

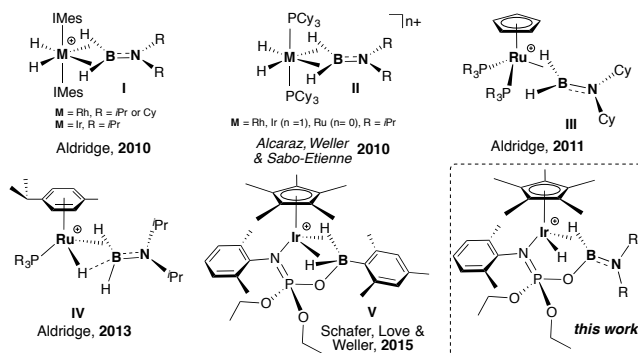
# Phosphoramidate-Supported Cp\*Ir(III) Aminoborane H<sub>2</sub>B=NR<sub>2</sub> Complexes: Synthesis, Structure, and Solution Dynamics

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**Abstract:** Reaction of the aminoboranes H<sub>2</sub>B=NR<sub>2</sub> (R = *i*Pr or Cy) with the cationic Cp\*Ir(III) phosphoramidate complex, [Cp\*Ir(κ<sup>2</sup>-N,O-Xyl(N)P(O)(OEt)<sub>2</sub>)] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup> generates the aminoborane complexes [Cp\*Ir(H)(κ<sup>1</sup>-N-η<sup>2</sup>-HB-Xyl(N)P(O)HBNR<sub>2</sub>)(OEt)<sub>2</sub>]] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup> (R = *i*Pr or Cy) in which coordination of a P=O bond with boron weakens the B=N multiple bond. For these complexes, solution- and solid-state as well as DFT computational techniques have been employed to substantiate B-N bond rotation of the coordinated aminoborane.

Aminoboranes (H<sub>2</sub>B=NR<sub>2</sub>) are the subject of great interest, particularly owing to their intermediacy in the dehydrocoupling of amine-boranes for access to BN-containing polymers.<sup>[1]</sup> From a structural standpoint, the aminoborane B=N π bond is an especially fascinating motif, where one partner (nitrogen) is responsible for the donation of two electrons, formally providing a coplanar array of atoms (H<sub>2</sub>B=NR<sub>2</sub>), which are sp<sup>2</sup>-hybridized at both nitrogen and boron. Consistent with a strong interaction, the energy associated with free B-N bond rotation has been calculated to be about 40 kcal·mol<sup>-1</sup>, depending on the nature of the R substituent.<sup>[2]</sup>

Despite isolobal analogies to 1,1-disubstituted olefins (H<sub>2</sub>C=CR<sub>2</sub>), only in the last five years have studies documenting the coordination chemistry of aminoboranes emerged. Aldridge has shown that *N*-heterocyclic carbene (NHC) complexes of both Ir(III) and Rh(III) bind aminoboranes in an η<sup>2</sup>:η<sup>2</sup> fashion (through two adjacent 3c-2e interactions) to provide [M(H)<sub>2</sub>(IMes)<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>BNR<sub>2</sub>)] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup>; M = Rh(III), R = *i*Pr or Cy, and M = Ir(III), R = *i*Pr, Ar<sup>F</sup><sub>4</sub> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (I, Chart 1).<sup>[3a]</sup> PCy<sub>3</sub>-substituted Ru(II), Rh(III), and Ir(III) complexes have also been shown to behave similarly (II, Chart 1).<sup>[1b]</sup> Indeed, Alcaraz and Sabo-Etienne have shown that the Ru derivative can be employed to trap the very reactive, aminoborane H<sub>2</sub>B=NH<sub>2</sub>, [Ru(H)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>:η<sup>2</sup>-H<sub>2</sub>BNH<sub>2</sub>)]<sup>[11]</sup> Alternative aminoborane coordination modes have also been documented. For example, Cp (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)- and Cp\* (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)-coordinated Ru(II) complexes have proven to be effective starting materials for access to η<sup>2</sup>-HB coordinated aminoborane complexes e.g. [CpRu(PPh<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>B=NCy<sub>2</sub>)] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup> (III, Chart 1), which exhibit B-H exchange between bridging and terminal modes.<sup>[4]</sup> In addition to a metal, auxiliary ligands (*coligands*) may also interact with a coordinated aminoborane. An example of this type has been reported for a hydride coligand of the η<sup>6</sup>-arene complex, [(*p*-cymene)Ru(PR<sub>3</sub>)<sub>2</sub>(H)(η<sup>2</sup>-H<sub>2</sub>B=N<sup>i</sup>Pr<sub>2</sub>); R = Ph or Cy] (IV, Chart 1), which interacts with the boron atom of H<sub>2</sub>B=N<sup>i</sup>Pr<sub>2</sub>. In this case, coplanarity between the H<sub>2</sub>B and NR<sub>2</sub> fragments is

