Reaction of the Transition Metal Hydrides $[Cp^*MH_2]_2$ ($Cp^* = \eta^5$-C_5Me_5; M = Fe, Ru) with BH_3·THF to Yield Metallaboranes. Improved Kinetic Control Leads to Novel Ferraboranes

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The reactions of $[Cp^*MH_2]_2$, $Cp^* = \eta^5$-C_5Me_5; M = Fe, Ru, with BH_3·THF have been explored. As with $[Cp^*RuCl_2]_2$, $[Cp^*RuH_2]_2$ readily reacts with borane to generate *nido*-1,2-$(Cp^*RuH)_2B_3H_7$. In contrast to the chloride, intermediates are detectible in the hydride reaction and product selectivity is higher. Benefits of the apparently lower reaction barrier appear in the reaction of $[Cp^*FeH_2]_2$ with BH_3·THF. The formation and isolation of the novel hydrogen-rich ferraborane *arachno*-1-$Cp^*FeB_4H_{11}$ from the iron hydride contrasts with the production of pentamethylferrocene from a pentamethylcyclopentadienyl iron halide. This metastable ferraborane has been characterized spectroscopically as well as by reaction with $Co_2(CO)_8$ to give a good yield of the more stable derivative *nido*-1-(Cp^*Fe)-2-$\{Co(CO)_3\}B_4H_8$ by metal fragment addition. The latter compound has been spectroscopically characterized in solution as well as in the solid state by a single-crystal X-ray diffraction study as an example of a mixed metal dimetallahexaborane.

Introduction

The stepwise addition of monoboranes to monocyclopentadienylmetal chlorides (Cp^*MCl_n), $Cp^* = \eta^5$-C_5Me_5, usually in dimeric form, has been shown to be an excellent method for the preparation of metallaboranes containing transition metals ranging from groups 5 to 9.[1−3] This synthetic route depends on the selective conversion of metal polyborohydrides to metallaboranes by hydrogen elimination. The method fails when competing pathways have lower overall barriers than that leading to a metallaborane, e.g., hydride formation by borane elimination, which can also lead to metal reduction or metallocene formation. For this reason, the route from monocyclopentadienyl halides is not found to be useful for the first-row metals Mn, Fe, and Ni. Metallocene formation is observed in the case of Mn (using $[Cp^*MnCl(THF)]_2$)[4] and Fe (using Cp^*FeCl),[5] and reduction to the metal is observed in the case of Ni (using $[Cp^*NiBr]_2$).[5] In the last case, not even the substantive protection of the Cp* ligand is sufficient to derail reductive degradation.

Metal borohydrides are known to dissociate into metal hydrides and borane, and some metal hydrides are known to coordinate borane to give metal borohydrides.[6−8] In addition there is substantial evidence in the literature showing that the reaction of metal hydrides with various boranes can lead to metallaboranes.[9−12] Thus, in our search for alternative metal precursors for ferraboranes containing the Cp*Fe fragment, we considered iron hydrides. When the synthesis, characterization, and some innovative organometallic chemistry of the compounds $[Cp^*MH_2]_2$, $Cp^* = \eta^5$-C_5Me_5, M = Fe, Ru, appeared in the literature, a mechanistically enlightening study suggested itself.[13,14] The ruthenium hydride presented the possibility of a direct comparison of the known reaction of $[Cp^*RuCl_2]_2$ with borane with that of $[Cp^*RuH_2]_2$. Similar reactivity for the ruthenium hydride and more favorable reaction barriers would then make $[Cp^*FeH_2]_2$ an excellent candidate for entry into the desired iron chemistry. In the event, both suppositions were found to be true and the novel ferraboranes described below were synthesized and characterized.[15]

Results

Dimeric Cp^*MX_2 compounds exhibit more than one structure type,[16] and as shown in Figure 1, the com-

