

Phosphoramidate-Supported Cp*Ir(III) Aminoborane H₂B=NR₂ Complexes: Synthesis, Structure, and Solution Dynamics

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Abstract: Reaction of the aminoboranes H₂B=NR₂ (R = *i*Pr or Cy) with the cationic Cp*Ir(III) phosphoramidate complex, [Cp*Ir(κ²-N,O-Xyl(N)P(O)(OEt)₂][BAR^F₄] generates the aminoborane complexes [Cp*Ir(H)(κ¹-N-η²-HB-Xyl(N)P(O)HNR₂)(OEt)₂][BAR^F₄] (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 (H₂B=NR₂) are the subject of great interest, particularly owing to their intermediacy in the dehydrocoupling of amine-boranes for access to BN-containing polymers.^[1] 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 (H₂B=NR₂), which are sp²-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⁻¹, depending on the nature of the R substituent.^[2]

Despite isolobal analogies to 1,1-disubstituted olefins (H₂C=CR₂), 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 η²:η² fashion (through two adjacent 3c-2e interactions) to provide [M(H)₂(IMes)₂(η²:η²-H₂BNR₂)] [BAR^F₄]; M = Rh(III), R = *i*Pr or Cy, and M = Ir(III), R = *i*Pr, Ar^F₄ = 3,5-(CF₃)₂C₆H₃ (I, Chart 1).^[3a] PCy₃-substituted Ru(II), Rh(III), and Ir(III) complexes have also been shown to behave similarly (II, Chart 1).^[1b] Indeed, Alcaraz and Sabo-Etienne has shown that the Ru derivative can be employed to trap the very reactive, aminoborane H₂B=NH₂, [Ru(H)₂(PCy₃)₂(η²:η²-H₂BNH₂)]^[11] Alternative aminoborane coordination modes have also been documented. For example, Cp (η⁵-C₅H₅)- and Cp* (η⁵-C₅Me₅)-coordinated Ru(II) complexes have proven to be effective starting materials for access to η²-HB coordinated aminoborane complexes e.g. [CpRu(PPh₃)₂(η²-H₂B=NCy₂)] [BAR^F₄] (III, Chart 1), which exhibit B-H exchange between bridging and terminal modes.^[4] 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 η⁶-arene complex, [(*p*-cymene)Ru(PR₃)₂(H)(η²-H₂B=N^{*i*}Pr₂); R = Ph or Cy] (IV, Chart 1), which interacts with the boron atom of H₂B=N^{*i*}Pr₂. In this case, coplanarity between the H₂B and NR₂ fragments is

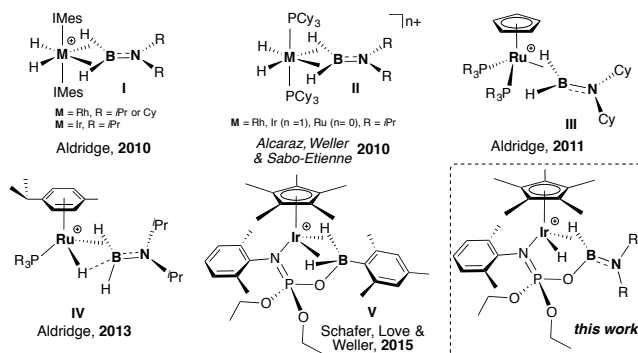
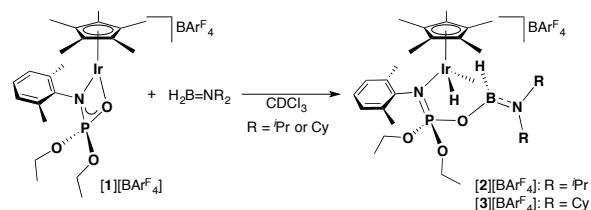


Chart 1. Overview of group 8 and 9 B-H aminoborane complexes

maintained due to retention of B-N multiple bond character.^[5] In a computational study by Bhunya and Paul, structures of this type were implicated as intermediates during the dehydropolymerization of H₂B·NH₃ using Brookhart's Ir(III) pincer complex [(POCOP)Ir(H)₂]; POCOP = κ⁻³-1,3-(OP^{*i*}Bu)₂C₆H₃.^[1d]