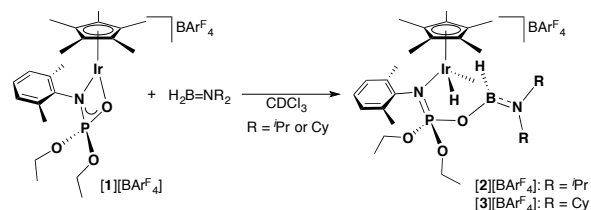


**Chart 1.** Overview of group 8 and 9 B-H aminoborane complexes

maintained due to retention of B-N multiple bond character.<sup>[5]</sup> In a computational study by Bhunya and Paul, structures of this type were implicated as intermediates during the dehydropolymerization of H<sub>2</sub>B·NH<sub>3</sub> using Brookhart's Ir(III) pincer complex [(POCOP)Ir(H)<sub>2</sub>]; POCOP = κ<sup>-3</sup>-1,3-(OP<sup>i</sup>Bu)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.<sup>[1d]</sup>

Herein, we show how incorporation of a hemilabile Lewis-basic coligand<sup>[6]</sup> impacts the coordination of an aminoborane molecule. Previously, we showed that treatment of [Cp\*Ir(κ<sup>2</sup>-N,O-Xyl(N)P(O)(OEt)<sub>2</sub>)] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup>; Xyl = 2,6-dimethylphenyl ([1] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup>) with H<sub>2</sub>BMes (Mes = 2,4,6-trimethylphenyl) provides access to the bis(B-H) agostic complex [Cp\*Ir(κ<sup>1</sup>-N-Xyl(N)P(η<sup>2</sup>:η<sup>2</sup>-H<sub>2</sub>B(O)Mes)(OEt)<sub>2</sub>]] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup> (V, Chart 1).<sup>[6a]</sup> For aminoboranes, we proposed that coordination, followed by Lewis-base stabilization (provided by the hemilabile *N,O*-chelating ligand) would encourage weakening or disruption of the B-N π system, possibly allowing for observable<sup>[7]</sup> B-N bond rotation. In related work, Sabo-Etienne and co-workers have recently reported that room temperature B-N bond rotation was accessible for a series of bis(σ-B-H) complexes having pendant Lewis basic functionality, [Ru(H)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>(η<sup>2</sup>:η<sup>2</sup>-H<sub>2</sub>BN(CH<sub>3</sub>)CH<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>E)]; n = 1, E = N(CH<sub>3</sub>)<sub>2</sub>, n = 1 E = OCH<sub>3</sub>, and n = 2 E = N(CH<sub>3</sub>)<sub>2</sub>.<sup>[1j]</sup> Interestingly, NMR spectroscopy and single crystal X-ray diffraction did not provide evidence for interaction of the Lewis basic moiety with the boron center.

Addition of 1 equiv. of aminoborane H<sub>2</sub>B=NR<sub>2</sub>, R = *i*Pr or Cy, to a CDCl<sub>3</sub> solution of [1] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup> results in an immediate color change from red to yellow over 5 min giving the hydride-bridged oxy aminoborane complexes, [Cp\*Ir(H)(κ<sup>1</sup>-N-η<sup>2</sup>-HB-Xyl(N)P(O)HBNR<sub>2</sub>)(OEt)<sub>2</sub>]] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup>, R = *i*Pr ([2] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup>) or Cy ([3] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup>) (Scheme 1). The identity of these six-membered

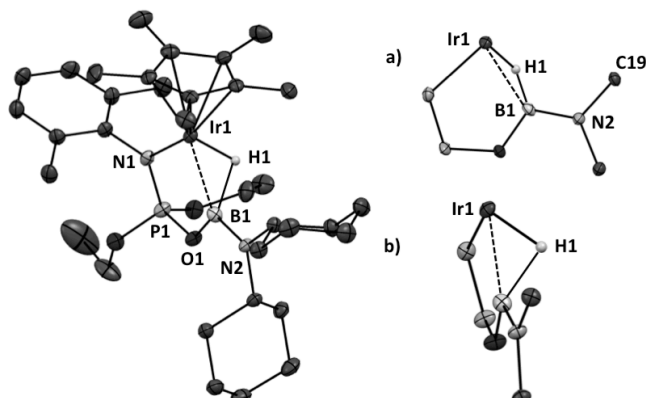


**Scheme 1.** Generation of the Cp\*Ir(III) aminoborane complexes [2] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup> and [3] [BAR<sup>F</sup><sub>4</sub>]<sup>+</sup>

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genuine iridacycles,<sup>[8]</sup> was unequivocally established by multinuclear NMR spectroscopy, X-ray crystallography (for [3][BAR<sup>F</sup><sub>4</sub>]), ATR-FT-IR, ESI-MS, elemental analysis, and computation (DFT). Yellow prisms of [3][BAR<sup>F</sup><sub>4</sub>], obtained from a hexanes-layered CH<sub>2</sub>Cl<sub>2</sub> solution at -35 °C, serve to elucidate the heavy atom connectivity (Figure 1). The structure comprises a Cp\*Ir(III) complex bonded in a  $\kappa^1$ -fashion by the *N*-



