Novel Approach to Multimetal Metallaborane Clusters. Synthesis of Hypoelectronic *nido*-$Cp^*_3IrRu_2B_5H_9$ from the Reaction of *arachno*-$Cp^*IrB_3H_9$ with *nido*-$(Cp^*RuH)_2B_3H_7$

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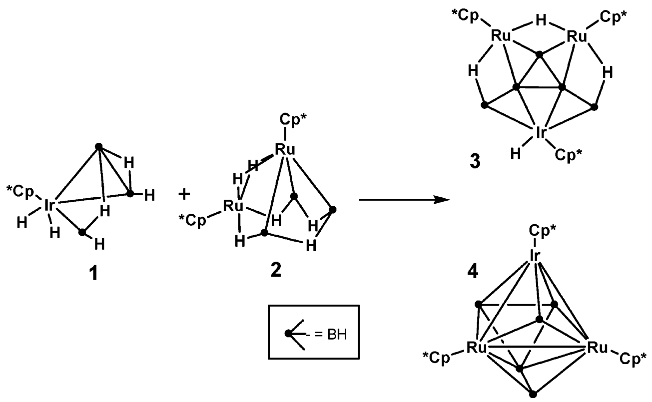
Summary: Two new mixed-metal metallaborane clusters, $Cp^*_3Ru_2IrB_5H_9$ and $Cp^*_3Ru_2IrB_5H_5$, were isolated from the reaction of an iridaborane with a ruthenaborane. The structures show the former to have an unusual nido eight-atom cluster shape with a low electron count and the latter to have the expected bicapped-octahedral geometry.

The structural chemistry of metallaboranes containing group 8 or 9 metals with cyclopentadienyl or carbonyl ancillary ligands is well understood in general.[1−3] In contrast, an understanding of the reactivity and mechanism is rudimentary even at the level of stoichiometric relationships.[4] Hence, our recent work has been focused on this area.[5] As reactivity relationships are more easily understood when the structural chemistry is well established, we have concentrated on ruthena-, rhoda-, and iridaboranes. Studied to date have been reactions with the following: borane and metal fragments (cluster expansion, metal fragment substitution, and ligand exchange),[6−8] Lewis bases (addition, degradation, and substitution on metal or boron sites),[9] and alkynes (insertion, hydroboration, and catalytic cyclotrimerization).[10,11] Consistent with the known organometallic chemistry, we find the reactivity to be a sensitive function of metal identity even for isoelectronic clusters with the same cluster shape and metal ancillary ligands: e.g., alkyne insertion into *nido*-$(Cp^*RuH)_2B_3H_7$ vs catalytic alkyne cyclotrimerization by *nido*-$(Cp^*Rh)_2B_3H_7$.[12]

An implication of this result is that the frontier orbital character is strongly perturbed on a change in the metal identity. We have yet to observe a self-reaction of a metallaborane: e.g., a bimolecular reaction of a monoiridaborane to give a diiridaborane cluster. However, if electronic structures of metallaboranes containing two different metals do differ significantly, a reaction between two different metallaboranes constitutes a potential source of novel cluster products. Historically, the reaction of two different polyboranes has provided access to larger borane structures: e.g., $B_{13}H_{19}$.[13] Hence, in a logical variant of our reactivity studies, we have now explored the reaction of an iridaborane, *arachno*-$Cp^*IrB_3H_9$ (**1**), with a ruthenaborane, *nido*-$(Cp^*RuH)_2B_3H_7$ (**2**), having the structures shown in Scheme 1. A mutual reaction does take place, and the products isolated suggest that it is an addition reaction. The novel products also possess structures that provide an interesting counterpoint to the compositions and structures of known eight-atom clusters.

Scheme 1



Reflux of an equimolar mixture of **1** and **2** in hexane for 14 h gave modest yields of two related products, **3** and **4**.[14] The spectroscopic data show that each contains one Ir, two Ru, and five B atoms. On the basis of the parent ion envelopes in the mass spectra, **3** contains more H atoms than **4**. The ^1H NMR of **3** reveals five terminal B−H protons in two broad resonances and three resonances in the metal hydride region corresponding to four protons in the ratio 1:2:1. On the basis of ^{11}B decoupling experiments, these are assigned to Ru−H−Ru, Ru−H−B, and Ir−H, respectively. Hence, **3** is formulated as $Cp^*_3IrRu_2B_5H_9$.