Herein, we show how incorporation of a hemilabile Lewis-basic coligand^[6] impacts the coordination of an aminoborane molecule. Previously, we showed that treatment of [Cp*Ir(κ²-N,O-Xyl(N)P(O)(OEt)₂][BAR^F₄]; Xyl = 2,6-dimethylphenyl ([1][BAR^F₄]) with H₂BMes (Mes = 2,4,6-trimethylphenyl) provides access to the bis(B-H) agostic complex [Cp*Ir(κ¹-N-Xyl(N)P(η²:η²-H₂B(O)Mes)(OEt)₂][BAR^F₄] (V, Chart 1).^[6a] 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^[7] 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)₂(PCy₃)₂(η²:η²-H₂BN(CH₃)CH₂(CH₂)_{*n*}E)]; *n* = 1, E = N(CH₃)₂, *n* = 1 E = OCH₃, and *n* = 2 E = N(CH₃)₂.^[1j] 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 H₂B=NR₂, R = *i*Pr or Cy, to a CDCl₃ solution of [1][BAR^F₄] results in an immediate color change from red to yellow over 5 min giving the hydride-bridged oxy aminoborane complexes, [Cp*Ir(H)(κ¹-N-η²-HB-Xyl(N)P(O)HNR₂)(OEt)₂][BAR^F₄], R = *i*Pr ([2][BAR^F₄]) or Cy ([3][BAR^F₄]) (Scheme 1). The identity of these six-membered



Scheme 1. Generation of the Cp*Ir(III) aminoborane complexes [2][BAR^F₄] and [3][BAR^F₄]

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genuine iridacycles,^[8] was unequivocally established by multinuclear NMR spectroscopy, X-ray crystallography (for [3][BAR^F₄]), ATR-FT-IR, ESI-MS, elemental analysis, and computation (DFT). Yellow prisms of [3][BAR^F₄], obtained from a hexanes-layered CH₂Cl₂ solution at -35 °C, serve to elucidate the heavy atom connectivity (Figure 1). The structure comprises a Cp*Ir(III) complex bonded in a κ¹-fashion by the *N*-

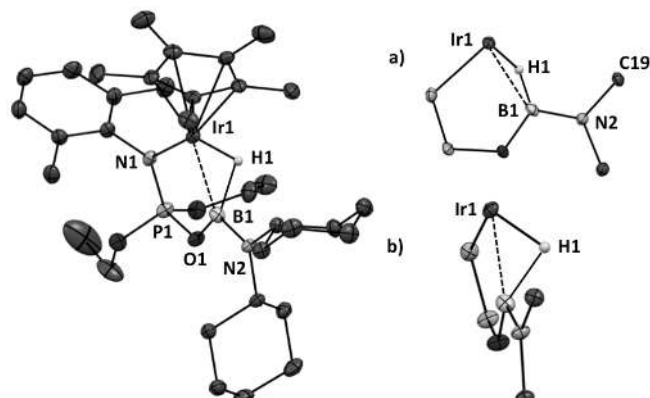


Figure 1. ORTEP depiction of the solid-state molecular structure of [Cp*Ir(H)(κ¹-*N*-η²-HB-Xyl(N)P(O)BNCy₂)(OEt)₂][BAR^F₄] [3][BAR^F₄] (displacement ellipsoids are shown at the 50% probability, hydrogens and BAR^F₄⁻ counterion omitted for clarity, Terminal Ir-H not located). Selected bond lengths [Å] 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), [φ]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 η²-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 sp³-hybridized boron [B(H)(OR)(NR₂)] 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.^[9] The sum of angles about nitrogen [Σ(∠RNR) = 358°] and boron-nitrogen bond distance [B(1)-N(2): 1.412(4) Å] also suggest B=N π character, as it is not significantly outside the range reported previously for B=N double bonds *e.g.* Cl₂B=NPh₂ [1.380(6) Å].^[10] The structure also features an ∠ Ir(1)⋯B(1)-N(2) bond angle of 133.6(2)°, which is similar to that observed for related η²-HB complexes: [CpRu(PPh₃)₂(η²-H₂B=NCy₂)] [BAR^F₄] [∠ Ru⋯B-N = 130.23°]^[4] and [Rh(IMes)₂(H)(η²-B(H)=NMe₂)] [BAR^F₄] [∠ Rh⋯B-N = 132.6(10)°].^[3b] The Ir(1)-B(1) bond distance of 2.190(3) Å is consistent with a Ir⋯H-B interaction.^[13]

