1: A solution of $K[NCPh_2]$ (0.094 mmol) in THF (10 mL) was transferred to a solution of $[Re(OTf)(CO)_3(bpy)]$ (0.050 g, 0.086 mmol) in THF (15 mL) at −78 °C. The color changed from yellow to dark green. After reaching room temperature, 15 min stirring, solvent evaporation, extraction (CH_2Cl_2, 2 × 10 mL), filtration, evaporation of the solvent, crystallization from THF/hexane yielded **1** in (0.045 g, 87 %). IR (THF): $\tilde{\nu} = 1999$, 1898, 1880 cm^{-1}; ^1H NMR(200 MHz, CD_2Cl_2): $\delta = 8.80$, 8.37, 8.11, 7.44 (m, 2H each; bpy), 7.24 (m, 6H; Ph), 6.96 ppm (m, 4H; Ph); $^{13}C\{^1H\}$ NMR (75.46 MHz, CD_2Cl_2): $\delta = 158.10$ [N=C], 157.14, 155.30, 143.25 [bpy], 142.30, 128.94, 127.53, 126.14 [2Ph], 125.54, 121.79 ppm [bpy].

Reaction of 1 with *p*TolNCO: *p*TolNCO (9.0 μL, 0.082 mmol) was added to a solution of **1** (0.050 g, 0.082 mmol) in THF (15 mL). Evaporation of the solvent, followed by crystallization from CH_2Cl_2/hexane yielded **4** (0.053 g, 87 %). IR (CH_2Cl_2): $\tilde{\nu} = 2014$, 1913, 1887, 1716 cm^{-1} (C=O); ^1H NMR(200 MHz, CD_2Cl_2): $\delta = 8.80$, 8.74, 8.16 (m, 2H each; bpy), 7.54–7.05 (m, 24H; bipy, Ph), 6.66, 6.64, 6.51, 6.48 (qAA′BB′, 4H; *p*Tol), 2.05 ppm (s, 3H; CH_3, *p*Tol).

Reaction of 1 with BzNCO: BzNCO (20 μL, 0.164 mmol) was added to a solution of **1** (0.050 g, 0.082 mmol) in THF (15 mL) and the mixture was stirred for 15 min. Workup as for **4** afforded orange crystals of **6** (0.060 g, 84 %). IR (THF): $\tilde{\nu} = 2019$, 1917, 1890, 1669, 1623 cm^{-1} (C=O and C=N); ^1H NMR (200 MHz, CD_2Cl_2): $\delta = 8.83$, 7.84, 7.75 (m, 2H each; bpy), 7.39–6.79 (m, 44H; bpy, Bz, Ph), 4.49 (s, 2H, CH_2), 4.29 ppm (s, 2H; CH_2).

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An Iridaborane Reaction Cycle Driven by PMe_3 and BH_3·THF: Synthesis and Characterization of $[Cp^*IrB_3H_7(PMe_3)]$ and $[Cp^*IrB_2H_6(PMe_3)]$**

Ramón Macías,* Thomas P. Fehlner, and Alicia M. Beatty

Polyhedral boron-containing compounds show an extensive structural chemistry that exhibits clear interconnections with organometallic and other p-block transition-element compounds.[1,2] However, until recently, limitations of synthetic methods have precluded systematic study of metallaboranes, and as a result their reactivity has remained largely unexplored relative to that of organometallic compounds.[3–6] This changed significantly with the development of a general route to a class of metallaboranes in which the metal can be varied from Group 5–9.[7] The results to date show that although metallaborane chemistry does overlap with organometallic chemistry, the former exhibits reactivities without parallel in other areas.[8,9]

The chemistry of the environment and of living organisms is often reversible and based on catalytic and stoichiometric cycles. Industrial chemistry is also highly reliant on the use of catalytic and stoichiometric cycles. The importance of such systems has provided much of the impetus for research in organometallic chemistry.[10,11] Even though significant examples exist,[12–14] polyhedral boron chemistry shows a marked lack of reaction cycles either catalytic or stoichiometric. Herein we report a novel stoichiometric cycle in which the iridaboranes, [1-(Cp*)-1-$(H)_2$-*arachno*-1-IrB_3H_7] (**1**)[15] and [1-(Cp*)-1-H-*arachno*-1-IrB_4H_9] (**2**)[15] ($Cp^* = \eta^5\text{-}C_5Me_5$) are interconverted via novel phosphane-substituted derivatives (Scheme 1). The chemistry is driven by acid/base chemistry of PMe_3 ($Me = CH_3$) and borane.