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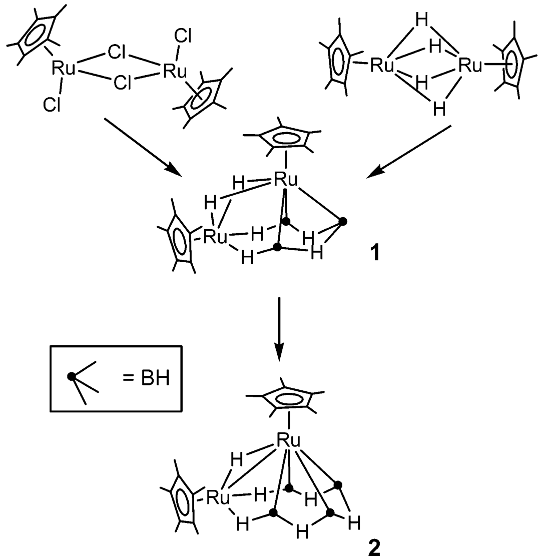

Figure 1. Comparison of the pentamethylcyclopentadienylmetal halide vs hydride routes for the formation of *nido*-1,2-$(Cp^*RuH)_2B_3H_7$, **1**.

pounds $[Cp^*RuH_2]_2$ and $[Cp^*RuCl_2]_2$ have different reported dimeric structures.[14,17] These structural differences and the associated electronic effects of the ligands can affect reactivity. For example, the reactive site in the halide dimers is believed to be the halogen atom and the substitution of halide by hydride should be a significant one. Further $[Cp^*RuH_2]_2$ is dimeric in solution and the solid state, whereas the form of Cp^*RuCl_2 in solution depends on conditions.[17] In addition to dimers, monomers and higher oligomers can be present. Even ionic forms are possible. These species are expected to reduce the selectivity of the chloride route relative to the hydride and may introduce mechanistic complications as well.

Reaction of $[Cp^*RuCl_2]_2$ with Monoboranes. To review, eqs 1−4 represent the stoichiometric pathway for the efficient production of *nido*-1,2-$(Cp^*RuH)_2B_3H_7$, **1**, from the reactions of $[Cp^*RuCl_2]_2$ with both $LiBH_4$ and $BH_3{\cdot}THF$ (Figure 1).[18] The known mixed valence compound $\{Cp^*_2Ru_2Cl_3\}$[17] is postulated as an intermediate in the borohydride reaction (eqs 1, 2). In the metathesis pathway the number of halogen atoms present on the intermediate, stable with respect to hydride formation, determines the boron content of the first former metallaborane.[19] Reaction of authentic $\{Cp^*_2Ru_2Cl_3\}$ with borane leads to the same ruthenaborane.

$$[Cp^*RuCl_2]_2 + LiBH_4 \rightarrow \{Cp^*_2Ru_2Cl_3\} + LiCl + {}^1/_2\,H_2 + BH_3 \quad (1)$$

$$\{Cp^*_2Ru_2Cl_3\} + 3\,LiBH_4 \rightarrow \{Cp^*_2Ru_2(BH_4)_3\} + 3\,LiCl \quad (2)$$

$$[Cp^*_2Ru_2(BH_4)_3] \rightarrow 1,2\text{-}(Cp^*RuH)_2B_3H_7 + 3/2\,H_2 \quad (3)$$

$$[Cp^*RuCl_2]_2 + BH_3{\cdot}THF \rightarrow \{Cp^*_2Ru_2Cl_3\} + BH_2Cl{\cdot}THF + {}^1/_2\,H_2 \quad (4)$$

$$[Cp^*_2Ru_2Cl_3] + 6\,BH_3{\cdot}THF \rightarrow \{Cp^*_2Ru_2(BH_4)_3\} + 3\,BH_2Cl{\cdot}THF \quad (5)$$

$$1,2\text{-}[Cp^*RuH]_2\,B_3H_7 + BH_3{\cdot}THF \rightarrow 1,2\text{-}(Cp^*Ru)_2B_4H_{10} + H_2 \quad (6)$$

In contrast, the reagent $BH_3{\cdot}THF$ serves dual roles: removal of Cl as BH_2Cl and addition to the metal fragment. Even so, we still suggest the triborohydride $\{Cp^*_2Ru_2(BH_4)_3\}$ as the crucial intermediate that leads to the ruthenaborane product by hydrogen elimination. Reaction of $[Cp^*RuCl_2]_2$ with $LiBH_4$ takes place at room temperature or below, whereas with $BH_3{\cdot}THF$ heating is required. Hence, in the latter reaction the largest barrier is encountered in the conversion of $[Cp^*RuCl_2]_2$ into $\{Cp^*_2Ru_2(BH_4)_3\}$. Utilization of a hydride, then, should either increase or decrease this barrier.

