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Communications

Routes to Compounds Containing M−B Bonds. Reaction of $[Cp^*FeH_2]_2$ with $BH_3{\cdot}THF$, Yielding the Hydrogen-Rich *arachno*-Ferrapentaborane 1-$Cp^*FeB_4H_{11}$ ($Cp^* = \eta^5$-C_5Me_5)

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Summary: The reaction of $[Cp^*FeH_2]_2$ *(*$Cp^* = \eta^5$-C_5Me_5*) with* $BH_3{\cdot}THF$ *under mild conditions produces the new arachno-ferraborane 1-*$Cp^*FeB_4H_{11}$ *via a boraallyl intermediate. Reaction of 1-*$Cp^*FeB_4H_{11}$ *with* $Co_2(CO)_8$ *yields the novel nido-dimetallahexaborane 1,2-(*Cp^*Fe*)-{*$Co(CO)_3$*}*B_4H_8*, which has been characterized by an X-ray diffraction structure determination.*

The reactions of monoboranes with mono(cyclopentadienyl)metal chlorides generate metallaboranes containing metals from groups 5−9.[1] Mild reaction conditions foster kinetic control that leads to good selectivity and high yields in most cases. However, three first-row metals (Mn, Fe, Ni) fail to yield metallaboranes via this route. The only metal-containing products observed were the metallocene (Mn, Fe) or metal (Ni). One of our main objectives has been to explore the effects of metal variation on metallaborane chemistry.[2] Hence, as metallaboranes derived from first-row metals have properties distinctly different from those of their heavier congeners, e.g., Co vs Rh and Ir[3−5] and Cr vs Mo and W,[6−8] we have sought alternate routes to access metallaboranes of Mn, Fe, and Ni. Here we report that a mono(cyclopentadienyl)iron hydride provides a useful synthetic route to a ferraborane of the type sought.

Our understanding of the formation of metallaboranes via the chloride route requires formation of a metal *poly*borohydride coupled with fast H_2 elimination and metallaborane formation relative to borane loss and hydride formation.[5] $[Cp^*FeX]_n$ (X = Cl, Br; $Cp^* = \eta^5$-C_5Me_5) has been poorly characterized,[9] and in situ reactions of the presumed $[Cp^*FeCl]_n$ with monoboranes may well never produce the requisite polyborohydride. Hence, we sought other means of chemically accessing an iron polyborohydride.

Metal borohydrides are in equilibrium with hydrides, and the equilibrium position of reaction 1 depends on the metal, the Lewis basicity of the solvent, and other parameters.[10−12] As a polyborohydride can undergo

$$M_m(BH_4)_n \leftrightarrow M_mH_n + nBH_3 \tag{1}$$

$$M_m(BH_4)_n \rightarrow M_mB_nH_{4n-2} + H_2 \tag{2}$$

$$M_mB_nH_{4n-2} + BH_3 \rightarrow M_mB_{n+1}H_{4n-1} + H_2 \tag{3}$$

dihydrogen elimination (reaction 2)[7,13] to form a metallaborane, the reaction of metal hydrides with $BH_3{\cdot}THF$ constitutes an alternative route to compounds with M−B bonds. The maximum number of boron atoms in the first-formed metallaborane should be determined by *n*. However, cluster building can continue, as reaction 3 has been established for nearly all the metals studied previously.[5]

Previous reports confirm the viability of hydrides as a source of metallaboranes;[14−16] however, different ancillary ligands make it difficult to judge whether these hydrides access the same reaction manifold as $[Cp^*MCl]_n$ precursors. To establish this point, we first compared the reactivity of $BH_3{\cdot}THF$ with $[Cp^*RuCl_2]_2$ vs that with $[Cp^*RuH_2]_2$.[17] The final product is the same in both reactions.[4,18] The hydride reacts with $BH_3{\cdot}THF$ (but not

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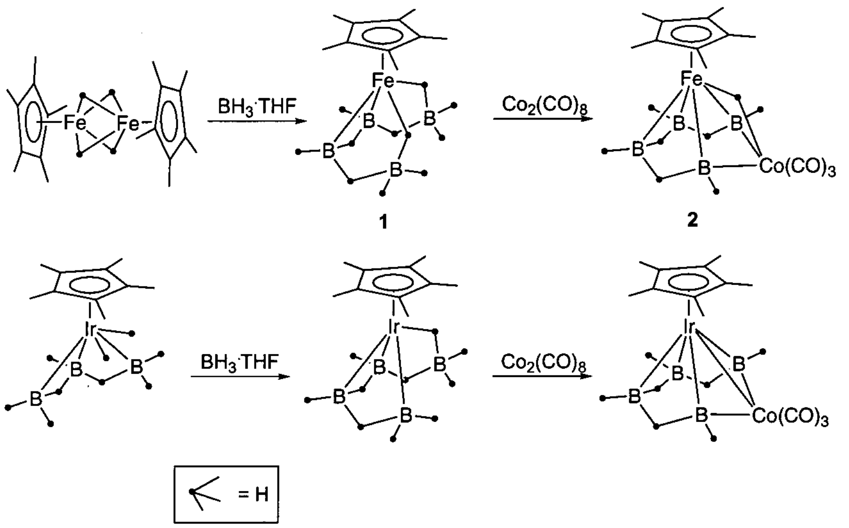
Scheme 1