**Figure 1.** ORTEP depiction of the solid-state molecular structure of [Cp\*Ir(H)( $\kappa^1$ -*N*- $\eta^2$ -HB-Xyl(N)P(OBHNCy<sub>2</sub>)(OEt)<sub>2</sub>][BAR<sup>F</sup><sub>4</sub>] [3][BAR<sup>F</sup><sub>4</sub>] (displacement ellipsoids are shown at the 50% probability, hydrogens and BAR<sup>F</sup><sub>4</sub><sup>-</sup> counterion omitted for clarity, Terminal Ir-H not located). Selected bond lengths [Å] and angles [°]: Ir(1)-H(1) 1.47(3), B(1)-H(1) 1.59(4), Ir(1)-N(1) 2.142(3), Ir(1)-B(1) 2.190(3), P(1)-O(1) 1.555(2), P(1)-N(1) 1.576(2), B(1)-N(2) 1.412(4), B(1)-O(1) 1.427(5), Ir(1)-H(1)-B(1) 91(2),  $\phi$ [Ir(1)-B(1)-N(2)-C(19)]: 4.5(4). a) view of iridacyclic core b) view along B-N bond.

phosphoramidate atom [Ir(1)-N(1): 2.142(3) Å] and a bridging 3c-2e  $\eta^2$ -HB interaction [Ir(1)-H(1): 1.47(3) Å and B(1)-H(1): 1.59(4) Å]. Though the terminal hydride atom could not be reliably located, it is implicated based on NMR spectroscopy and DFT calculations (*vide infra*). The boron fragment most closely resembles a *sp*<sup>3</sup>-hybridized boron [B(H)(OR)(NR<sub>2</sub>)] centre [sum of angles around B = 341°], owing to oxygen coordination [B(1)-O(1): 1.427(5) Å]. For comparison, the average B-O distance found for tricoordinate boronic acids are in the range of 1.35-1.38 Å.<sup>[9]</sup> The sum of angles about nitrogen [ $\Sigma(\angle \text{RNR}) = 358^\circ$ ] and boron-nitrogen bond distance [B(1)-N(2): 1.412(4) Å] also suggest B=N  $\pi$  character, as it is not significantly outside the range reported previously for B=N double bonds *e.g.* Cl<sub>2</sub>B=NPh<sub>2</sub> [1.380(6) Å].<sup>[10]</sup> The structure also features an  $\angle$  Ir(1)⋯B(1)-N(2) bond angle of 133.6(2)°, which is similar to that observed for related  $\eta^2$ -HB complexes: [CpRu(PPh<sub>3</sub>)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>B=NCy<sub>2</sub>)] [BAR<sup>F</sup><sub>4</sub>] [ $\angle$  Ru⋯B-N = 130.23°]<sup>[4]</sup> and [Rh(IMes)<sub>2</sub>(H)( $\eta^2$ -B(H)=NMe<sub>2</sub>)] [BAR<sup>F</sup><sub>4</sub>] [ $\angle$  Rh⋯B-N = 132.6(10)°].<sup>[3b]</sup> The Ir(1)-B(1) bond distance of 2.190(3) Å is consistent with a Ir⋯H-B interaction.<sup>[13]</sup>

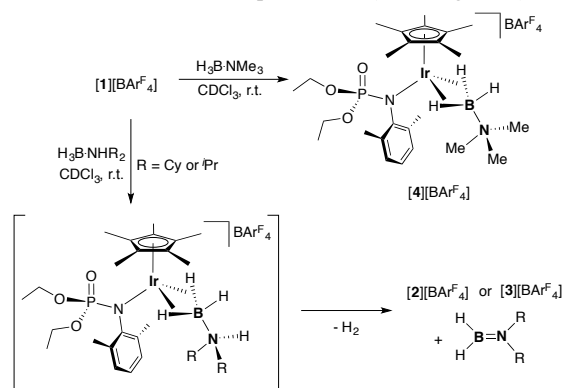
In the <sup>1</sup>H NMR spectrum (298 K) of [2][BAR<sup>F</sup><sub>4</sub>] and [3][BAR<sup>F</sup><sub>4</sub>] one signal is observed for both bridging and terminal hydride groups at  $\delta = -9.89$  and  $-9.86$ , respectively. Cooling to 178 K provides no change in the line shape or chemical shift of this signal, indicating rapid exchange between terminal Ir-H and bridging Ir⋯H-B units. Remarkably, the coordinated aminoborane moiety was found to be highly fluxional on the NMR time scale. For [2][BAR<sup>F</sup><sub>4</sub>] (CD<sub>2</sub>Cl<sub>2</sub>, 298 K) the N<sup>i</sup>Pr<sub>2</sub> fragment was observed as two broad resonances centered at  $\delta = 3.40$  (CH(CH<sub>3</sub>)<sub>2</sub>) and 1.27 (CH(CH<sub>3</sub>)<sub>2</sub>). On cooling to 178 K, two heptets at  $\delta = 3.38$  [h, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, 1H] and 3.12 [h, <sup>3</sup>J<sub>H,H</sub> = 6.3 Hz, 1H] as well as two corresponding doublets at  $\delta = 1.24$  [d, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, 6H] and 1.03 [d, <sup>3</sup>J<sub>H,H</sub> = 6.3 Hz, 6H], were observed, consistent with a time-averaged C<sub>s</sub>-symmetric complex. These findings are consistent with temperature-dependent B-N bond rotation. Analysis of these lineshapes gives a minimal barrier to rotation  $\Delta G^\ddagger_{\text{rot}} = 14.3 \pm 0.3$  kcal·mol<sup>-1</sup> (*T*<sub>c</sub> = 301 K) consistent with the observed <sup>1</sup>H NMR spectroscopic data at 298 K (see the Supporting Information). The <sup>31</sup>P and <sup>11</sup>B NMR spectra show no change down to 178 K. For the