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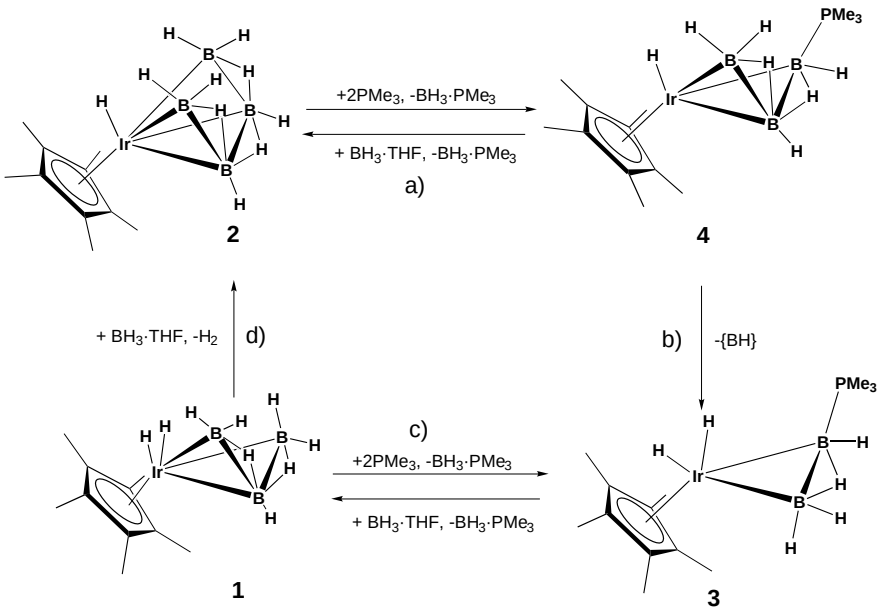

Scheme 1. a) C_6D_6 solution, PMe_3 (forward) and BH_3·THF (reverse), room temperature; b) solid state or solution, room or lower temperatures; c) C_6D_6 solution, PMe_3 (forward) and BH_3·THF (reverse), room temperature; d) THF solution, excess of BH_3·THF, 60 °C.

PMe_3 reacts at room temperature with **1** to give BH_3PMe_3 and the new three-vertex iridatriborane, [1-(Cp*)-1-$(H)_2$-*arachno*-1-IrB_2H_4-2-(PMe_3)] (**3**). By contrast, **2** reacts with the PMe_3 to give [1-(Cp*)-1-(H)-*arachno*-1-IrB_3H_6-2-(PMe_3)] (**4**), which decomposes slowly in solution (and the solid state) to give **3** (Scheme 1). Compound **4** has been characterized by NMR spectroscopy and mass spectrometry. The ^{11}B-{^1H} NMR spectrum shows three signals with a relative intensity ratio of 1:1:1: the signal at the highest field being a doublet. Accordingly, the ^{31}P-{^1H} NMR spectrum shows a broad quartet indicating a B–PMe_3 bond. ^1H NMR spectroscopy demonstrates the existence of three B-H terminal hydrogen atoms, two B-H-B bridging hydrogen atoms, and one Ir-H hydride as well as the presence of a Cp* ring and a PMe_3 ligand. The proposed structure of **4** (Scheme 1) is that of well-known metal "borallyl" complexes such as **1**,[15] [$(PPh_3)_2$(CO)-$HIrB_3H_7$],[16] [(Cp*)$Co(CO)B_3H_7$],[17] and Group 10 metallatetraboranes.[18–23]

An X-ray diffraction analysis of **3** shows that the molecular structure[24] (Figure 1) is analogous to that of previously reported metallatriboranes of formulation, $K[M(CO)_4(\eta^2$-$B_2H_5)]$ (M = Fe, Ru, Os) and $[M(\eta^5$-$C_5H_5)(CO)_2(\eta^2$-$B_2H_5)]$ (M = Fe, Ru).[25] The PMe_3 group is bound to the boron atom B2 of the {IrB_2} triangle *tran*s to the η^5-C_5Me_5 ligand; a configuration probably driven by steric effects. The B2–B3 bond length in compound **3** is significantly longer than that in $[(\eta^5$-$C_5H_5)(CO)_2Fe(\eta^2$-$B_2H_5)]$ (1.815(4) versus 1.773(8) Å). In addition, the B–B bridging hydrogen atom H6 is asymmetrically bound to the boron atoms B2 and B3; that is, the distance to the PMe_3-substituted boron atom B2 is 0.15 Å shorter. These structural distortions presumably reflect the unsymmetrical electronic distribution imposed by the phosphane ligand in the substituted metalladiboranes compared with the distribution in the unsubstituted analogues.

