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Novel Iridaboranes from the Reactions of $Cp^*_2Ir_2H_xCl_{4-x}$, $x = 0-2$, with $LiBH_4$. Existence of a Concurrent Reaction Channel in the Conversion of Metal Chlorides to Metal Hydrides

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*Summary: Reaction of either $Cp^*_2Ir_2Cl_4$ or $Cp^*_2Ir_2HCl_3$ with $LiBH_4$ leads to formation of the new iridaborane $Cp^*Ir(H)_2B_3H_7$, **1** (a borallyl complex), in parallel with Cp^*IrH_4. In contrast, reaction of $Cp^*_2Ir_2H_2Cl_2$ with $LiBH_4$ leads exclusively to $Cp^*_2Ir_2(H)_3B_2H_5$, **3**, which is isolobal with **1**.*

The reaction of a metal chloride with a group 13 hydride constitutes one of the standard methods of preparing molecular metal hydrides.[1] Although this reaction is often written as a replacement of Cl^- by H^- with the fate of the group 13 species unspecified, it is known that metathesis of Cl^- by a pseudo halide, e.g., BH_4^-, is the first step. Indeed, in many instances the metal borohydride can often be isolated and characterized.[2] "Workup", e.g., addition of a Lewis base, removes a Lewis acid by displacement, e.g., BH_3, or hydrolysis generates the hydride.[3,4]

It follows that a metal reagent with more than one chloride can be used to produce a polyborohydride, thereby permitting the elimination of H_2 with formation of metallaboranes to compete with hydride formation. Indeed, following in the footsteps of Messerle,[5] we have shown that the reaction of dinuclear Cp^*MCl_n complexes with $LiBH_4$, as well as BH_3THF, constitutes a general route to metallaboranes for a variety of transition metals.[6−8] Although competition between H_2 elimination and metal hydride formation in polyborohydrides seems logical, it was only when we explored the iridium system that its consequences became explicit.

In terms of hydrides, the iridium system has been well studied.[9−11] In addition, there are a number of mononuclear and dinuclear iridaboranes,[12,13] but the relevant compound is $Cp^*_2Ir_2(H)_2(\mu\text{-}H)(\mu\text{-}BH_4)$ (Scheme 1).[14] It is formed in the reaction of $[Cp^*_2Ir_2H_3]^+$ with borohydride and was shown to possess a bridging borohydride ligand.[14] Here we describe the formation of a new mononuclear borallyl complex formed concurrently with a known hydride in the reaction of $Cp^*_2Ir_2Cl_4$ or $Cp^*_2Ir_2HCl_3$ with $LiBH_4$. This is contrasted with the formation of an unusual dinuclear diborane complex generated from the reaction of $Cp^*_2Ir_2H_2Cl_2$ with $LiBH_4$. These results reveal a complex, but understandable, competition between H_2 and borane elimination, yielding iridaboranes and hydrides.

As shown in Scheme 1, the reaction of $Cp^*_2Ir_2Cl_4$ with excess $LiBH_4$ produces a pair of products in high yield. The known hydride Cp^*IrH_4 is accompanied by the new metallaborane $Cp^*Ir(H)_2B_3H_7$, **1** (≈40% each). On the basis of the spectroscopic data,[15] **1** is formulated as a dihydrido borallyl complex, a member of a growing set of such compounds.[16−24] Although a structure determination was frustrated by rapid decay in the X-ray beam, the structure of $Cp^*Ir(CO)B_3H_7$, **2**, formed as the principal product of the reaction of **1** with $Co_2(CO)_8$, has been obtained and is shown in Figure 1. It is a mono metal analogue of B_4H_{10} (Scheme 2),[25] and comparison

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(15) Spectroscopic data for **1**: MS(FAB), $(P^+{-}H_2) = 368$, 3 B, 1 Ir atoms. Calcd for weighted average of isotopomers lying within the instrument resolution, 368.1630, obsd, 368.1611. NMR: ^{11}B (hexane, 22 °C), δ −7.7 (dt, $J_{B-H} = 140$ Hz, 50 Hz, $\{^1H\}$, s, 1B), −14.3 (d, $J_{B-H} = 120$ $\{^1H\}$, s, 2B); ^1H (C_6D_6, 22 °C), 3.11 (partially collapsed quartet, pcq, 4H, B−H_t), 2.29 (pcq, 1H, B−H_t), 1.62 (s, 15H, C_5Me_5), −5.14 (s, br, 2H, B−*H*−B), −14.51 (s, 2H, Ir−*H*). IR (C_6D_6, cm^{-1}): 2512 w, 2472 m, 2420 s (B−H_t), 2167 m (Ir−H). Anal. Calcd for $C_{10}H_{24}B_3Ir$: C, 32.55; H, 6.56. Found: C, 33.93; H, 6.35.

