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Utilization of Transition-Metal Properties To Control Polyborane Formation. Synthesis of the *arachno*-Diiridahexaborane(12) 2,5-$\{Cp^*IrH\}_2B_4H_8$ and Its Conversion to the *nido*-Diiridahexaborane(10) 1,2-$\{Cp^*Ir\}_2(\mu\text{-}H)B_4H_7$ ($Cp^* = \eta^5\text{-}C_5Me_5$)

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*Summary: Metal-assisted borane condensation is demonstrated by the formation of the hexaborane(12) analogue arachno-2,5-$\{Cp^*IrH\}_2B_4H_8$ (**3**) by the reaction of two $BH_3{\cdot}THF$ moieties with the metal centers of the tetraborane(10) analogue $\{Cp^*IrH\}_2(\mu\text{-}H)B_2H_5$ (**1**). Mild thermolysis of **3**, which contains separated B_2H_4 fragments, results in H_2 elimination and the formation of the hexaborane(10) analogue nido-1,2-$\{Cp^*Ir\}_2(\mu\text{-}H)B_4H_7$ (**2**), containing a contiguous B_4H_7 fragment.*

With few exceptions known metallaboranes with frameworks containing five or more atoms exhibit closo or nido shapes.[1−6] Indeed, the greater the number of metal atoms, the greater the apparent tendency to eliminate hydrogen to form more closed structures. However, our metallaborane chemistry based on mono(cyclopentadienyl)metal fragments[7] has demonstrated that the choice of transition metal can be used to modify the facility of this process. Thus, earlier transition metals facilitate hydrogen loss, leading to highly condensed clusters with unusual framework structures containing W and Re, which we have characterized as hypoelectronic.[8−10] On the other hand, the group 9 metals Co and Rh form very stable *nido*-metallaboranes.[11,12] Ruthenaboranes lie somewhere between; e.g., the *nido*-diruthenahexaborane $Cp^*_2Ru_2B_4H_{10}$ ($Cp^* = \eta^5\text{-}C_5Me_5$) smoothly converts to the BH-capped *nido*-diruthenapentaborane $Cp^*_2Ru_2B_4H_8$, which is stable.[13]

Recently we have reported some initial experiments on the related Ir system[14] where we found that the initial products are hydrogen-rich arachno clusters from which H_2 is much less readily lost. For example, although $Cp^*_2Rh_2B_2H_6$ (an analogue of *nido*-B_4H_8) is the product of the reaction of $[Cp^*RhCl_2]_2$ with 4 $LiBH_4$,[13] $\{Cp^*IrH\}_2(\mu\text{-}H)B_2H_5$ (**1**) (an analogue of *arachno*-B_4H_{10}) is the product of the reaction of $[Cp^*IrHCl]_2$ with 2 $LiBH_4$. Furthermore, $Cp^*_2Ir_2B_2H_8$ shows little tendency to form $Cp^*_2Ir_2B_2H_6$. Hence, we have now explored the formation of larger arachno systems via the addition of borane to **1**. In doing so we have synthesized the first example of an *arachno*-dimetallahexaborane and demonstrated its clean conversion to a *nido*-dimetallahexaborane.

The reaction of **1** with an excess of $BH_3{\cdot}THF$ at elevated temperature leads to the formation of *nido*-1,2-$\{Cp^*Ir\}_2(\mu\text{-}H)B_4H_7$ (**2**) in excellent yield.[15] Examination of the reaction by ^{11}B NMR shows that the formation of **2** proceeds through an intermediate which was subsequently isolated in modest yield under less aggressive conditions and characterized as *arachno*-2,5-$\{Cp^*IrH\}_2B_4H_8$ (**3**).[16] In a separate experiment **3** was shown to smoothly convert into **2**.

The structure of **2** is evident via a comparison of its ^1H and ^{11}B NMR spectra with those of *nido*-1,2-$Cp^*_2Ru_2B_4H_{10}$; however, its shape was verified by a solid-state structure determination (Figure 1) as that of a *nido*-1,2-$Cp^*_2Ir_2B_4H_8$ analogue of B_6H_{10}.[17] It is worth noting that 1,2-$Cp^*_2Ir_2B_4H_8$ is the fourth member of the series of compounds $Cp^*_2M_2B_4H_8$ (M = Cr,[18] Re,[19] Ru,[13]