cyclohexyl analogue [3][BAR<sup>F</sup><sub>4</sub>], similar phenomena were noted, giving  $\Delta G^\ddagger_{\text{rot}} = 15.5 \pm 0.3$  kcal·mol<sup>-1</sup> (*T*<sub>c</sub> = 301 K).

Ring-expansion of the parent four-membered iridacycle [1][BAR<sup>F</sup><sub>4</sub>] ( $\delta_{\text{B}} = 41.5$ ) is also evidenced by a change in <sup>31</sup>P{<sup>1</sup>H} NMR chemical shift to  $\delta_{\text{P}} = 10.1$  ( $\Delta\delta_{\text{P}} = -31.4$  ppm) for [2][BAR<sup>F</sup><sub>4</sub>] and  $\delta_{\text{P}} = 9.6$  ( $\Delta\delta_{\text{P}} = -31.9$  ppm) for [3][BAR<sup>F</sup><sub>4</sub>], consistent with the formation of a six-membered metallacycle.<sup>[6a]</sup> By <sup>11</sup>B{<sup>1</sup>H} NMR spectroscopy, a broad signal for the oxy-stabilized aminoborane is observed at  $\delta_{\text{B}} = 27.5$  ( $\omega_{1/2} = 210$  Hz) for [2][BAR<sup>F</sup><sub>4</sub>] and 27.5 ( $\omega_{1/2} = 350$  Hz) for [3][BAR<sup>F</sup><sub>4</sub>]. These values are shifted slightly upfield compared to free H<sub>2</sub>B=N<sup>i</sup>Pr<sub>2</sub> ( $\delta_{\text{B}} = 35.2$ )<sup>[11]</sup> and related  $\sigma$ -B-H complexes of H<sub>2</sub>B=N<sup>i</sup>Pr<sub>2</sub>; [Ir(H)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>( $\eta^2$ : $\eta^2$ -H<sub>2</sub>BN<sup>i</sup>Pr<sub>2</sub>)] [BAR<sup>F</sup><sub>4</sub>] ( $\delta_{\text{B}} = 46$ ),<sup>[3]</sup> and [CpRu(PPh<sub>3</sub>)<sub>2</sub>( $\eta^2$ -H<sub>2</sub>BN<sup>i</sup>Pr<sub>2</sub>)] [BAR<sup>F</sup><sub>4</sub>] ( $\delta_{\text{B}} = 38$ ).<sup>[4]</sup> This is consistent with the move to a four-coordinate boron atom. ESI(+)-MS also provides a molecular ion signal at *m/z* = 697.32 (calcd. 697.32) for [2]<sup>+</sup> and *m/z* = 777 for [3]<sup>+</sup> of the appropriate isotope pattern. Finally, ATR FT-IR spectroscopy of [2][BAR<sup>F</sup><sub>4</sub>] and [3][BAR<sup>F</sup><sub>4</sub>] provides one broad band at 2025 and 2019 cm<sup>-1</sup>, corresponding to Ir-H-B stretching vibrations.