$LiBH_4$) at lower temperatures, and the milder conditions gave higher yields and permitted the observation of distinct intermediates preceding the formation of $[Cp^*RuH_2]_2B_3H_7$ when the reaction was monitored by NMR spectroscopy. Encouraged by these results, we extended the investigation to iron.

Reaction of $[Cp^*FeH_2]_2$[19] with borane at 22 °C is facile, leading to two major products—Cp^*_2Fe and a new ferraborane, **1**, in a ratio of ~1:2 based on integration of the Cp* methyl resonances in the ^1H NMR.[20] The mass spectrum gave a minimal molecular formula of $Cp^*FeB_4H_9$; however, the number and intensities of the resonances in the proton NMR require two additional hydrogen atoms, yielding $Cp^*FeB_4H_{11}$ (**1**), which corresponds to an eight-skeletal-electron-pair, five-fragment metallaborane analogous to *arachno*-B_5H_{11}.[21,22] The equal-intensity doublet and triplet in the ^{11}B NMR is only consistent with the Cp*Fe fragment in an apical position, i.e., 1-$Cp^*FeB_4H_{11}$, as shown in Scheme 1. All other spectroscopic data are consistent with the postulated structure. Crystals of X-ray quality were never obtained.

Crystallographically characterized *arachno*-metallapentaboranes are known, e.g., 1-$\{(PR_3)_2(CO)Ir\}B_4H_9$,[23] 1-$\{Cp^*Co\}B_4H_{10}$,[3] and 3-$\{Cp^*(PMe_3)Ru\}B_4H_9$,[24] and the framework spectroscopic parameters of **1** are comparable with those of the first two. In the case of *arachno*-1-$Cp^*IrB_4H_{10}$,[5] we were able to stucturally characterize a derivative formed cleanly in high yield, 1,2-$(Cp^*Ir)\{Co(CO)_3\}B_4H_7$, to provide structural corroboration. In the same manner, reaction of **1** with $Co_2(CO)_8$ cleanly generated in high yield a robust *nido*-dimetallahexaborane, 1,2-$(Cp^*Fe)\{Co(CO)_3\}B_4H_8$ (**2**), which is isoelectronic with $(Cp^*Ir)\{Co(CO)_3\}B_4H_7$.[25] Its structure in the solid state (Figure 1)[26] along with the spectroscopic data show that it is related to **1** in the same way as **3** is to **4** (Scheme 1).

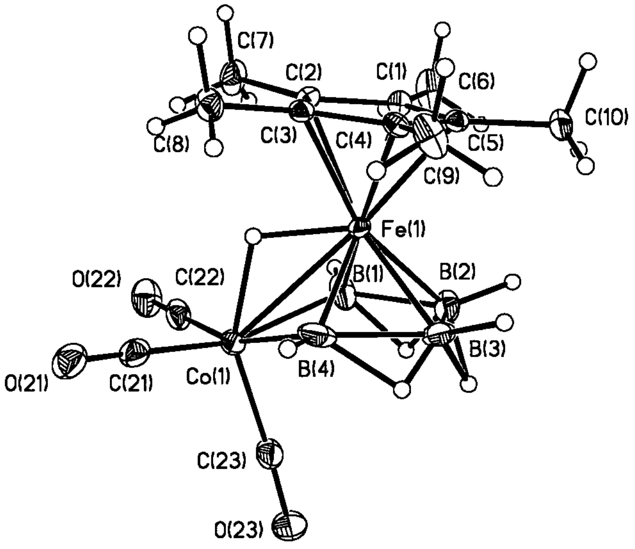


Figure 1. Molecular structure of 1,2-$(Cp^*Fe)\{Co(CO)_3\}B_4H_8$ (**2**), with 30% probability ellipsoids. Selected bond lengths (Å): Fe(1)−B(1) = 1.982(3), Fe(1)−B(4) = 1.983(3), Fe(1)−B(2) = 2.030(3), Fe(1)−B(3) = 2.039(3), Fe(1)−Co(1) = 2.5828(4), Co(1)−B(4) = 2.115(3), B(1)−B(2) = 1.744(5), B(2)−B(3) = 1.781(7), B(3)−B(4) = 1.764(6).