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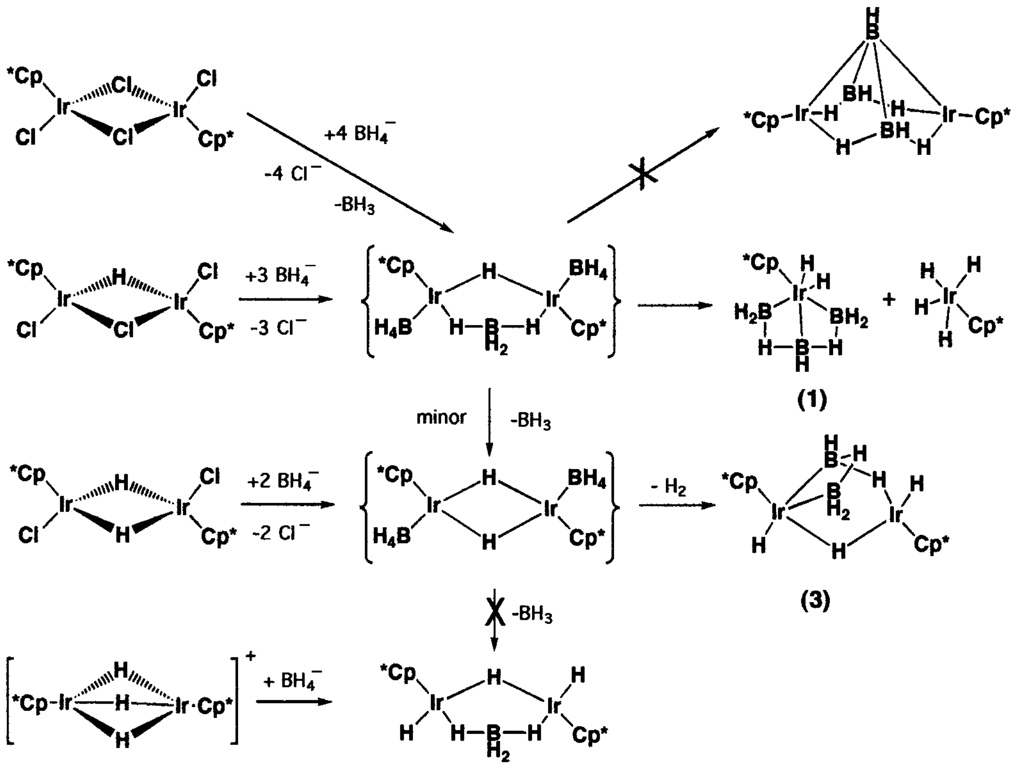
Scheme 1



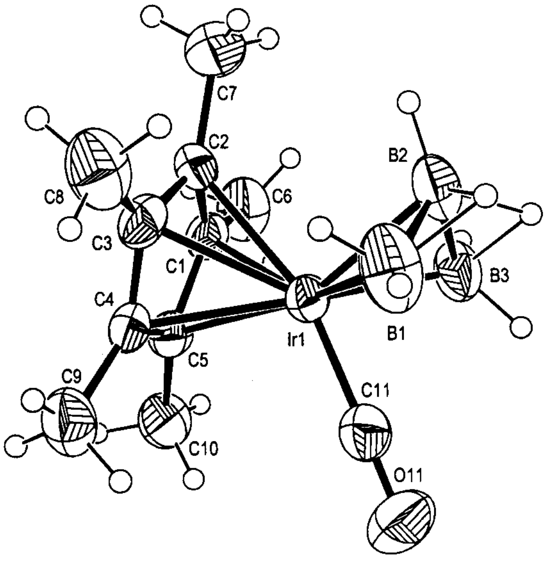
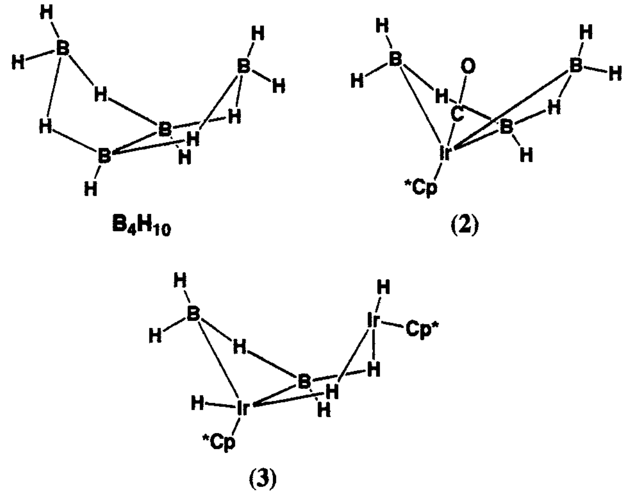