As heating is required for the reaction of $[Cp^*RuCl_2]_2$ with $BH_3{\cdot}THF$, it is not possible to avoid conversion of some of the diruthenapentaborane formed initially into a diruthenahexaborane, 1,2-$(Cp^*Ru)_2B_4H_{10}$, **2** (eq 6). Hence, $LiBH_4$ is selective for the diruthenapentaborane, and $BH_3{\cdot}THF$ is convenient for forming the diruthenahexaborane in a single-pot reaction. A drawback of the borohydride route is the formation of $Cp^*_3Ru_3B_3H_8$ as a significant byproduct.[20] Presumably it arises from the presence of a trimer produced from Cp^*RuCl_2 in solution and, interesting compound or not, it reduces the selectivity of the preparation.

Reaction of $[Cp^*RuH_2]_2$ with Monoboranes. ^1H and ^{11}B NMR show that the reaction of $[Cp^*RuH_2]_2$ with $BH_3{\cdot}THF$ at 0 °C produces **1** as the sole product containing boron in 30 min. Solvent removal at 0 °C yields **1** in nearly quantitative (93%) yield. Compound **2** results overnight from the addition of 4 molar equiv of $BH_3{\cdot}THF$ to $[Cp^*RuH_2]_2$ (90%). Reaction of $[Cp^*RuH_2]_2$ with $LiBH_4$ under the same conditions is null. Equation 7 expresses the stoichiometric result. Clearly the ruthenium hydride yields the same principal product as the chloride, but the greater selectivity for the diruthenapentaborane product suggests that the overall barrier for reaction is significantly lower.

$$[Cp^*RuH_2]_2 + 3\,BH_3{\cdot}THF \rightarrow 1,2\text{-}[Cp^*RuH]_2\,B_3H_7 + 2\,H_2 \quad (7)$$

Monitoring the reaction at low temperature (−30 to 0 °C) by NMR shows the growth and decay of intermediates containing Cp*Ru, borane, and Ru−H−B fragments as **1** (3 $BH_3{\cdot}THF$) or **2** (4 $BH_3{\cdot}THF$) is formed. Although these data were not sufficient to define the structures of these intermediates, their observation here, but not in the case of the ruthenium chloride reaction, is also consistent with lower barriers for the hydride reaction. This qualitative observation also demonstrates that it is the barrier to the formation of the intermediates rather than their loss that is lowered. Part of this barrier must be associated with the initial reaction of the borane with the hydride; hence, the

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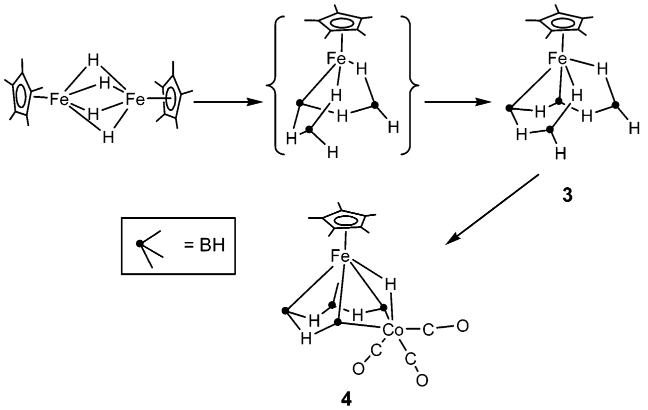

Figure 2. Summary of the reaction of $[Cp^*FeH_2]_2$ with borane to give $1\text{-}Cp^*FeB_4H_{11}$, **3**, and its subsequent reaction with $Co_2(CO)_8$ to give $1\text{-}\{Cp^*Fe\}\text{-}2\text{-}Co(CO)_3B_4H_8$, **4**.

observation suggests more facile formation of metallaboranes from hydrides versus chlorides.