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(14) A hexane solution of $(Cp^*RuH)_2B_3H_7$ (68 mg, 0.132 mmol, in 20 mL) with $Cp^*IrB_3H_9$ (50 mg, 0.135 mmol) was refluxed for 14 h. Following extraction with CH_2Cl_2, preparative TLC (20% CH_2Cl_2 in hexane) yielded a brown band of **3** (20 mg, 17%) and a yellow band of **4** (10 mg, 9%). Repeated chromatography was required to separate **3** from the closely following band of $(Cp^*Ru)_2B_4H_{10}$. Spectroscopic data are as follows. **3**: ^{11}B NMR (C_6D_6, 128 MHz, 22 °C) δ 104.5 (br, 1B), 82.6 (br, 2B), 5.5 (d, $J_{B-H} = 118$ Hz, {^1H}, s, 2B); ^1H NMR (C_6D_6, 400 MHz, 22 °C) δ 11.67 (3H), 1.87 (15H), 1.80 (30H), 1.65 (2H), −14.84 (Ru−H−Ru, 1H), −14.91 (Ru−H−B, 2H), −17.20 (Ir−H, 1H); MS (FAB) *m*/*z* 859 ($M^+ - 4H$). **4**: ^{11}B NMR (C_6D_6, 128 MHz, 22 °C) δ 118.0 (br, 1B), 100.4 (br, 1B), 71.4 (d, $J_{B-H} = 108$ Hz, {^1H}, s, 2B), −1.5 (d, $J_{B-H} = 110$ Hz, {^1H}, s, 1B); ^1H NMR (C_6D_6, 400 MHz, 22 °C) br peaks spanning δ 9.5−8.0, 1.92 (15H), 1.78 (30H); MS (FAB) *m*/*z* 859 (M^+).

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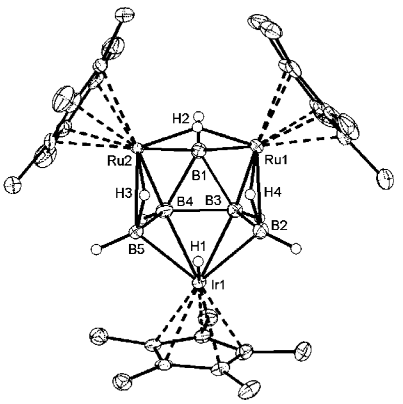


Figure 1. Molecular structure of $Cp^*_3IrRu_2B_5H_9$ (**3**). Selected bond distances (Å): Ir1−B5 = 2.130(5), Ir1−B2 = 2.147(5), Ir1−B4 = 2.219(5), Ir1−B3 = 2.222(5), Ru1−B1 = 2.130(5), Ru1−B2 = 2.146(5), Ru1−B3 = 2.286(5), Ru2−B5 = 2.122(5), Ru2−B1 = 2.156(5), Ru2−B4 = 2.295(5), B1−B3 = 1.765(7), B1−B4 = 1.753(6), B2−B3 = 1.812(7), B3−B4 = 1.775(6), B4−B5 = 1.826(7).

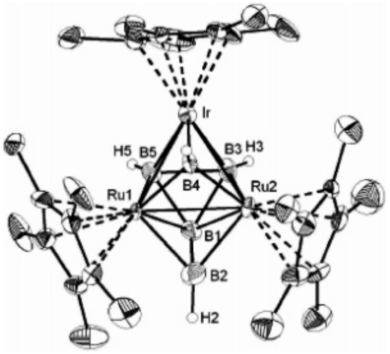
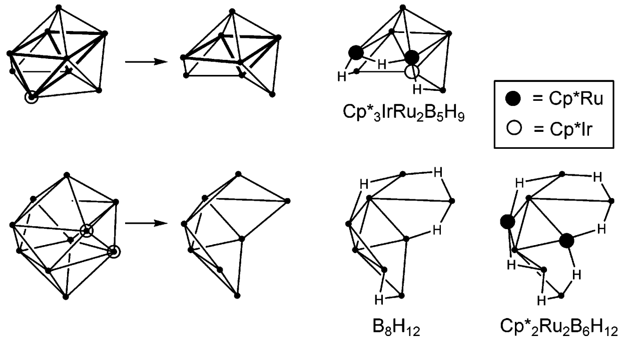