Complexes [2][BAR<sup>F</sup><sub>4</sub>] and [3][BAR<sup>F</sup><sub>4</sub>] can also be independently synthesized *via* dehydrogenation. Reaction of [1][BAR<sup>F</sup><sub>4</sub>] with H<sub>3</sub>B-NR<sub>2</sub>H (R = <sup>i</sup>Pr or Cy) at 298 K in CDCl<sub>3</sub> (Scheme 2), provides [2][BAR<sup>F</sup><sub>4</sub>] and [3][BAR<sup>F</sup><sub>4</sub>] in 21% and 56% yield respectively along with small amounts of free H<sub>2</sub>B=NR<sub>2</sub> (by <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy). In contrast, treatment of [1][BAR<sup>F</sup><sub>4</sub>] with 1 equiv. of H<sub>3</sub>B-NMe<sub>3</sub>, where no dehydrogenative pathway is available, gives [Cp\*Ir( $\kappa^1$ -*N*-Xyl(N)P(O)(OEt)<sub>2</sub>( $\eta^2$ : $\eta^2$ -H<sub>3</sub>B-NMe<sub>3</sub>)] [BAR<sup>F</sup><sub>4</sub>], [4][BAR<sup>F</sup><sub>4</sub>], as shown by NMR spectroscopy and ESI(+)-MS.<sup>[12]</sup> The <sup>1</sup>H NMR spectrum features a broad singlet, which sharpens on <sup>11</sup>B decoupling at  $\delta = -4.93$  of integration 3H, indicating rapid site exchange between the three B-H units on the NMR timescale, which are not frozen out down to 190 K. Comparable solution-state behavior has been observed for [Ir(H)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>( $\eta^2$ : $\eta^2$ -H<sub>3</sub>B-NMe<sub>2</sub>R)] [BAR<sup>F</sup><sub>4</sub>] (R = H or Me).<sup>[13]</sup> In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum a signal is observed at  $\delta = 7.44$  characteristic of open  $\kappa^1$ -*N* phosphoramidate coordination.<sup>[6a]</sup> The <sup>11</sup>B NMR spectrum shows a broad signal at  $\delta_{\text{B}} = -1.21$  ( $\omega_{1/2} = 205$  Hz;  $\delta_{\text{B}} = -7.3$  for “free” H<sub>3</sub>B-NMe<sub>3</sub>) consistent with metal coordination of the four-coordinate borane.<sup>[13]</sup>

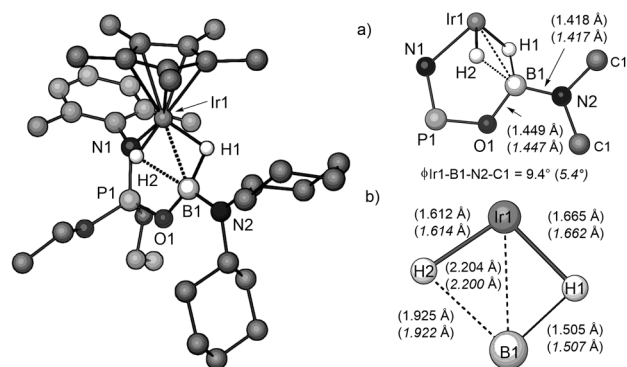
To provide a clearer description of the Ir-H<sub>2</sub>B core of [2]<sup>+</sup> and [3]<sup>+</sup>, DFT calculations were performed ([3]<sup>+</sup>; Figure 2).<sup>[14]</sup> The



**Scheme 2.** Generation of the bis( $\sigma$ -B-H) Ir(III) complex [4][BAR<sup>F</sup><sub>4</sub>]

calculated bond metrics for the optimized structure of [3]<sup>+</sup> are in excellent agreement with the solid-state structure of [3][BAR<sup>F</sup><sub>4</sub>] (Table S2). The Ir-H<sub>2</sub>B unit is best described as a monohydrido Ir(III) complex having one 3c-2e  $\eta^2$ -HB interaction with the oxy-supported aminoborane [HB(OR)(NR<sub>2</sub>)] (Figure 2). The Ir-H distances are similar for both bridging and terminal hydrides [Ir(1)-H(1): 1.665 Å; Ir(1)-H(2): 1.612 Å for [3]<sup>+</sup>], however the B-H distances vary greatly [B(1)-H(1): 1.505 Å; B(1)-H(2): 1.925 Å in [3]<sup>+</sup> *cf.* B-H: 1.207 Å for the optimized structure of H<sub>2</sub>B=NCy<sub>2</sub>]. The B(1)⋯H(2) distance is similar to that found in a hydrido-boryl

complex of Os resulting from aminoborane B-H bond cleavage in which the B $\cdots$ H<sub>hydride</sub> separation was calculated to be 1.946 Å.<sup>[7a]</sup> In both [2]<sup>+</sup> and [3]<sup>+</sup> the Ir(1)-B(1)-O(1) and NR<sub>2</sub> planes were found to be nearly coplanar [ $\phi$ Ir(1)-B(1)-N(2)-C(1): 5.4° for [2]<sup>+</sup>, 9.4° for [3]<sup>+</sup>]. By comparison to H<sub>2</sub>B=NCy<sub>2</sub>, the B(1)-N(2) bond was also found to be slightly lengthened (1.403 *cf.* 1.418 Å for [3]<sup>+</sup>). The DFT calculated <sup>11</sup>B NMR chemical shifts<sup>[14]</sup> for [2]<sup>+</sup> and [3]<sup>+</sup> are in excellent agreement with experimental data ( $\delta_B$  = 27.4 and 27.5, respectively) and show an upfield shift ( $\Delta\delta_B$  = *ca.* -3.5) relative to the calculated values for the free aminoboranes.<sup>[15]</sup>



**Figure 2.** DFT-calculated structure of [3]<sup>+</sup> with non-coordinating hydrogen atoms omitted for clarity. a) diagram of the iridacyclic core b) diagram of the Ir-H<sub>2</sub>B core. Interatomic distances correspond to those for [3]<sup>+</sup> (top) and [2]<sup>+</sup> (bottom, *italics*).

