). IR (hexane, cm^{-1}): 2492 w, 2458 w (B−H$_t$).

Data for 5. MS (EI; *m/z*): P$^+$(max) 589 (isotopic pattern for 2Ru, 2Cl, and 4B atoms); mass calcd for $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{36}{}^{11}\mathrm{B}_4{}^{101}\mathrm{Ru}_2{}^{37}\mathrm{Cl}_2$ 593.2322, obsd 593.2489. ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 115.32 (s, br, 1B−Cl), 26.01 (s, 1B−Cl), 18.60 (s, br, 1B), −33.04 (d, $J_{\mathrm{B-H}} = 115$ Hz, 1B). ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 5.06 (partially collapsed quartet (pcq), 1BH$_t$), 1.76 (s, 15H, Cp*), 1.70 (s, 15H, Cp*), .45 (s, br, 1B−H−B), −1.16 (pcq, 1BH$_t$), −10.95 (s, br, 1Ru−H−B), −12.16 (s, br, 1Ru−H−B), −14.95 (s, 1Ru−H−Ru). IR (hexane, cm^{-1}): 2496 w, 2454 w (B−H$_t$).

6 and **7** mixture: MS (EI; *m/z*): P$^+$(max) 625 (isotopic pattern for 2Ru, 3Cl, and 4B atoms); mass calcd for $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{35}{}^{11}\mathrm{B}_4{}^{101}\mathrm{Ru}_2{}^{37}\mathrm{Cl}_3$ 628.0029, obsd 627.9997. ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 131.67 (s, br, 1B), 118.60 (s, 1B−Cl), 23.71 (s, 1BH$_t$), 21.36 (s, 2B−Cl), 18.53 (s, 1B−Cl), −11.32 (s, br, 2B−Cl). ^{1}H NMR (C$_6$D$_6$, 22 °C): 10.76 (partially collapsed quartet (pcq), 1BH$_t$), 5.26 (pcq, 1BH$_t$), 1.69 (s, 15H, Cp*), 1.66 (s, 15H, Cp*), 1.64 (s, 30H, Cp*), .74 (s, br, 1B−H−B), 0.42 (s, br, 1B−H−B), −9.81 (d, 2Ru−H−B), −9.92 (q, 1Ru−H−B), −11.07 (s, 1Ru−H−B), −15.26 (s, 1Ru−H−Ru), −16.15 (s, 1Ru−H−Ru). IR (hexane, cm^{-1}): 2454 w (B−H$_t$).

Preparation of *closo*-1-(SMe$_2$)-2,3-(η^5-C$_5$Me$_5$Ru)$_2$(μ_3-H)-B$_5$HCl$_3$ (8 and 9) and *closo*-2,3-(η^5-C$_5$Me$_5$Ru)$_2$B$_6$H$_3$Cl$_3$ (10). In a typical reaction, *nido*-1,2-(η^5-C$_5$Me$_5$Ru)$_2$(μ-H)$_2$B$_3$H$_7$ (**1**; 0.3 g, 0.58 mmol) was loaded into a 100 mL dried Schlenk flask with 20 mL of freshly distilled toluene to generate a yellow solution. BHCl$_2$·SMe$_2$ (0.43 mL, 3.58 mmol) was added very slowly by syringe, and the reaction mixture was placed into an oil bath having a temperature of 95 °C and was heated for 30 h, converting the yellow solution to a red solution. The reaction mixture was warmed to room temperature, the solvent was evaporated, and the residue was extracted into hexane and the extract filtered through a small neutral alumina column. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with hexane−CH$_2$Cl$_2$ (5/5 v/v) yielded (Cp*Ru)$_2$(μ_3-H)B$_4$(B−SMe$_2$)HCl$_3$ (**8**; 4%, 0.01 g), (Cp*Ru)$_2$(μ_3-H)B$_4$(B−SMe$_2$)HCl$_3$ (**9**; 16%, 0.06 g) and (Cp*Ru)$_2$B$_6$H$_3$Cl$_3$ (**10**; 0.04 g, 12%).

Data for 8. MS (FAB; *m/z*): P$^+$(max) 697 (isotopic pattern for 2Ru, 3Cl, 1S, and 5B atoms); mass calcd for $^{12}\mathrm{C}_{22}{}^{1}\mathrm{H}_{38}{}^{11}\mathrm{B}_5{}^{101}\mathrm{Ru}_2{}^{37}\mathrm{Cl}_3{}^{32}\mathrm{S}$ 698.0312, obsd 698.0334. ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 115.91 (s, 1B−Cl), 51.69 (s, 1B−Cl), 50.47 (d, 1B−H), 28.51 (s, 1B−Cl), −10.60 (s, 1B−SMe$_2$). ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 6.61 (partially collapsed quartet (pcq), 1BH$_t$), 1.92 (s, 15H, Cp*), 1.91 (s, 15H, Cp*), 1.52 (s, 6H, (B−(SMe)$_2$), −13.22 (q, μ_3-H, RuHB−Cl). IR (hexane, cm^{-1}): 2496 w (B−H$_t$).