The fact that $[Cp^*RuH_2]_2$ is a well-defined compound in solution leads to a more selective reaction than the ruthenium chloride/borohydride route. That is, the chloride route generates a triruthenaborane byproduct and requires a chromatographic step: a procedure that inevitably reduces isolated yield. Consequently, the isolated yields are considerably higher (90% vs 80%) in the hydride route. On the other hand, the ruthenium hydride route is less attractive overall, as $[Cp^*RuH_2]_2$ must be generated from $[Cp^*RuCl_2]_2$ (65%). Net yield from purchased compounds is lower, and the overall time required is considerably higher. Hence, the hydride route will find the most use for metals for which chromatography is not possible, e.g., Cr,[21] or for metals not amenable to the chloride route. It is the latter point that is addressed here.

Reaction of $[Cp^*FeH_2]_2$ with $BH_3{\cdot}THF$. Addition of $BH_3{\cdot}THF$ to a hexane solution of $[Cp^*FeH_2]_2$ results in immediate gas evolution and a color change from a dark green to an orange-brown. Chromatography yields a purple band, which is a mixture containing an unstable, non-boron-containing, iron hydride byproduct, and a yellow band, which contains a mixture of two compounds: Cp^*_2Fe and a new ferraborane, **3**, in a ≈1:2 ratio. Attempts to completely remove the former from the latter by sublimation, recrystallization, and control of reaction stoichiometry were unsuccessful. A sample of **3**, which is sufficiently pure (90% **1**, 10% Cp^*_2Fe by NMR) for definitive spectroscopic characterization, was obtained from the first 50% cut of the yellow band obtained from three successive columns. Orange **3** is air sensitive and slowly decomposes into Cp^*_2Fe on attempted crystallization. As suitable single crystals could not be obtained, characterization is based on spectroscopic data only.

The molecular formula from mass spectrometric measurements combined with Wade's rules[22,23] suggest that **3** is 8 skeletal electron pair (sep) *arachno*-$Cp^*FeB_4H_{11}$, i.e., a metal analogue of B_5H_{11} (Figure 2). The ^{11}B NMR exhibits a doublet and triplet in a 1:1 ratio, suggesting a plane of symmetry and positioning of the Cp*Fe fragment in the apical position in the cluster as shown in Figure 2. Three sets of $B-H_{term}$ protons are seen in the ^1H NMR as well as two types of B−H−B protons (1:2 ratio) plus one type of B−H−Fe with intensities relative to the Cp* Me signal consistent with the *arachno*-$1\text{-}Cp^*FeB_4H_{11}$ structure shown in Figure 2. Selective $^1H\{^{11}B\}$ experiments revealed the proton connectivity to the two types of boron, consistent with the structure shown. Hence, in **3** a Cp*FeH fragment formally replaces the apical BH fragment in B_5H_{11}, and the compound is one of a class of compounds we have called hydrogen-rich metallaboranes.[24]

As with the ruthenium model system, we searched for intermediates. One boron-containing intermediate was observed by ^{11}B NMR. It exhibits the NMR signature of a "borallyl" metallaborane, i.e., lower field doublet of doublets of area 2 and higher field doublet of area 1. Many borallyl complexes are known[25,26] and are equally well described as *arachno*-metallatetraboranes. The abundance of this intermediate was enhanced by using lower ratios of $[Cp^*FeH_2]_2{:}BH_3THF$, and it was reduced by using higher ratios. This stoichiometric control is similar to that found for the ruthenium hydride reaction in which the three-boron product or the four-boron product could be selected by the borane-to-metal ratio. Unfortunately, the three-boron iron compound could not be isolated.