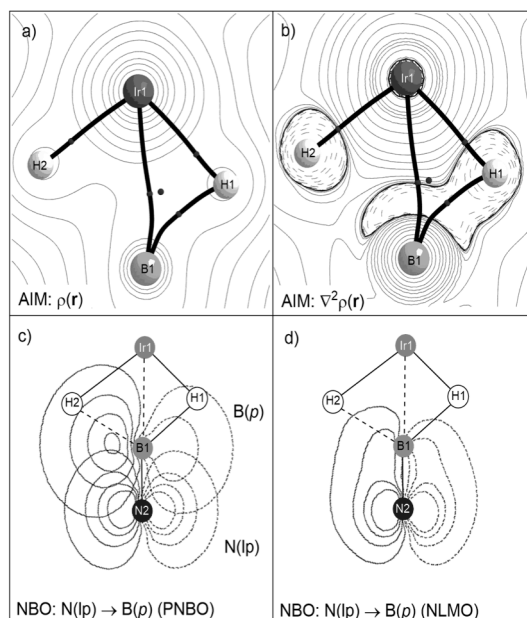
An atoms in molecules (AIM)<sup>[16]</sup> analysis of the electron density topology was performed to probe the bonding. AIM has previously been employed to assist in the assignment of structures wherein the nature of (R<sub>n</sub>BH<sub>n</sub>) $\cdots$ M interactions has been unclear.<sup>[17]</sup> Contour plots of the electron density and the Laplacian of the electron density (showing local concentration and depletion) for the Ir-H<sub>2</sub>B unit in [3]<sup>+</sup> are shown in Figures 3a and 3b. For complexes [2]<sup>+</sup> and [3]<sup>+</sup>, two bond critical points (bcps) indicating the presence of a bond were found between Ir and H, while only one boron-hydrogen bcp was located pointing to an (H)Ir $\cdots$ H-B interaction in [2][BAR<sup>F</sup><sub>4</sub>] and [3][BAR<sup>F</sup><sub>4</sub>] (*vide supra*). An Ir-B bond critical point was also found with a high ellipticity value [ $\epsilon$  = 2.44 for [3]<sup>+</sup>] in close proximity to the ring critical point associated with the Ir $\cdots$ H-B interaction. These data suggest that the local electron density topology is unstable, and that minor energetic perturbations might lead to changes in structure.<sup>[16b,17a]</sup> Indeed pathways for hydride exchange were identified for [2]<sup>+</sup> and [3]<sup>+</sup>, proceeding with low energy barriers (see the Supporting Information).<sup>[14]</sup> This observation is consistent with the <sup>1</sup>H NMR spectrum for the Ir-H<sub>2</sub>B unit of [2][BAR<sup>F</sup><sub>4</sub>] and [3][BAR<sup>F</sup><sub>4</sub>], which even at 178 K provides a single peak for both bridging and terminal hydrides.

Natural bond orbital (NBO) calculations<sup>[18]</sup> were also performed to quantify the extent of the B-N  $\pi$  interaction in these complexes. Figure 3c shows the overlap between N(*lp*) and B(*p*) pre-orthogonal natural bonding orbitals (PNBOs) resulting in the formation of a B=N  $\pi$  natural localized molecular orbital (NLMO; Figure 3d) which is 80% N and 15% B in character. The natural population analysis (NPA) data reveal an increase in negative charge at N(2) [0.10e in [2]<sup>+</sup>; 0.11e in [3]<sup>+</sup>] upon aminoborane coordination, as anticipated for a slightly diminished N(*lp*)  $\rightarrow$  B(*p*) interaction. Second order perturbation analysis provides an estimate of the energetic stabilization ( $E^{(2)}$ ) provided by these interactions. The N(*lp*)  $\rightarrow$  B(*p*) stabilization energy for both complexes was found to be smaller than that for the free aminoboranes, H<sub>2</sub>B=NR<sub>2</sub> (R = <sup>i</sup>Pr, Cy) by *ca.* 6 kcal·mol<sup>-1</sup> [65.9 kcal·mol<sup>-1</sup> for [2]<sup>+</sup>, 66.8 kcal·mol<sup>-1</sup> for [3]<sup>+</sup>; *cf.* 72.6 and 72.3 kcal·mol<sup>-1</sup> for H<sub>2</sub>B=N<sup>i</sup>Pr<sub>2</sub> and H<sub>2</sub>B=NCy<sub>2</sub> respectively]. Consistent with nitrogen planarity for [2]<sup>+</sup> and [3]<sup>+</sup>, the nitrogen lone pair was calculated to be purely *p* in character, while the acceptor B(*p*)