Data for 9. MS (FAB; *m/z*): P$^+$(max) 697 (isotopic pattern for 2Ru, 3Cl, 1S, and 5B atoms); mass calcd for $^{12}\mathrm{C}_{22}{}^{1}\mathrm{H}_{38}{}^{11}\mathrm{B}_5{}^{101}\mathrm{Ru}_2{}^{37}\mathrm{Cl}_3{}^{32}\mathrm{S}$ 698.0312, obsd 698.0334. ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 130.33 (br, 1B−H), 47.98 (s, 2B−Cl), 25.56 (s, 1B−Cl), −12.39 (s, 1B−SMe$_2$). ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 11.04 (partially collapsed quartet (pcq), 1BH$_t$), 1.89 (s, 30H, Cp*), 1.51 (s, 6H, (B−(SMe)$_2$), −12.72 (q, μ_3-H, Ru−H−BCl). IR (hexane, cm^{-1}): 2498 w (B−H$_t$).

Data for 10. MS (FAB; *m/z*): P$^+$(max) 646 (isotopic pattern for 2Ru, 3Cl, and 6B atoms); mass calcd for $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{33}{}^{11}\mathrm{B}_6{}^{101}\mathrm{Ru}_2{}^{37}\mathrm{Cl}_3$ 648.0293, obsd 648.0271. ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 119.91 (s, br, 1BH$_t$), 99.04 (s, B−Cl). 68.28 (d, $J_{\mathrm{B-H}} = 137$ Hz, 1BH$_t$), 66.53 (s, 1B−Cl), 14.78 (s, 1B−Cl), −7.75 (d, $J_{\mathrm{B-H}} = 128$ Hz, 1BH$_t$). ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 8.35 (partially collapsed quartet (pcq), 1BH$_t$), 7.83 (pcq, 1BH$_t$), 1.15 (pcq, 1BH$_t$), 1.66 (s, 15H, Cp*), 1.61 (s, 15H, Cp*). IR (hexane, cm^{-1}): 2504 w, 2446 w (B−H$_t$).

Preparation of (η^5-C$_5$Me$_5$Ru)$_2$B$_6$H$_{10}$Cl$_2$ (11). In a typical reaction *nido*-(η^5-C$_5$Me$_5$Ru)$_2$B$_6$H$_{12}$ (0.3 g, 0.54 mmol) in 15 mL of toluene was stirred with BHCl$_2$·SMe$_2$ (0.32 mL, 2.73 mmol) at 85 °C for 18 h, converting the yellow solution to an orange-yellow solution. The reaction mixture was warmed to room temperature, the solvent was evaporated, and the residue was extracted into hexane and the extract filtered through a small neutral alumina column. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using a fast silica gel column. Elution with hexane−CH$_2$Cl$_2$ (8/2 v/v) yielded (η^5-C$_5$Me$_5$Ru)$_2$B$_6$H$_{10}$Cl$_2$ (**11**; 0.27 g, 82%).

11: MS (FAB; *m/z*): P$^+$(max) 614 (isotopic pattern for 2Ru, 2Cl, and 6B atoms), $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{40}{}^{11}\mathrm{B}_6{}^{101}\mathrm{Ru}_2{}^{37}\mathrm{Cl}_2$, calcd 619.0142, obsd 619.0198. ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 38.11 (d, $J_{\mathrm{B-H}} = 112$ Hz, 4B), 11.24 (s, 2B−Cl). ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 6.88 (partially collapsed quartet (pcq), 4 BH$_t$), 1.68 (s, 30 H, 2Cp*), −0.32 (s, br, 2B−H−B), −13.75 (q, 4 Ru−H−B). IR (hexane, cm^{-1}): 2508 w, 2450 w (B−H$_t$). Anal. Calcd (found) for $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{40}{}^{11}\mathrm{B}_6{}^{101}\mathrm{Ru}_2{}^{37}\mathrm{Cl}_2$: C, 38.84 (40.23); H, 6.52 (6.87).

Preparation of (η^5-C$_5$Me$_5$Ru)$_2$B$_8$H$_{11}$Cl (12). In a typical reaction (η^5-C$_5$Me$_5$Ru)$_2$B$_8$H$_{12}$ (0.2 g, 0.35 mmol) in 15 mL of toluene was stirred with BHCl$_2$·SMe$_2$ (0.20 mL, 1.75 mmol) at 85 °C for 18 h, converting the red solution to a deep red solution. The reaction mixture was warmed to room temperature, the solvent was evaporated, and the residue was extracted into hexane and the extract filtered through a small neutral alumina column. After removal of solvent from the filtrate, the residue was subjected to chromatographic workup using silica gel TLC plates. Elution with hexane−CH$_2$Cl$_2$ (8/2 v/v) yielded (η^5-C$_5$Me$_5$Ru)$_2$B$_8$H$_{11}$Cl (**12**; 0.15 g, 75%).