A comparison of these observations with the iridium system is informative. The reaction of $[Cp^*IrCl_2]_2$ with borohydride yields *arachno*-$\{(Cp^*IrH_2)B_3H_7\}$ plus Cp^*IrH_4 in approximately equal abundances.[27] The evidence of a borallyl intermediate in the iron system accompanied by a substantial amount of metal hydride byproduct suggests a similar course for the $[Cp^*FeH_2]_2$ reaction with borane. Further, *arachno*-$\{(Cp^*IrH_2)B_3H_7$ adds $BH_3{\cdot}THF$ to give *arachno*-$\{(Cp^*IrH)B_4H_9$, as is observed in the case of iron albeit less definitively.[26] In short, the stoichiometric pathway given by eqs 8 and 9 and illustrated in Figure 2 is firmly based on precedent as well as the empirical observations.

$$[Cp^*FeH_2]_2 + 3\ BH_3{\cdot}THF \rightarrow \{1\text{-}(Cp^*FeH_2)B_3H_7\} + Cp^*FeH_n \quad (8)$$

$$\{1\text{-}(Cp^*FeH_2)\,B_3H_7\} + BH_3{\cdot}THF \rightarrow 1\text{-}Cp^*FeB_4H_{11} + H_2 \quad (9)$$

Selected Derivative Chemistry of 3. *Arachno*-metallaboranes are expected to lose H_2 and close to give more stable *nido*-species, e.g., the pyrolysis of *arachno*-$1\text{-}Cp^*CoB_4H_{10}$[28,29] to give *nido*-$1\text{-}Cp^*CoB_4H_8$.[30,31] However, **3** decomposed on heating above 45 °C without the production of the expected *nido*-$Cp^*FeB_4H_9$ or any other

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metallaborane based on ^{11}B NMR analysis. Apparently hydrogen elimination has a higher barrier than some other degradation pathway, and the expected analogue of *nido*-1-Cp*CoB_4H_8, *nido*-1-Cp*FeB_4H_9, is not formed. Possibly this is due to the fact that the fifth endohydrogen of the putative *nido*-derivative would have to bridge between apical and basal sites of the square-pyramidal cluster.

The reaction of open metal clusters with $Co_2(CO)_8$ constitutes a useful way of generating derivatives that are often more stable than the original cluster.[32] This approach has been useful in metallaborane chemistry as well, where metal fragment addition, metal fragment replacement, and simple CO addition to the Cp*M center have been observed.[33-36] Thus, the reaction of **3** with $Co_2(CO)_8$ was examined with expectations of producing a derivative that could be structurally characterized in the solid state.

Reaction of **3** with $Co_2(CO)_8$ proceeds smoothly at room temperature to form a single major product (besides $Co_4(CO)_{12}$) which is easily isolated by chromatography. The orange compound is of considerably higher stability than **3** and has a molecular formula Cp*$FeB_4H_8Co(CO)_3$ based on the parent ion mass. Three H atoms have been replaced by the three-electron $Co(CO)_3$ fragment, thereby producing an 8 sep, six-fragment *nido*-dimetallahexaborane. The ^{11}B NMR of the new compound indicates the presence of a plane of symmetry, and both of the boron resonances are now simple doublets. Loss of the triplet in the ^{11}B NMR is accompanied by loss of one of the intensity 2 $B-H_{term}$ resonances in the ^{1}H NMR. Both IR, with its typical $M(CO)_3$ fingerprint, and the mass spectrum, with characteristic *m*/*e* 28 neutral mass losses, verify the incorporation of a $Co(CO)_3$ fragment. Single crystals were obtained, and the X-ray diffraction study provided the solid state structure shown in Figure 3. Solid state and solution data are in full agreement and confirm the structure of this derivative of **3** as *nido*-1-{Cp*Fe}-2-$Co(CO)_3B_4H_8$, **4**, as shown in Figure 2. *nido*-1-{Cp*Ir}-2-$Co(CO)_3B_4H_7$, produced by the reaction of *arachno*-1-Cp*IrB_4H_{10} with $Co_2(CO)_8$, provides both a structural and reaction analogue for comparison.