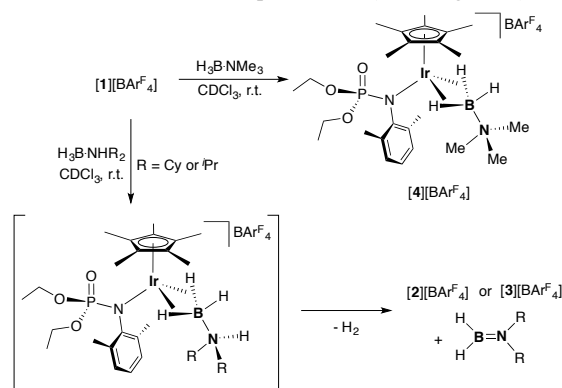
In the ¹H NMR spectrum (298 K) of [2][BAR^F₄] and [3][BAR^F₄] one signal is observed for both bridging and terminal hydride groups at δ = -9.89 and -9.86, respectively. Cooling to 178 K provides no change in the line shape or chemical shift of this signal, indicating rapid exchange between terminal Ir-H 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^F₄], (CD₂Cl₂, 298 K) the NⁱPr₂ fragment was observed as two broad resonances centered at δ = 3.40 (CH(CH₃)₂) and 1.27 (CH(CH₃)₂). On cooling to 178 K, two heptets at δ = 3.38 [h, ³J_{H,H} = 6.6 Hz, 1H] and 3.12 [h, ³J_{H,H} = 6.3 Hz, 1H] as well as two corresponding doublets at δ = 1.24 [d, ³J_{H,H} = 6.6 Hz, 6H] and 1.03 [d, ³J_{H,H} = 6.3 Hz, 6H], were observed, consistent with a time-averaged C_s-symmetric complex. These findings are consistent with temperature-dependent B-N bond rotation. Analysis of these lineshapes gives a minimal barrier to rotation Δ*G*[‡]_{rot} = 14.3 ± 0.3 kcal·mol⁻¹ (T_c = 301 K) consistent with the observed ¹H NMR spectroscopic data at 298 K (see the Supporting Information). The ³¹P and ¹¹B NMR spectra show no change down to 178 K. For the

cyclohexyl analogue [3][BAR^F₄], similar phenomena were noted, giving Δ*G*[‡]_{rot} = 15.5 ± 0.3 kcal·mol⁻¹ (T_c = 301 K).

Ring-expansion of the parent four-membered iridacycle [1][BAR^F₄] (δ_B = 41.5) is also evidenced by a change in ³¹P{¹H} NMR chemical shift to δ_P = 10.1 (Δδ_P = -31.4 ppm) for [2][BAR^F₄] and δ_P = 9.6 (Δδ_P = -31.9 ppm) for [3][BAR^F₄], consistent with the formation of a six-membered metallacycle.^[6a] By ¹¹B{¹H} NMR spectroscopy, a broad signal for the oxy-stabilized aminoborane is observed at δ_B = 27.5 (ω_{1/2} = 210 Hz) for [2][BAR^F₄] and 27.5 (ω_{1/2} = 350 Hz) for [3][BAR^F₄]. These values are shifted slightly upfield compared to free H₂B=NⁱPr₂ (δ_B = 35.2)^[11] and related σ-B-H complexes of H₂B=NⁱPr₂; [Ir(H)₂(PCy₃)₂(η²-η²-H₂BNⁱPr₂)] [BAR^F₄] (δ_B = 46),^[3] and [CpRu(PPh₃)₂(η²-H₂BNⁱPr₂)] [BAR^F₄] (δ_B = 38).^[4] 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]⁺ and *m/z* = 777 for [3]⁺ of the appropriate isotope pattern. Finally, ATR FT-IR spectroscopy of [2][BAR^F₄] and [3][BAR^F₄] provides one broad band at 2025 and 2019 cm⁻¹, corresponding to Ir-H-B stretching vibrations.