orbital was found to be composed of 96% *p*-character. Surprisingly, it was found that the B(*p*) orbital has a greater population in [2]<sup>+</sup> and [3]<sup>+</sup> than in the free aminoboranes [0.57e *cf.* 0.36 e], which we attribute to Ir-H(2)( $\sigma$ )  $\rightarrow$  B(*p*) donation and modest B-O  $\pi$  character.

Having established the structure for these systems, the potential energy surfaces (PES) for B-N bond rotation were subsequently determined for [2]<sup>+</sup> and [3]<sup>+</sup> (representative PES for [3]<sup>+</sup> shown in Figure 4). The surfaces obtained were found to be asymmetric due to the orientation <sup>i</sup>Pr and Cy groups, but overall, isomerization *via* rotation of these groups was determined to be facile at 298 K. The electronic energy barriers to rotation ( $\Delta E^{\ddagger}_{rot}$ ) approximated by local maxima on the PES are consistent with the activation parameters determined previously by <sup>1</sup>H NMR spectroscopy [ $\Delta E^{\ddagger}_{rot} \sim 12.4$  and 11.1 kcal·mol<sup>-1</sup> *cf.*  $\Delta G^{\ddagger}_{rot} = 14.3 \pm 0.3$  and  $15.5 \pm 0.3$  kcal·mol<sup>-1</sup> for [2]<sup>+</sup> and [3]<sup>+</sup>]. Similar calculations were performed on the free aminoboranes, H<sub>2</sub>B=NR<sub>2</sub> (R = <sup>i</sup>Pr, Cy) and show significant barriers to rotation ( $\Delta E^{\ddagger}_{rot}$ ) of 37.3 kcal·mol<sup>-1</sup> (R = <sup>i</sup>Pr) and 37.1 kcal·mol<sup>-1</sup> (R = Cy); *ca.* 26 kcal·mol<sup>-1</sup> higher than in [2]<sup>+</sup> and [3]<sup>+</sup>.

Careful examination of the PESs for B-N bond rotation in [3]<sup>+</sup> resulted in the identification of a high-energy intermediate<sup>[19]</sup> [3-rot]<sup>+</sup> existing in a shallow well near the local maximum for rotation by 180° (Figure 5). For this intermediate, the NR<sub>2</sub> and H<sub>2</sub>B

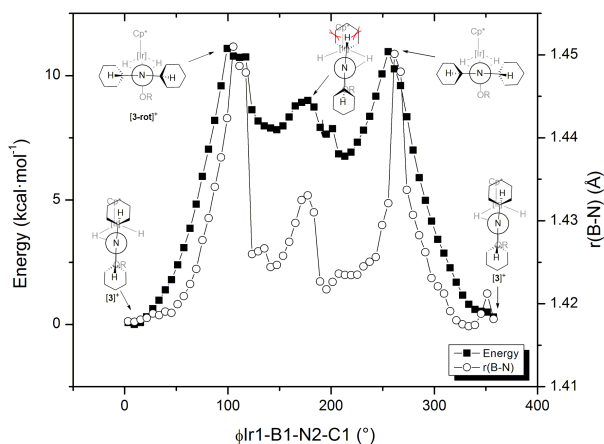


**Figure 3.** AIM and NBO analysis of [3]<sup>+</sup>: a) contour plot of  $\rho(r)$  with bond paths shown as black tubes, bcps as red points and rcps as purple points. b) contour plot of  $\nabla^2\rho(r)$  with positive contours shown as solid black lines, negative contours shown as dashed red lines [3]<sup>+</sup> c) PNBO overlap N(2)-B(1)-H(2) plane d) N-B  $\pi$  NLMO in the N(2)-B(1)-H(2) plane.