Data for 12. MS (FAB; *m/z*): P$^+$(max) 601 (isotopic pattern for 2Ru and 6B atoms), $^{12}\mathrm{C}_{20}{}^{1}\mathrm{H}_{41}{}^{11}\mathrm{B}_8{}^{101}\mathrm{Ru}_2{}^{37}\mathrm{Cl}$, calcd 608.1728, obsd 608.1702. ^{11}B NMR (C$_6$D$_6$, 22 °C): δ 106.07 (d, $J_{\mathrm{B-H}} = 137$ Hz, 1B), 63.07 (d, $J_{\mathrm{B-H}} = 122$ Hz, 1B), 30.34 (d, $J_{\mathrm{B-H}} = 119$ Hz, 1B), 17.19 (d, $J_{\mathrm{B-H}} = 139$ Hz, 1B), 14.97 (s, 1B−Cl), 13.68 (d, $J_{\mathrm{B-H}} = 111$ Hz, 1B), 3.25 (d, $J_{\mathrm{B-H}} = 91$ Hz, 1B), −24.07 (d, $J_{\mathrm{B-H}} = 142$ Hz, 1B). ^{1}H NMR (C$_6$D$_6$, 22 °C): δ 9.92 (pcq, 1BH$_t$), 5.91 (pcq, 1BH$_t$), 5.63 (pcq, 1BH$_t$), 5.01 (pcq, 1BH$_t$), 3.40 (pcq, 1BH$_t$), 3.10 (pcq, 1BH$_t$), 0.93 (pcq, 1BH$_t$), 1.64 (s, 15 H, 1Cp*), 1.36 (s, 15 H, 1Cp*), 1.01 (s, br, 1B−H−B), −0.35 (s, br, 1B−H−B), −2.23 (s, br, 1B−H−B), −17.60 (s, br, 1Ru−H−B). IR (hexane, cm^{-1}): 2502 w, 2449 w (B−H$_t$).

X-ray Structure Determinations. *nido*-1,2-(η^5-C$_5$Me$_5$Ru)$_2$-(μ-H)B$_4$H$_7$Cl$_2$ (2). A crystalline sample of **2** was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Non-hydrogen atoms were found by successive full-matrix least-squares refinement on F^2 and refined with anisotropic thermal parameters. Crystal data: formula, C$_{20}$H$_{38}$B$_4$Cl$_2$Ru$_2$; crystal system, space group: tetragonal, $I4_1/a$; unit cell dimensions, $a = 33.5236(10)$ Å, $b = 33.5236(10)$ Å, $c = 8.7943(4)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 16$; final R indices ($I > 2\sigma(I)$) R1 = 0.0241, wR2 = 0.0576.

***pileo*-2,3-(η^5-C$_5$Me$_5$Ru)$_2$(μ-H)B$_4$H$_5$Cl$_2$ (3).** A crystalline sample of **3** was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. The asymmetric unit contains one dimer, in which one of the Cp* rings exhibits a 2-fold disorder (51% and 49% relative occupancies). Note: it is possible that a small amount of the Cl$_3$ compound is present or that a static disorder is present in which Cl1 is located on B1 for a small percentage of the molecules. Crystal data: formula, C$_{20}$H$_{36}$B$_4$Cl$_2$Ru$_2$; crystal system, space group: triclinic, $P\bar{1}$; unit cell dimensions, $a = 9.0023(3)$ Å, $\alpha = 76.6780(10)°$, $b = 9.5781(4)$ Å, $\beta = 79.1590(10)°$, $c = 16.0270(6)$ Å, $\gamma = 67.7320(10)°$, $Z = 2$; final R indices ($I > 2\sigma(I)$) R1 = 0.0225, wR2 = 0.0556.

***pileo*-2,3-(η^5-C$_5$Me$_5$Ru)$_2$(μ-H)B$_4$H$_4$Cl$_3$ (7).** A crystalline sample of **7** was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. The asymmetric unit contains one dimer. Note: it is possible that a small amount of the Cl4 compound is present or that a static disorder is present in which Cl1, Cl2, or Cl3 actually resides on atom B4 for a small percentage of the molecules. Crystal data: formula, $C_{20}H_{35}B_4Cl_3Ru_2$; crystal system, space group, monoclinic, $P2_1/n$; unit cell dimensions, $a = 10.5503(4)$ Å, $\alpha = 90°$, $b = 13.9118(5)$ Å, $\beta = 105.0630(10)°$, $c = 17.6855(7)$ Å, $\gamma = 90°$, $Z = 4$; final R indices ($I > 2\sigma(I)$) R1 = 0.0228, wR2 = 0.0575.