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[15] $\{Cp^*IrH\}_2(\mu\text{-}H)B_2H_5$ (0.1 g, 0.14 mmol) was dissolved in 5 mL of freshly distilled hexane in a 100 mL Schlenk tube. $BH_3{\cdot}THF$ (0.56 mL, 0.56 mmol) was added at room temperature. The solution was stirred for 48 h at 65 °C. Column chromatography was applied, and elution with hexane gave a yellow solution. Removal of the solvents in vacuo afforded 80 mg of yellow microcrystals of **2** (78%). Spectroscopic data for **2**: MS (FAB) $P^+ = 706$, 4 B, 2 Ir atoms, calcd for $^{12}C_{20}{}^1H_{38}{}^{11}B_4{}^{193}Ir_2$ 708.2605, obsd 708.2596; ^{11}B NMR (hexane, 22 °C) δ 42.3 (d, $J_{B-H} = 150$ Hz, $\{^1H\}$, s, 2B), −1.8 (d, s, $J_{B-H} = 141$ Hz, 2B); ^1H NMR (C_6D_6, 22 °C) 6.38 (pcq, 2H, $B-H_t$), 3.07 (pcq, 2H, $B-H_t$), 2.04 (s, 15H, C_5Me_5), 1.80 (s, 15H, C_5Me_5), −0.98 (s, br, 2H, $B-H-B$), −4.52 (s, br, 1H, $B-H-B$), −21.44 (s, 1H, $Ir-H$); IR (hexane, cm^{-1}) 2464 w, 2420 m ($B-H_t$). Anal. Calcd for $C_{20}H_{38}B_4Ir_2$: C, 34.02; H, 5.42. Found: C, 34.22; H, 5.55.

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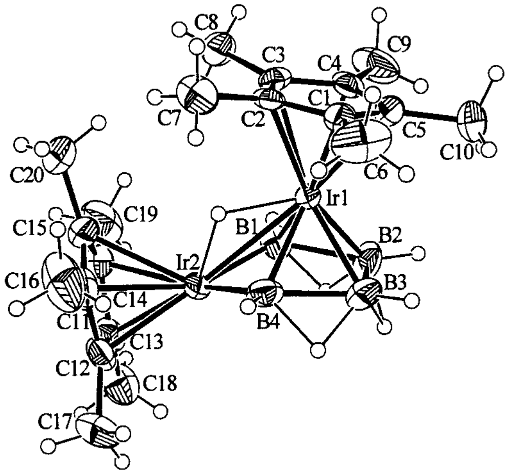


Figure 1. Molecular structure of *nido*-$\{Cp^*Ir\}_2(\mu\text{-}H)B_4H_7$ (**2**). Selected bond distances (Å) and angles (deg): Ir1−B2 = 2.088(13), Ir1−B3 = 2.106(13), Ir1−B1 = 2.118(11), Ir1−B4 = 2.120(13), B1−B2 = 1.869(19), B2−B3 = 1.83(2), B3−B4 = 1.87(2); B2−Ir1−B3 = 51.9(6), B2−Ir1−B1 = 52.8(6), B3−Ir1−B1 = 89.6(6), B2−Ir1−B4 = 89.6(6), B3−Ir1−B4 = 52.4(6), B4−Ir2−B1 = 90.4(6), B4−Ir2−Ir1 = 50.1(4), B1−Ir2−Ir1 = 50.0(3), B2−B1−Ir2 = 114.9(9), B3−B2−B1 = 106.9(9), B2−B3−B4 = 106.5(9), B3−B4−Ir2 = 115.1(9).

Ir), possessing identical compound stoichiometries but different metal identities.

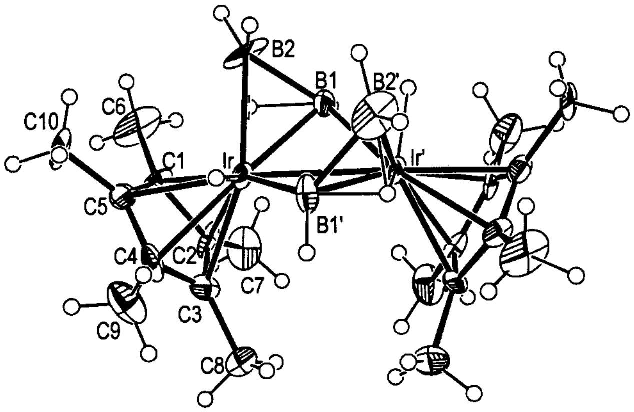
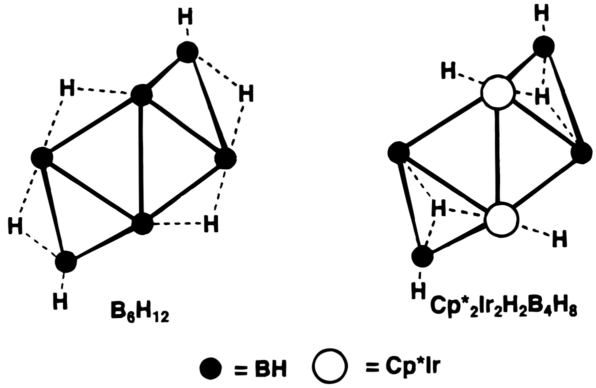