The spectroscopic data of **3** are fully in accord with its solid-state structure. The ^{11}B-{^1H} NMR spectrum consists of two signals with a relative intensity ratio of 1:1, with the peak at the highest field being a doublet, indicating that this boron atom is bound to the phosphane ligand. This is supported by the ^{31}P-{^1H} NMR spectrum that exhibits a well-defined quartet. Interestingly, although the ^1H NMR selective decoupling experiments demonstrate that the boron atom B3 in **3** bears two terminal hydrogen atoms, there is no observable coupling with the bridging hydrogen atom perfectly consistent with the long B3–H6 bond length found in the solid state.

The reaction of BH_3·THF with **3** proceeds by addition of BH_3 to the cluster framework; concomitant liberation of BH_3PMe_3 regenerates the original four-vertex *arachno*-iridaborane **1**.

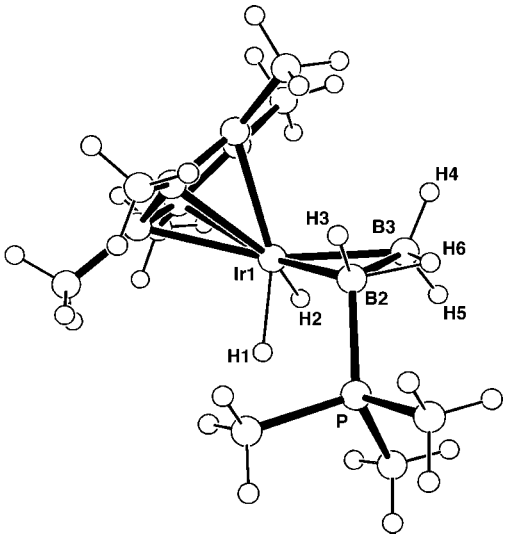

Figure 1. Molecular structure of compound **3**. Selected bond lengths [Å] and interatomic angles [°]: Ir1-B2 2.146(3), Ir1-B2 2.157(3), P-B2 1.931(3), B2-B3 1.815(4); B2-Ir1-B3 49.89(10), B3-B2-P 119.76(18), B3-B2-Ir1 65.38(12), P1-B2-Ir1 115.22(13).

Similarly, compound **4** reacts with BH_3·THF, yielding the five-vertex *arachno*-metallaborane **2** (Scheme 1). This type of reactivity suggests that the use of BH_3PMe_3 as a leaving group in **3** and **4** may permit, for example, the insertion of different Lewis acids in the cluster framework of the iridaboranes.

Monitoring the reactions by NMR spectroscopy shows that the cleavage of **1** and **2** by PMe_3 is fast and quantitative at room temperature. Likewise, the regeneration of **1** and **2** upon addition of BH_3·THF to solutions of **3** and **4** takes place quantitatively in a few minutes at ambient temperature. By contrast, the decomposition of **4** to give **3** is slow in solution under the same conditions with a measured half-life of four

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days. To our surprise, in the solid state the half-life is four hours.

The cleavage of polyboranes and metallaboranes by abstraction of BH_3PR_3 with formation of phosphane derivatives has considerable precedent.[26] Particularly relevant here is the generation of *nido*-[{Cp*Ru}$_2$(PR_3)B_2H_6] ($PR_3 = PMe_3$, PMe_2Ph) from the reaction of PR_3 with the five-vertex *nido*-[{Cp*Ru}$_2B_3H_9$].[27] Here the phosphane ligand is found coordinated to the ruthenium center rather than to a boron atom. Indeed, the thermal decomposition of the PMe_2Ph derivative generates benzene to give *nido*-[{Cp*Ru}$_2$-(μ-PMe_2)(B_2H_5)]. By contrast, in **3** and **4** PMe_3 is preferentially bound to a boron atom rather than to an iridium center. In the case of an osmahexaborane, [$(PPh_3)_2$(CO)OsB_5H_9], reaction with PPh_3 generates [{$(PPh_3)_2$(CO)OsB_4H_7}-(BH_2PPh_3)] in which a pendant BH_2PPh_3 group is bound to a basal boron atom. On heating, the original starting osmahexaborane is formed, or it decomposes to give [$(PPh_3)_2$(CO)OsB_4H_8] and BH_3PPh_3.[28] These differing behaviors reflect the influence of the metal fragments. As with organometallic chemistry, the reactivity of a bound polyborane is strongly affected by the metal, thereby demonstrating the potential of similarly effective control of the chemistry with metal properties.