Discussion

One limitation of the monocyclopentadienylmetal halide route to metallaboranes can be circumvented by using hydrides as alternative metal fragment sources. This has permitted one more metal to be added to the matrix of metallaboranes produced by this synthetic strategy, i.e., metallaboranes that contain Cp*M, M = Ta, Cr, Mo, W, Re, Fe, Ru, Co, Rh, Ir, fragments.

The pertinent *arachno*-metallapentaboranes related to **3** are illustrated in Figure 4. Neither **3** nor *arachno*-1-Cp*IrB_4H_{10} can be converted into the *nido*-form. The observation that hydrogen elimination for both is less favorable than decomposition does not prove that these *nido*-forms are intrinsically unstable. In fact, the degradation barrier for the iron compound is probably low and Ir−H bonds are strong for the iridium compound. It is interesting to note that *arachno*-1-Cp*WB_4H_{13}, which was characterized as an intermediate in the formation of *nido*-2-Cp*WB_4H_{11}, eliminates hydrogen below room temperature.[37] *arachno*-1-Cp*CoB_4H_{10} eliminates hydrogen at 70 °C.[28] These four compounds only differ in the number of hydrogen atoms and the metal type. Congruent with the continuing theme of our work, the properties of these open metallaboranes depend strongly on the metal. These results provide additional support for the idea that the potential of main group−transition metal chemistry[38] is large.

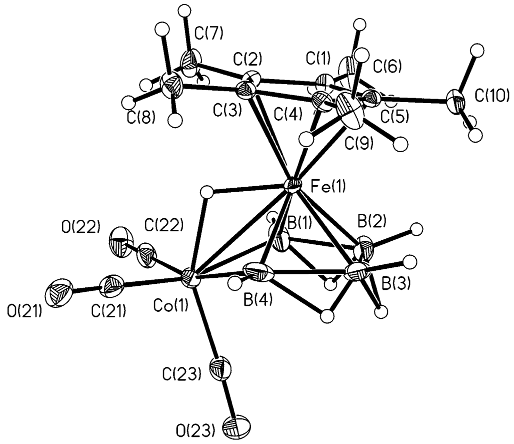

Figure 3. Molecular structure of *nido*-1-{Cp*Fe}-2-$Co(CO)_3B_4H_8$, **4**. Selected bond distances (Å): Fe(1)−B(1) 1.982(3), Fe(1)−B(4) 1.983(3), Fe(1)−B(2) 2.030(3), Fe(1)−B(3) 2.039(3), Fe(1)−Co(1) 2.5828(4), Co(1)−B(1) 2.115(3), Co(1)−B(4) 2.115(3), B(1)−B(2) 1.744(5), B(2)−B(3) 1.781(7).

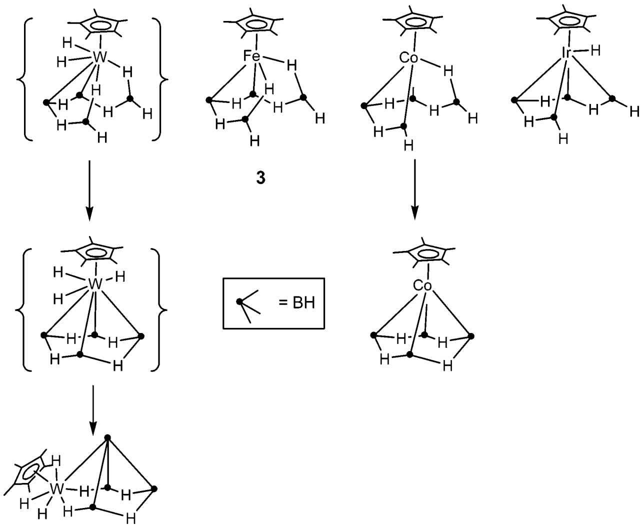

Figure 4. Comparison of known monometallapentaboranes containing the Cp*M fragment.