Figure 1. Molecular structure of $Cp^*Ir(CO)B_3H_7$, **2**. Selected bond distances (Å) and angles (deg): Ir1−C11 1.829(17), Ir1−B1 2.236(19), Ir1−B2 2.147(17), Ir1−B3 2.170(18), B1−B2 1.87(3), B2−B3 1.82(3), C11−O11 1.182(18), C11−Ir1−B2 104.6(7), C11−Ir1−B3 83.0(8), B2−Ir1−B3 49.8(7), B2−Ir1−B1 50.4(8), B3−Ir1−B1 89.0(8), B2−B1−Ir1 62.3(8), B3−B2−B1 113.9(15), B3−B2−Ir1 65.8(8), B1−B2−Ir1 67.3(8), B2−B3−Ir1 64.4(8).

of the spectroscopic data of **2**[26] with those of **1** establishes the structure of the latter.

Scheme 2



Consistent with known chemistry, we suggest rapid metathesis of Cl^- by BH_4^-, BH_3 loss, and product formation (Scheme 1). This suggests the intermediate, $\{Cp^*_2Ir_2(H)(BH_4)_3\}$, shown in Scheme 1. The generation of identical products from the reaction of $Cp^*_2Ir_2Cl_3H$[10] with $LiBH_4$ is consistent with this hypothesis. Contrast these results with the reaction of $Cp^*_2Co_2Cl_2$ or $Cp^*_2Rh_2Cl_4$ with $LiBH_4$.[24,27] In both cases, $Cp^*_2M_2B_2H_6$, M

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[25] Crystal data for **2**: colorless crystal, $C_{11}H_{22}B_3IrO$, monoclinic, space group $P2_1/c$, $a = 7.2512(4)$ Å, $b = 14.4243(18)$ Å, $c = 28.001(4)$ Å, $\beta = 97.40(1)°$, $V = 2904.3(6)$ Å^3, $Z = 8$, fw = 394.92, $D_{calc} = 1.806$ g/cm^3, $\mu = 9.171$ mm^{-1}, Mo Kα, $\lambda = 0.71073$ Å, $T = 293$ K, Enraf-Nonius CAD4, crystal size 0.15 × 0.15 × 0.10 mm^3, $2\theta_{max} = 50.02°$, R1 = 0.0475, wR2 = 0.1067 for 3665 observed unique reflections ($I > 2\sigma(I)$) and R1 = 0.0822, wR2 = 0.1324 for all 5127 unique reflections including those with negative intensities.

[26] Spectroscopic data for **2**: MS(FAB), $P^+ = 396$, 3 B, 1 Ir atoms, fragment peak corresponding to loss of one CO. Calcd for weighted average of isotopomers lying within the instrument resolution, 396.1579, obsd, 396.1592. NMR: ^{11}B (hexane, 22 °C), δ −4.9 (dt, $J_{B-H} = 140$ Hz, 55 Hz, $\{^1H\}$, s, 1B), −11.6 (t, $J_{B-H} = 120$, $\{^1H\}$, s, 2B); ^1H (C_6D_6, 22 °C), 3.21 (overlapping pcq, 4H, B−H_t), 3.10 (overlapping pcq, 1H, B−H_t), 1.54 (s, 15H, C_5Me_5), −4.68 (s, br, 2H, B−H−B). IR (hexane, cm^{-1}): 2519 w, 2493 w, 2435 m (B−H_t), 2027 vs (CO). Anal. Calcd for $C_{11}H_{22}B_3IrO$: C, 33.45; H, 5.61. Found: C, 34.36; H, 5.78.

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= Co, Rh, is produced. For rhodium, reduction to $Cp^*_2Rh_2Cl_2$ by H_2 elimination from the dihydride precedes metallaborane formation, but no like reduction chemistry is observed with Ir.

The reaction of $Cp^*_2Ir_2H_2Cl_2$[10] with $LiBH_4$ was examined and found to produce $Cp^*_2Ir_2(H)_3(B_2H_5)$, **3**, in an isolated yield of 85%.[28] Trace amounts of **3** were observed in the reaction of $[Cp^*IrCl_2]_2$ with $LiBH_4$, showing that loss of BH_3 from $\{Cp^*_2Ir_2(H)(BH_4)_3\}$ is not competitive with formation of **1**. The spectroscopic data for **3** are consistent with the static structure in the solid state (Figure 2).[29] The new compound consists of a dinuclear $Cp^*_2Ir_2H_2(\mu\text{-}H)$ fragment bridged asymmetrically by a B_2H_5 ligand for which prototypes exist.[30,31] Compounds **1** and **3** are related in that replacement of a BH vertex of **1** by an isolobal Cp*Ir vertex generates **3** (Scheme 2).