Experimental Section

Reaction of **1** and **2** with PMe_3: A mixture of **1** and **2** (1:5 ratio; 15 mg, 0.04 mmol) was treated with PMe_3 in [D_6]benzene. Compound **1** gave rise to **3** (minor component), whereas **2** afforded **4** (major component). Compound **4** decomposed in solution (and in the solid state) to give **3**.

3: ^{11}B NMR ([D_6]benzene, 22 °C, 128 MHz): $\delta = -19.1$ (t, ^1J(B,H) = 103 Hz; {^{1}H}, s, 1B), -24.7 ppm (td, ^1J(B,H) + ^1J(B,P) = 107 Hz, ^1J(B,H) = 42 Hz; {^{1}H}, d, ^1J(B,P) = 98 Hz, 1B); ^{1}H NMR ([D_6]benzene, 22 °C, 400 MHz): $\delta = 3.05$ (d, 20 Hz, 1H, B-H_t), 2.83 (s, 1H; B-H_t), 2.13 (s, 15H; C_5Me_5), 1.59 (m, $J = 10$ Hz, 1H; B-H_t), +0.69 (d, ^2J(H,P) = 11 Hz, 9H, PMe_3; {^{31}P}, s), -6.36 (quintet, 9 Hz, 1H; B-H-B), -17.06 (s, 1H; Ir-H), -19.04 ppm (d, ^3J(H,P) = 17 Hz, 1H, Ir-H; {^{31}P}, s); ^{31}P NMR ([D_6]benzene, 22 °C, 162 MHz): $\delta = -16.3$ ppm (quartet, ^1J(B,P) = 95 Hz, PMe_3); IR (KBr): $\tilde{\nu} = 2407$, 2373 (B-H_t); 2153 cm^{-1} (Ir-H); HR-MS(EI): *m*/*z* calcd for $C_{13}H_{28}B_2PIr$: 430.17478, [$M^+ - H_2$]; found 430.17317; elemental analysis (%) calcd for $C_{13}H_{30}B_2PIr$: C 36.21, H 7.01; found: C 36.40, H 6.99.

4: ^{11}B ([D_6]benzene, 22 °C, 128 MHz): $\delta = -5.3$ (d, ^1J(B,H) = 134 Hz; {^{1}H}, s, 1B), -12.9 (t, ^1J(B,H) = 109 Hz; {^{1}H}, s, 1B), -20.1 ppm (t, ^1J(B,H) + ^1J(B,P) = 112 Hz; {^{1}H}, d, ^1J(B,P) = 103 Hz, 1B); ^{1}H ([D_6]benzene, 22 °C, 400 MHz): $\delta = 3.96$ (s, 1H; B-H_t), 3.07 (s, 1H; B-H_t), 2.45 (dd, $J = 19$, 7 Hz; B-H_t), 2.11 (s, 15H; C_5Me_5), 1.99 (s, 1H; B-H_t), 0.63 (d, ^2J(H,P) = 11 Hz, 9H, PMe_3; {^{31}P}, s), -4.32 (s, 1H; B-H-B), -4.78 (dq, 1H, $J = 19.4$, 6.3 Hz, B-H-B), -18.50 ppm (d, ^3J(H,P) = 21 Hz, 1H, Ir-H; {^{31}P}, s); ^{31}P ([D_6]benzene, 22 °C; 162 MHz): $\delta = -9.7$ ppm (quartet, ^1J(^{11}B,^{31}P) 10.0 Hz; PMe_3); IR (hexane): $\tilde{\nu} = 2518$, 2472, 2425 (B-H_t); 2282 cm^{-1} (Ir-H); LR-MS (EI): *m*/*z* calcd for $C_{18}H_{31}B_3IrP$: 444, [M^+]; found envelop with cut-off at 445 and maximum at 442; the isotopic pattern suggests that the ions [M^+] and [$M^+ - H_2$] are overlapped with a major contribution of the latter.

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