Figure 2. Molecular structure of *arachno*-2,5-$\{Cp^*IrH\}_2$-B_4H_8 (**3**). Selected bond distances (Å) and angles (deg): Ir−Ir′ = 2.7814(9), Ir−B1 = 2.160(14), Ir−B1′ = 2.18(2), Ir−B2 = 2.19(2), B1−B2 = 1.85(3), B1−Ir′ = 2.18(2); B1−Ir−B1′ = 93.2(7), B1−Ir−B2 = 50.2(8), B1′-Ir−B2 = 99.3(7), B1−Ir−Ir′ = 50.5(4), B1′−Ir−Ir′ = 49.8(4), B2−Ir−Ir′ = 87.2(6), B2−B1−Ir = 65.8(9), B2−B1−Ir′ = 118.0(11), Ir−B1−Ir′ = 79.7(5).

Chart 1



The NMR data on **3** are consistent with three structures which differ in the positioning of the metal atoms. Hence, a solid-state structure determination (Figure 2) was required to identify **3** as *arachno*-2,5-$\{Cp^*IrH\}_2$-B_4H_8.[20] As this constitutes the first crystallographic structure determination of a B_6H_{12} metal analogue, the structural metrics deserve further elaboration. Although B_6H_{12} itself has been known for a long time,[21] it has never been crystallographically characterized. However, its structure is well-established on the basis of NMR,[22] gas-phase electron diffraction,[23] and theoretical geometry and chemical shift calculations.[24] The observed framework of **3** is compared with that of B_6H_{12} in Chart 1. Both contain C_2 axes, and that for **3** bisects the Ir−Ir edge and is perpendicular to it. Likewise, both contain two outer BH_2 fragments rendered equivalent by the C_2 axis. If we take into account the larger edge distances associated with the metals in **3**, the shapes of the networks are very similar. The greatest difference lies in the positioning of the bridging hydrogens, which is perhaps understandable, as the precise positioning of these hydrogens in B_6H_{12} is important in reproducing the ^{11}B chemical shifts.[24] In **3** both the structural work and the $^1H\{\text{selective }^{11}B\}$ NMR spectra suggest two equivalent terminal Ir−H hydrogens rather than Ir−H−B bridges, as one might expect for a true analogue. Further the structural study suggests, but does not prove, the presence of triply bridging hydrogens on the IrB(1)B(2) triangles (Figure 2). The $^1H\{\text{selective }^{11}B\}$

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(16) $\{Cp^*IrH\}_2(\mu\text{-}H)B_2H_5$ (0.15 g, 0.22 mmol) was dissolved in 10 mL of freshly distilled hexane in a 100 mL Schlenk tube. $BH_3\cdot THF$ (0.88 mL, 0.88 mmol) was added at room temperature. The solution was stirred for 24 h at 60 °C. The ^{11}B NMR spectrum showed a mixture of **2** and **3**. Column chromatography was applied, and elution with hexane gave a yellow solution which contains **2**. Then elution with ether gave a red solution, which was slowly evaporated under nitrogen to give yellow microcrystals with some red solid. Washing with 2-propanol to remove the red solid gives 0.05 g of yellow microcrystals of **3** (32%). Spectroscopic data for **3**: MS (FAB) $P^+ = 708$, 4 B, 2 Ir atoms, calcd for $^{12}C_{20}{}^1H_{40}{}^{11}B_4{}^{193}Ir_2$ 710.2761, obsd 710.2809; ^{11}B NMR (hexane, 22 °C) δ 34.5 (d, $J_{B-H} = 110$ Hz, $\{^1H\}$, s, 2B), −14.7 (dd, $J_{B-H} = 120$ Hz, $\{^1H\}$, s, 2B); ^1H NMR (C_6D_6, 22 °C) 6.09 (pcq, 2H, B−H_t), 3.83 (pcq, 2H, B−H_t), 2.84 (pcq, 2H, B-H_t), 1.67 (s, 30H, C_5Me_5), −1.89 (s, br, 2H, B−*H*−B), −15.44 (s, 2H, Ir−*H*); IR (toluene, cm^{-1}) 2455 w, 2414 m (B−H_t). Anal. Calcd for $C_{20}H_{40}Ir_2B_4$: C, 33.92; H, 5.69. Found: C, 35.08; H, 6.12 (reflecting the difficulty of isolating an intermediate in the overall conversion of **1** to **2)**.

(17) Crystal data for **2**: yellow platelike crystal, $C_{20}H_{38}B_4Ir_2$, monoclinic, space group $P2_1/n$, $a = 8.3011(14)$ Å, $b = 19.742(3)$ Å, $c = 114.552(3)$ Å, $\beta = 93.448(15)°$, $V = 2380.5(7)$ Å^3, $Z = 4$, fw 706.14, $D_{calcd} = 1.970$ g/cm^3, $\mu = 11.171$ mm^{-1}, Mo Kα, $\lambda = 0.710\,73$ Å, $T = 293$ K, Enraf-Nonius CAD4, crystal size 0.38 × 0.12 × 0.06 mm^3, $2\theta_{max} = 49.96°$, R1 = 0.0382, wR2 = 0.0942 for 3339 observed unique reflections ($I > 2\sigma(I)$) and R1 = 0.0551, wR2 = 0.1007 for all 4177 unique reflections, including those with negative intensities.