***closo*-1-(SMe$_2$)-2,3-(η^5-C$_5$Me$_5$Ru)$_2$(μ_3-H)B$_5$HCl$_3$ (8).** A crystalline sample of **8** was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Non-hydrogen atoms were found by successive full-matrix least-squares refinement on F^2 and refined with anisotropic thermal parameters. The asymmetric unit contains one Ru dimer and 5/12 of a hexane solvent molecule. Hydrogen atoms on the disordered hexane molecule were not included in the refinement. Crystal dataL formula, $C_{24.50}H_{43.84}B_5Cl_3Ru_2S$; crystal system, space group: orthorhombic, *Pbca*; unit cell dimensions, $a = 22.027(3)$ Å, $b = 12.4145(14)$ Å, $c = 23.813(3)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 8$; final R indices ($I > 2\sigma$(I)) R1 = 0.0348, wR2 = 0.1026.

***closo*-1-(SMe$_2$)-2,3-(η^5-C$_5$Me$_5$Ru)$_2$(μ_3-H)B$_5$HCl$_3$ (9).** A crystalline sample of **9** was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal dataL formula, $C_{22}H_{38}B_5Cl_3Ru_2S$; crystal system, space group, monoclinic, $P2_1/n$; unit cell dimensions, $a = 8.4861(4)$ Å, $\alpha = 90°$, $b = 20.9284(10)$ Å, $\beta = 91.4140(10)°$, $c = 15.9540(7)$ Å, $\gamma = 90°$, $Z = 4$; final R indices ($I > 2\sigma(I)$) R1 = 0.0203, wR2 = 0.0478.

***closo*-2,3-(η^5-C$_5$Me$_5$Ru)$_2$B$_6$H$_3$Cl$_3$ (10).** A crystalline sample of **10** was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. The asymmetric unit contains one dimer. Note: a small percentage of product containing a chloride positional impurity is suspected, as evidenced by an improbably long B4−H2 distance. Crystal data: formula, $C_{20}H_{33}B_6Cl_3Ru_2$; crystal system, space group, monoclinic, $P2_1/c$; unit cell dimensions, $a = 9.0660(5)$ Å, $\alpha = 90°$, $b = 32.7224(17)$ Å, $\beta = 111.4440(10)°$, $c = 9.1682(5)$ Å, $\gamma = 90°$, $Z = 4$; final R indices ($I > 2\sigma(I)$) R1 = 0.0436, wR2 = 0.1052.

***nido*-2,4-(η^5-C$_5$Me$_5$Ru)$_2$B$_6$H$_{10}$Cl$_2$ (11).** A crystalline sample of **11** was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Non-hydrogen atoms were found by successive full-matrix least-squares refinement on F^2 and refined with anisotropic thermal parameters. The asymmetric unit contains one dimer and one dichloromethane solvent molecule. Note: a small percentage of products containing chloride positional impurities is suspected, as a large residual electron density is located 1.7 Å from B6. Crystal data: formula, $C_{21}H_{42}B_6Cl_4Ru_2$; crystal system, space group: monoclinic, $P2_1/c$; unit cell dimensions, $a = 14.5799(9)$ Å, $\alpha = 90°$, $b = 11.3893(7)$ Å, $\beta = 94.3710(10)°$, $c = 17.7889(11)$ Å, $\gamma = 90°$, $Z = 4$; final R indices ($I > 2\sigma(I)$) R1 = 0.0323, wR2 = 0.0736.

***nido*-2,3-(η^5-C$_5$Me$_5$Ru)$_2$B$_8$H$_{11}$Cl (12).** Crystals of **12** were examined under a light hydrocarbon oil. The specimen crystal was mounted with a small amount of silicone grease to the tip of a thin glass fiber attached to a tapered copper mounting pin and transferred to the goniometer of a Bruker D8-Apex diffractometer equipped with an Oxford Cryosystems 700 Series low-temperature apparatus operating at 100 K. The structure is a racemic twin, and the Flack parameter is 0.59(7). The hydrogen bridging Ru(2) and B(8) could not be found and was not included in the model. Crystal data: formula, $C_{20}H_{41}B_8ClRu_2$; crystal system, space group, orthorhombic, $P2_12_12_1$; unit cell dimensions, $a = 9.705(4)$ Å, $\alpha = 90°$, $b = 13.701(4)$ Å, $\beta = 90°$, $c = 19.123(6)$ Å, $\gamma = 90°$, $Z = 4$; final R indices ($I > 2\sigma(I)$) R1 = 0.0451, wR2 = 0.1095.

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Supporting Information Available: CIF files giving X-ray crystallographic data for **2**, **3**, and **7**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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