Figure 2. Molecular structure of $Cp^*_3IrRu_2B_5H_5$ (**4**). Selected bond distances (Å): Ir−B3 = 2.148(8), Ir−B4 = 2.071(7), Ir−B5 = 2.120(7), Ru1−B1 = 2.232(8), Ru1−B2 = 2.089(10), Ru1−B4 = 2.103(7), Ru1−B5 = 2.137(7), Ru2−B1 = 2.250(9), Ru2−B2 = 2.105(10), Ru2−B3 = 2.158(9), Ru2−B4 = 2.125(7), B1−B2 = 1.718(15), B1−B3 = 1.724(12), B1−B5 = 1.720(12), B3−B5 = 1.841(11).

Compound **4** showed no high-field proton resonances at all and is formulated as $Cp^*_3IrRu_2B_5H_5$. Both can be derived from the sum of the compositions of the starting clusters ($Cp^*_3IrRu_2B_6H_{18}$) by formal loss of BH_3 and three or five H_2 groups for **3** and **4**, respectively. As loss of BH_3 and H_2 is a common feature of borane as well as metallaborane cluster chemistries, the reaction is most simply viewed as metallaborane combination followed by main-group-fragment loss.

With eight cluster atoms and nine and seven skeletal electron pairs (sep) respectively, **3** and **4** should exhibit closo and bicapped-closo structures.[15,16] However, not only are there several isomeric possibilities but also metallaboranes containing one-electron Cp*Ru fragments need not follow the usual structural paradigm.[17] The required solid-state structure studies were carried out, and the results are shown in Figures 1 and 2. Cluster **4** does exhibit the expected bicapped-octahedral structure, consistent with its sep count. It is similar to $Cp^*_2Mo_2Fe(CO)_3B_5H_9$, albeit with four fewer bridging hydrogen atoms, in accord with the difference between group 8 and group 6 metals.[18]

Scheme 2



The structure of **3** is not routine and presents an interesting problem in the context of known structures of eight-atom clusters. As shown at the top of Scheme 2, **3** exhibits a cluster shape that can be derived from a tricapped trigonal prism by removal of one five-connected vertex. Thus, it has a nido geometry but, with only 9 sep rather than the prescribed 10 sep, it is hypoelectronic: i.e., fewer valence electrons than apparently are required by its geometric structure.[19] As also shown in Scheme 2, B_8H_{12}, a borane that does have 10 sep, exhibits a geometry derived by removing two adjacent vertices from a bicapped square antiprism. Hence, it has formal arachno geometry and might also be classified as hypoelectronic. Most classify it as nido on the basis of its electron count. The same geometry is exhibited by the 10-sep ruthenaborane $Cp^*_2Ru_2B_6H_{12}$ and, hence, we have described it as “normal”.[17] What is the source of this behavior? Muetterties[20] aptly characterized the eight-atom cluster as an “extraordinarily plastic aggregate”, and it is probably the differing numbers of bridging hydrogens, four for B_8H_{12}, six for $Cp^*_2Ru_2B_6H_{12}$, and three for **3**, that lie behind the differences in observed shapes.[21] Indeed, King has demonstrated that, with four bridging hydrogens, B_8H_{12} is topologically unable to adopt the structure of **3**.[22] Further, cluster rearrangement on protonation is known in metal cluster chemistry, although these are metal cluster isomers with proper electron counts.[23]

The structural observations illustrate the richness of eight-vertex cluster chemistry, but the most significant finding is the apparent way in which different metals in metallaboranes generate complementary reaction partners. We know that both **1** and **2** react readily with main-group and transition-metal sources of electrophilic species, whereas only **2** reacts readily with more basic species such as alkynes. Hence, we speculate that it is this difference which leads to the reactivity observed. A more precise explanation must await additional detailed work, including the characterization of intermediate products.

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Supporting Information Available: CIF files for the structures of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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