The fate of a metal polyborohydride complex is determined by competition between elimination of BH_3 and H_2. The former yields hydrides and is enhanced by factors that stabilize the Lewis acid, namely, basic solvents or donor substituents. On the other hand, elimination of H_2 from the polyborohydride leads to B−B and M−B bond formation, i.e., metallaboranes. Thus, for the proposed $\{Cp^*_2Ir_2(H)_2(BH_4)_2\}$ intermediate, H_2 elimination leads to **3**. In contrast, H_2 elimination from $\{Cp^*_2Ir_2(H)(BH_4)_3\}$ to give $Cp^*_2Ir_2B_3H_7$, the analogue of known $Cp^*_2M_2B_3H_7$, M = Co,[27] Rh,[32] is not competitive with cleavage to yield **1** and Cp^*IrH_4. The stability of the hydride is the likely driving force here. To compare these iridaboranes with related ones of cobalt and rhodium, the cluster-building reactions of **1** and **3** with main group and metal fragments have been surveyed, and the derivatives formed will be described in the full publication.

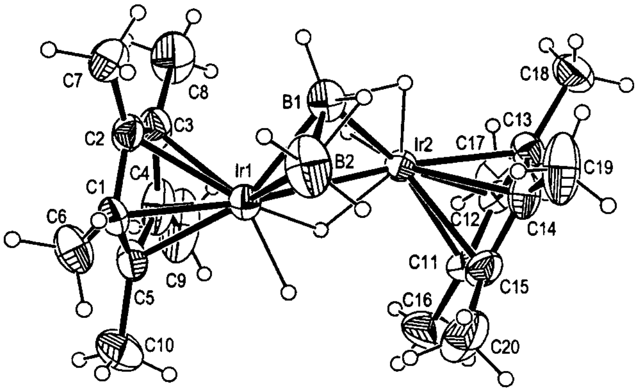

Figure 2. Molecular structure of $Cp^*_2Ir_2(H)_3(B_2H_5)$, **3**. Selected bond distances (Å) and angles (deg): Ir1−Ir2 2.8227(8), Ir1−B1 2.169(13), Ir1−B2 2.23(2), Ir2−B1 2.178(14), B1−B2 1.83(2), B1−Ir1−B2 49.2(6), B2−Ir1−Ir2 80.1(4), B1−Ir2−Ir1 49.4(3), B2−B1−Ir1 67.1(7), B2−B1−Ir2 109.6(9), Ir1−B1−Ir2 81.0(5), B1−B2−Ir1 63.7(6).

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Supporting Information Available: Information on detailed experimental procedures for **1**−**3** and data collection and reduction, structure solution and refinement, and tables of 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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(28) Spectroscopic data for **3**: MS(FAB), $P^+ = 684$, 2 B, 2 Ir atoms. Calcd for weighted average of isotopomers lying within the instrument resolution, 684.2262, obsd, 684.2259. NMR: ^{11}B (hexane, 22 °C), δ 14.2 (d, $J_{B-H} = 130$ Hz, $\{^1H\}$, s, 1B), −14.6 (apparent t, $\{^1H\}$ s, 1B); ^1H (C_6D_6, 22 °C), 4.77 (overlapping pcq, 1H, B−H_t), 4.19 (overlapping pcq, 1H, B−H_t), 2.89 (pcq, 1H, B−H_t), 1.95 (s, 15H, C_5Me_5), 1.89 (s, 15H, C_5Me_5), −2.75 (s, br, 1H, B−*H*−B), −13.99 (s, 1H, Ir−*H*−B), −17.83 (s, 1H, Ir−*H*), −17.89 (s, 1H, Ir−*H*), −18.76 (s, 1H, Ir−*H*). IR (hexane, cm^{-1}): 2440 m, 2389 m (B−H_t), 2172 w, 2102 m (Ir−H). Anal. Calcd for $C_{20}H_{38}B_2Ir_2$: C, 35.09; H, 5.60. Found: C, 35.18; H, 5.51.

(29) Crystal data for **3**: brown crystal, $C_{20}H_{38}B_2Ir_2$, triclinic, space group $P\bar{1}$, $a = 8.551(2)$ Å, $b = 10.306(2)$ Å, $c = 14.884(2)$ Å, $\alpha = 107.113(13)°$, $\beta = 92.554(12)°$, $\gamma = 111.67(2)°$, $V = 1147.5(4)$ Å^3, $Z = 2$, fw = 684.52, $D_{calc} = 1.981$ g/cm^3, $\mu = 11.585$ mm^{-1}, Mo Kα, $\lambda = 0.71073$ Å, $T = 293$ K, Enraf-Nonius CAD4, crystal size 0.35 × 0.18 × 0.18 mm^3, $2\theta_{max} = 50.02°$, R1 = 0.0389, wR2 = 0.0963 for 3201 observed unique reflections ($I > 2\sigma(I)$) and R1 = 0.0503, wR2 = 0.1013 for all 4006 unique reflections including those with negative intensities.

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