Experimental Section

General Procedures. All operations were carried out using standard Schlenk techniques.[39] Solvents were distilled im-

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mediately before use under nitrogen gas from the following drying agents: sodium benzophenone ketyl for hexanes, pentane, THF, and diethyl ether; molten sodium metal for toluene. Benzene-d_6 and toluene-d_8 (Acros) were dried and stored over potassium metal mirrors in a Young's tube and degassed using freeze/pump/thaw cycles. Silica gel (23−62 mesh) (ICN) was dried at 140 °C overnight before use. BH_3·THF (1 M) was obtained from Acros and $Co_2(CO)_8$ was obtained from Strem, and both were used as received. $[Cp^*RuH_2]_2$[13] and $[Cp^*FeH_2]_2$ were prepared according to the literature[14] with these modifications to the latter: during the preparation of Cp*FeCl(tmeda) sonication was used and stirring at −20 °C in a Peltier cooler rather than −78 °C for 3 days was satisfactory. Mass spectra were obtained on a JEOL JMS-AX505HA using perfluorokerosene as standard. NMR spectra were measured on 300 and 500 MHz Varian UnityPlus FT and 400 MHz Bruker DPX Avance spectrometers. Residual protons were used as internal reference for ^1H (C_6D_6, δ_H 7.15 ppm), and a sealed tube containing $[Me_4N][B_3H_8]$ was used as an external reference for ^{11}B (acetone-d_6 δ_B −29.7 ppm). Infrared spectra were measured on a Perkin-Elmer Paragon 1000 FT-IR spectrometer in a KBr solution cell. Elemental analyses were performed by M-H-W Laboratories.

Synthesis of *nido*-2,3-$(Cp^*RuH)_2B_3H_7$, 1. In a typical reaction, 400 mg of $[Cp^*RuH_2]_2$ (0.84 mmol) was dissolved in 10 mL of freshly distilled toluene. BH_3·THF (1 M, 2.52 mmol; 2.42 mL) was added via syringe at −30 °C. Gas evolution was observed along with a change in color from dark red to a red-orange after about 5 min. Warming the reaction to 0 °C and removing the solvent left pure (NMR) yellow **1** (0.40 g, 0.78 mmol, 93%).

Synthesis of *arachno*-1-$Cp^*FeB_4H_{11}$, 3. In a typical reaction, 60 mg of $[Cp^*FeH_2]_2$ (0.16 mmol) was loaded into a round-bottom Schlenk flask. Fresh hexane (20 mL) was added, and the dark green solution was allowed to stir. Excess 1 M BH_3·THF (0.93 mL) was added via syringe, upon which immediate gas evolution was noted. After stirring at RT for 2 h, the solvent was removed and the residue dried under vacuum. The orange solid was chromatographed on silica gel, and the second yellow-orange band removed with pentane contained a 2:1 ratio of $Cp^*FeB_4H_{11}$:Cp^*_2Fe by ^1H NMR. The purity of the compound could be improved to 9:1 by repetitive chromatography retaining the first half of the band only. **3** is an air-sensitive vibrant orange, crystalline solid and is soluble in common organic solvents. Approximate NMR yield is 40%. Attempted crystallization yielded only Cp^*_2Fe.

Spectroscopic Data. ^{11}B NMR (C_6D_6, 22 °C): 8.36 (d, $^1J_{BH} = 139$ Hz, $\{^1H\}$ 2B), −14.21 (br, t, $^1J_{BH} \approx 77$ Hz, $\{^1H\}$2B). $^1H\{^{11}B\}$ NMR (C_6D_6, 22 °C): 3.56 (2H, BH_t), 1.77 (2H, BH_t), 1.36 (15H, C_5Me_5), 1.29 (br, 2H, BH_t), −3.23 (1H, B-*H*-B), −3.37 (2H, B-*H*-B), −15.85 (d, 2H, Fe-*H*-B, $^2J_{HH} = 20$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): 93.40 (C_5Me$_5$), 9.59 (C_5Me_5). IR (C_6D_6, cm^{-1}): 2524 (w, B-H), 2456 (w, B-H), 2405 (w, B-H). EI$^+$MS: *m/z* 244 ($M^+ - H_2$); calcd for $C_{10}H_{24}FeB_4$ 244.15994 ($M^+ - H_2$), measd 244.15754.