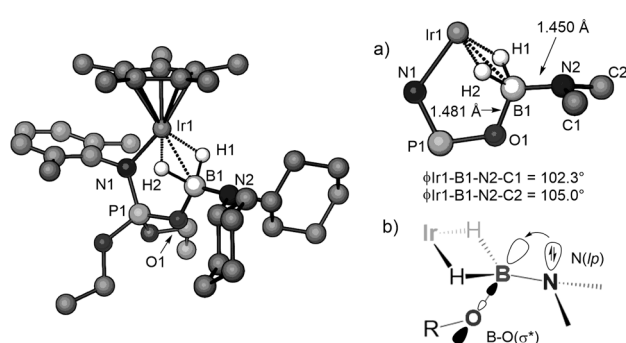
planes are nearly coplanar with both hydrides bound to boron [ $r$ (B-H1): 1.432;  $r$ (B-H2): 1.428 Å]. The B(1)-N(2) bond length (1.450 Å) was found to be slightly shorter than what is observed for a 90° B-N bond rotation of H<sub>2</sub>B=NCy<sub>2</sub> (1.467 Å). The shortened B(1)-N(2) bond, in combination with an elongation of the B(1)-O(1) bond relative to [3]<sup>+</sup> [1.481 Å *cf.* 1.449 Å] suggests that [3-rot]<sup>+</sup> retains some B-N  $\pi$  character, which we suggest results from N(*lp*)  $\rightarrow$  B-O( $\sigma^*$ ) donation. This notion is also supported by only a small degree of nitrogen pyramidalization in [3-rot]<sup>+</sup> [ $\Sigma$  ( $\angle$ RNR): 354° *cf.* 345° for H<sub>2</sub>B=NCy<sub>2</sub>]. Consistent with this proposal, NBO analysis of [3-rot]<sup>+</sup> shows significant N(*lp*)  $\rightarrow$  B-O( $\sigma^*$ ) donation [ $E^{(2)} = 14.5$  kcal·mol<sup>-1</sup>]. As the N(*lp*)  $\rightarrow$  B(*p*) stabilization energy of the aminoborane only decreases by *ca.* 6 kcal·mol<sup>-1</sup> upon coordination to Ir, the decrease in B-N bond order alone cannot



account for the large decrease observed for the B-N bond rotational barriers of  $[2][\text{BAR}^{\text{F}}_4]$  and  $[3][\text{BAR}^{\text{F}}_4]$ . In accord, we propose that transition state stabilization *via*  $\text{N}(lp) \rightarrow \text{B-O}(\sigma^*)$  donation, concomitant with ground state destabilization due to steric repulsion between the aminoborane R substituents and the  $\text{Cp}^*$  ring (owing to the conformational rigidity imposed by the supporting phosphoramidate ligand) in  $[2][\text{BAR}^{\text{F}}_4]$  and  $[3][\text{BAR}^{\text{F}}_4]$  are responsible for free rotation about the B-N bond at 298 K.



**Figure 4.** DFT-calculated potential energy surface and change in B(1)-N(2) bond length for rotation about the B-N bond in  $[3]^+$ .



**Figure 5.** DFT-calculated structure of  $[3\text{-rot}]^+$  with non-coordinating hydrogen atoms omitted for clarity. a) view of the geometry about boron b)  $\text{N}(lp) \rightarrow \text{B-O}(\sigma^*)$  donation.

In summary, we have shown that B-H activated  $\text{Cp}^*\text{Ir(III)}$  aminoborane complexes are cleanly prepared from  $[1][\text{BAR}^{\text{F}}_4]$  and  $\text{H}_2\text{B}=\text{NR}_2$ . These complexes exhibit dynamic solution-state behaviour, owing to stabilization of the aminoborane by the hemilabile phosphoramidate coligand. This interaction facilitates rotation about the B-N bond in an organometallic aminoborane complex, which has been independently corroborated by  $^1\text{H}$  NMR spectroscopy and DFT calculations. Furthermore, we have demonstrated the propensity of hemilabile ligands to participate in the cooperative binding and activation of aminoboranes/aminoboranes, providing a foundation for understanding possible dehydrogenative pathways using such systems.

## Acknowledgements

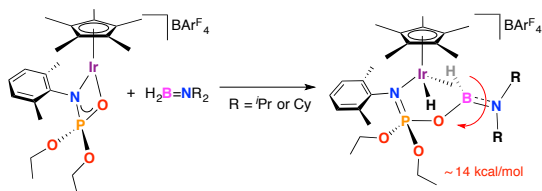
We thank the following for support of this research: NSERC (Discovery, Research Tools, and Instrumentation Grants to JAL and LLS; a MSFSS travel award to MWD) the University of British Columbia (VPRI travel award to MWD), the Peter Wall Institute for Advanced Studies, and the government of Canada (Vanier Scholarship to MWD and EGB). This work was undertaken, in part, thanks to funding from the Canada Research Chairs program (LLS). Dr. Brian O. Patrick is thanked for help with refinement of X-ray data and Dr. Pierre Kennepohl is thanked for helpful discussions.

**Keywords:** B-H activation • hemilability • aminoborane • dehydropolymerization • DFT

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## COMMUNICATION



**Rotation for DumBNies:** Free B-N bond rotation has been observed in a Cp\*Ir(III) aminoborane phosphoramidate complex. Solution- and solid-state techniques as well as density functional theory have been employed to substantiate the titled complexes as monohydride mono(BH) agostic Ir(III) complexes, culminating from phosphoramidate stabilization and B-H activation.

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Phosphoramidate-Supported Cp\*Ir(III)  
Aminoborane Complexes: Synthesis,  
Structure, and Solution Dynamics