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(20) Crystal data for **3**: yellow square pyramid-like, $C_{20}H_{40}B_4Ir_2$, tetragonal space group $P4_12_12$, $a = 8.7599(7)$ Å, $b = 8.7599(7)$ Å, $c = 30.4203(10)$ Å, $V = 2334.3(3)$ Å^3, $Z = 4$, fw 708.16, $D_{calcd} = 1.970$ g/cm^3, $\mu = 11.392$ mm^{-1}, Mo Kα, $\lambda = 0.710\,73$ Å, $T = 293$ K, Enraf-Nonius CAD4, crystal size 0.25 × 0.24 × 0.24 mm^3, $2\theta_{max} = 49.94°$, R1 = 0.0429, wR2 = 0.0968 for 1873 observed unique reflections ($I > 2\sigma(I)$) and R1 = 0.0498, wR2 = 0.1003 for all 2053 unique reflections, including those with negative intensities.

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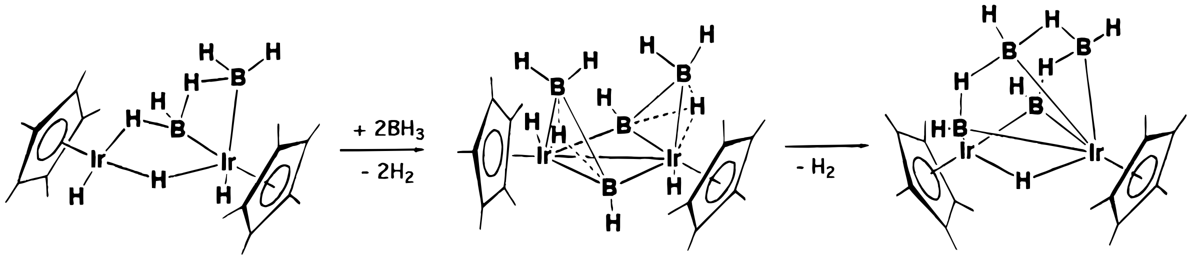
Scheme 1



$Cp^*_2Ir_2H_3B_2H_5$, 1 **$Cp^*_2Ir_2H_2B_4H_8$, 3** **$Cp^*_2Ir_2HB_4H_7$, 2**

NMR shows association with both B(1) and B(2), but unfortunately, the chemical shift does not rule out triply bridging protons. Both differences suggest that the affinity of the Cp*Ir fragment for hydrogen perturbs the framework relative to B_6H_{12}.

As shown in Scheme 1, the conversion of **1** to **2** via **3** is transparent, at least in an operational sense. Addition of two monoboranes to the Ir−Ir edge with elimination of 2 H_2 leads directly to **3**. One further elimination of H_2, accompanied by B−H−B bond formation and Ir−B bond plus skeletal hydrogen rearrangement, leads to **2**. We have previously reported low-temperature spectroscopic evidence for the formation of an arachno intermediate in the synthesis of $Cp^*WH_3B_4H_8$ from Cp^*WCl_4.[25] Thus, it is clear that the construction of a polyborane fragment on a metal center from monoboranes proceeds via hydrogen-rich intermediates with kinetic stabilities that depend on the identity of the transition metal.

The connection between the cluster expansion reactions of the iridaboranes and pure boranes is more than simple analogy. For example, Shore and co-workers have demonstrated the addition of borane to polyhedral anions to yield anions containing an additional borane fragment; e.g.

$$B_5H_8^- + {}^1/_2B_2H_6 \rightarrow B_6H_{11}^-$$

giving B_6H_{12} after protonation.[26] The utilization of anions with a basic site generated by the removal of a bridging proton creates the selectivity observed—a selectivity not found in the condensation of neutral boranes.[27] In the iridaborane system described here, as well as in previously described Rh and Ru systems,[13] it is the metal fragment that provides an electron-rich site for electrophilic attack. Hence, in the reaction of **1** with borane, our observations demonstrate that the contiguous B_4 fragment found in **2** results from the joining of the two B_2 fragments of **3** and does not originate from addition of borane to the B_2 fragment of **1**. Clearly, this constitutes metal-assisted borane condensation.

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Supporting Information Available: Tables giving details of the data collection and reduction and structure solution and refinement, crystallographic parameters, atomic coordinates and equivalent isotropic temperature factors, bond distances and bond angles, and anisotropic displacement parameters for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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