The formation of a mononuclear metallaborane from $[Cp^*FeH_2]_2$ was unexpected, as, with the notable exception of $[Cp^*IrCl_2]_2$, dinuclear metallaboranes are the

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(20) Spectroscopic data for **1** are as follows. ^{11}B NMR (C_6D_6, 22 °C; δ): 8.36 (d, $^1J_{BH} = 139$ Hz, $\{^1H\}$ 2B), −14.21 (br, t, $^1J_{BH} \approx 77$ Hz, $\{^1H\}$ 2B). ^1H NMR (C_6D_6, 22 °C; δ): 3.56 (br q, 2H, BH_t), 1.77 (br q, 2H, BH_t), 1.36 (s 15H, C_5Me_5), 1.29 (br q, 2H, BH_t), −3.23 (br s, 1H, $B{-}H{-}B$), −3.37 (br s, 2H, $B{-}H{-}B$), −15.85 (pcq, 2H, $Fe{-}H{-}B$, $^2J_{HH} = 20$ Hz). ^{13}C NMR (C_6D_6; δ): 93.40 (C_5Me_5), 9.59 (C_5Me_5). IR (hexane; cm^{-1}): 2524 (w, BH), 2456 (w, BH), 2405 (w, BH). EI^+ MS (*m/z*): calcd 244.159 94 ($M^+ - H_2$), measd 244.157 54. NMR yield based on Fe: 38%.

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(25) Spectroscopic data for **2** are as follows. ^{11}B NMR (C_6D_6, 22 °C; δ): 55.0 (d, $^1J_{BH} = 146$ Hz, $\{^1H\}$ 2B), 8.98 (d, $^1J_{BH} = 143$ Hz, $\{^1H\}$ 2B). ^1H NMR (C_6D_6, 22 °C; δ): 5.44 (q, 2H, BH_t), 3.29 (q, 2H, BH_t), 1.36 (s, 15H, C_5Me_5), −0.82 (br s, 2H, B−H−B), −2.88 (br s, 1H, $B{-}H{-}B$), −16.9 (s, 1H, Fe−H−Co). IR (hexane; cm^{-1}): 2506 (w, BH), 2494 (w, BH), 2064 (s, CO), 2016 (s, CO), 1995 (s, CO). EI^+ MS (*m/z*): calcd 386.070 07 (M^+), measd 386.067 28. Anal. Calcd for $C_{13}H_{23}FeB_4CoO_3$: C, 40.52; H, 6.02. Found: C, 40.65; H, 6.17. Isolated yield based on Fe: 85%.

(26) Crystal data for **2**: empirical formula $C_{13}H_{23}B_4CoFeO_3$; monoclinic crystal system; unit cell parameters $a = 9.2109(6)$ Å, $b = 16.4715(11)$ Å, $c = 11.7973(8)$ Å, $\beta = 101.2170(10)°$; space group $P2_1/n$; $Z = 4$; $T = 100(2)$ K; full-matrix least-squares refinement on F^2; indices (all data) R1 = 0.0394, wR2 = 0.0930.

major products formed from $[Cp^*MCl_n]_2$. In the case of Ir we have suggested that $Cp^*_2Ir_2(BH_4)_3H$ disproportionates into the observed products $Cp^*IrB_3H_9$ and Cp^*IrH_4.[5] If a similar process for Fe is written, eqs 4a,b

$$[Cp^*FeH_2]_2 + 3BH_3{\cdot}THF \rightarrow Cp^*_2Fe_2(BH_4)_3H + 3THF \quad (4a)$$

$$Cp^*_2Fe_2(BH_4)_3H + THF \rightarrow Cp^*FeB_3H_{10} + Cp^*FeH_3THF \quad (4b)$$

$$Cp^*FeB_3H_{10} + BH_3{\cdot}THF \rightarrow \mathbf{1} + H_2 \quad (4c)$$

suggest borallyl and hydride intermediates preceding the formation of **1**. Indeed, a ^{11}B NMR analysis of the reaction at low BH_3:$[Cp^*FeH_2]_2$ ratio reveals an additional ferraborane that exhibits the NMR fingerprint of a coordinated borallyl fragment.[27−29] Likewise, an unknown hydride is observed, and it may be this species that ultimately gives rise to the Cp^*_2Fe. $Cp^*FeB_3H_{10}$ is a perfectly reasonable intermediate in the formation of **1**, as borane cleanly converts the borallyl complex $(Cp^*IrH_2)B_3H_7$ to $Cp^*IrB_4H_{10}$ (Scheme 1).[5] Hence, the suggested route to **1** is given by eqs 4a−c.

In summary, **1** is a metastable metallaborane that can be generated efficiently from a hydride precursor. Although formed along with stable Cp^*_2Fe, the synthesis of a cobalt derivative demonstrates that **1** can be used in situ for studies of the reactivity of this novel hydrogen-rich *arachno*-ferraborane.

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Supporting Information Available: Text giving experimental procedures and characterization data for new compounds and X-ray structure information for **2**, including tables of crystal data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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