NMR Data for Intermediate $\{Cp^*FeB_3H_{10}\}$. ^{11}B NMR (hexane, 22 °C): −3.68 (d, $J_{BH} = 136$ Hz, $\{^1H\}$ 2B), −9.55 (dd, $\{^1H\}$ 1B). ^1H (C_6D_6, 22 °C): 1.14 (s, 15H, C_5Me_5), −6.62 (br, 2H, B-*H*-B), −13.95 (s, br, 2H, Fe-*H*-B).

Synthesis of *nido*-1-$\{Cp^*Fe\}$-2-$Co(CO)_3B_4H_8$, 4. $Cp^*FeB_4H_{11}$/Cp^*_2Fe (140 mg, 2:1 ratio ≈ 92 mg, 0.37 mmol of $Cp^*FeB_4H_{11}$) was dissolved in 20 mL of fresh hexane. $Co_2(CO)_8$ (120 mg, 0.37 mmol) was added to a Schlenk flask equipped with a stir bar, and the ferraborane solution was added by cannula. The solution rapidly changed to orange-brown and then red after 1 h. The solvent was removed under vacuum and the orange-brown residue chromatographed with pentane. Concentration of the first, bright orange, band yielded orange, air-stable crystals at −20° C suitable for X-ray analysis.

Table 1. Crystal Data and Structure Refinement for 4

empirical formula	$C_{13}H_{23}B_4CoFeO_3$
fw	385.33
T	100(2) K
λ (Mo, Kα)	0.71073 Å
cryst syst	monoclinic
space group	$P2(1)/n$
a	9.2109(6) Å
b	16.4715(11) Å
c	11.7973(8) Å
β	101.2170(10)°
V	1755.7(2) Å^3
Z	4
D_{calc}	1.458 g·cm^{-3}
μ(Mo Kα)	1.774 mm^{-1}
F(000)	792
cryst size	0.3 × 0.3 × 0.3 mm
θ range	2.15−28.29°
monochromator	graphite
index ranges	h: − 12→12
	k: − 21→21
	l: − 15→15
total no. of data	18 431
unique	4348
GooF	1.049
R1	0.0370
wR2	0.0915
largest diff peak, hole	1.810 and −0.502 e/Å^3

Spectroscopic Data. ^{11}B NMR (C_6D_6, 22 °C): 55.00 (d, $^1J_{BH} = 146$ Hz, $\{^1H\}$ 2B), 8.98 (d, $^1J_{BH} = 143$ Hz, $\{^1H\}$ 2B). $^1H\{^{11}B\}$ NMR (C_6D_6, 22 °C): 5.44 (2H, BH_t), 3.29 (2H, BH_t), 1.36 (15H, C_5Me_5), −0.82 (2H, B-*H*-B), −2.88 (1H, B-*H*-B), −16.9 (1H, Fe-*H*-Co). IR (C_6D_6; cm^{-1}): 2506 (w, BH), 2494 (w, BH), 2064 (s, CO), 2016 (s, CO), 1995 (s, CO). EI$^+$MS: *m/z* M$^+$ 386, calcd for $C_{13}H_{23}FeB_4CoO_3$ 386.07007, measd 386.06728. Anal. Calcd for $C_{13}H_{23}FeB_4CoO_3$: C, 40.52; H, 6.02. Found: C, 40.65; H, 6.17. Yield based on 0.37 mmol of Fe used: 85%.

X-ray Structure of 4. A crystalline sample in inert oil was mounted on a glass pin and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated using a Bruker Apex system and are summarized in Table 1. The structure was solved by direct methods using SHELXS-97 and refined using SHELXL-97 (Sheldrick, G. M., University of Göttingen). Non-hydrogen atoms were found by successive full matrix least-squares refinement on F^2 and refined with anisotropic thermal parameters. Hydrogen atoms were placed at idealized positions (except B-H and M-H hydrogen atoms, which were located from the difference maps), and a riding model with fixed thermal parameters [$u_{ij} = 1.2U_{ij}$(eq) for the atom to which they are bonded] was used for subsequent refinements of the hydrogen atoms.

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

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