Complexes [2][BAR^F₄] and [3][BAR^F₄] can also be independently synthesized *via* dehydrogenation. Reaction of [1][BAR^F₄] with H₃B·NR₂H (R = ⁱPr or Cy) at 298 K in CDCl₃ (Scheme 2), provides [2][BAR^F₄] and [3][BAR^F₄] in 21% and 56% yield respectively along with small amounts of free H₂B=NR₂ (by ¹H and ¹¹B NMR spectroscopy). In contrast, treatment of [1][BAR^F₄] with 1 equiv. of H₃B·NMe₃, where no dehydrogenative pathway is available, gives [Cp*Ir(κ¹-*N*-Xyl(N)P(O)(OEt)₂(η²-H₃B·NMe₃)] [BAR^F₄], [4][BAR^F₄], as shown by NMR spectroscopy and ESI(+)-MS.^[12] The ¹H NMR spectrum features a broad singlet, which sharpens on ¹¹B decoupling at δ = -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)₂(PCy₃)₂(η²-η²-H₃B·NMe₂R)] [BAR^F₄] (R = H or Me).^[13] In the ³¹P{¹H} NMR spectrum a signal is observed at δ = 7.44 characteristic of open κ¹-*N* phosphoramidate coordination.^[6a] The ¹¹B NMR spectrum shows a broad signal at δ_B = -1.21 (ω_{1/2} = 205 Hz; δ_B = -7.3 for “free” H₃B·NMe₃) consistent with metal coordination of the four-coordinate borane.^[13]

To provide a clearer description of the Ir-H₂B core of [2]⁺ and [3]⁺, DFT calculations were performed ([3]⁺; Figure 2).^[14] The



Scheme 2. Generation of the bis(σ-B-H) Ir(III) complex [4][BAR^F₄]

calculated bond metrics for the optimized structure of [3]⁺ are in excellent agreement with the solid-state structure of [3][BAR^F₄] (Table S2). The Ir-H₂B unit is best described as a monohydrido Ir(III) complex having one 3c-2e η²-HB interaction with the oxy-supported aminoborane [HB(OR)(NR₂)] (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]⁺], however the B-H distances vary greatly [B(1)-H(1): 1.505 Å; B(1)-H(2): 1.925 Å in [3]⁺ *cf.* B-H: 1.207 Å for the optimized structure of H₂B=NCy₂]. 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_{hydride} separation was calculated to be 1.946 Å.^[7a] In both [2]⁺ and [3]⁺ the Ir(1)-B(1)-O(1) and NR₂ planes were found to be nearly coplanar [ϕ Ir(1)-B(1)-N(2)-C(1): 5.4° for [2]⁺, 9.4° for [3]⁺]. By comparison to H₂B=NCy₂, the B(1)-N(2) bond was also found to be slightly lengthened (1.403 cf. 1.418 Å for [3]⁺). The DFT calculated ¹¹B NMR chemical shifts^[14] for [2]⁺ and [3]⁺ 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.^[15]

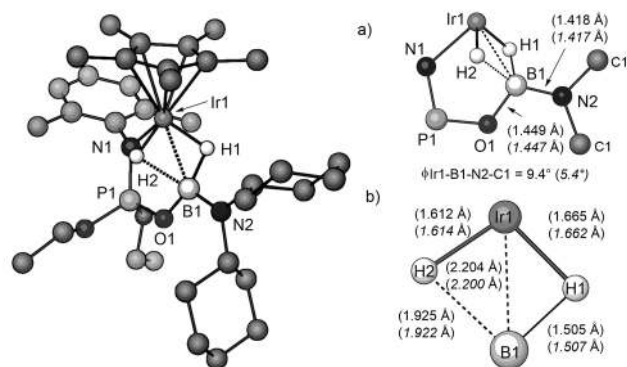


Figure 2. DFT-calculated structure of [3]⁺ with non-coordinating hydrogen atoms omitted for clarity. a) diagram of the iridacyclic core b) diagram of the Ir-H₂B core. Interatomic distances correspond to those for [3]⁺ (top) and [2]⁺ (bottom, *italics*).

An atoms in molecules (AIM)^[16] 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_nBH_n) \cdots M interactions has been unclear.^[17] Contour plots of the electron density and the Laplacian of the electron density (showing local concentration and depletion) for the Ir-H₂B unit in [3]⁺ are shown in Figures 3a and 3b. For complexes [2]⁺ and [3]⁺, 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][BAR₄^F] and [3][BAR₄^F] (*vide supra*). An Ir-B bond critical point was also found with a high ellipticity value [$\epsilon = 2.44$ for [3]⁺] 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.^[16b,17a] Indeed pathways for hydride exchange were identified for [2]⁺ and [3]⁺, proceeding with low energy barriers (see the Supporting Information).^[14] This observation is consistent with the ¹H NMR spectrum for the Ir-H₂B unit of [2][BAR₄^F] and [3][BAR₄^F], which even at 178 K provides a single peak for both bridging and terminal hydrides.

Natural bond orbital (NBO) calculations^[18] were also performed to quantify the extent of the B-N π 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 π 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]⁺; 0.11e in [3]⁺] 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, H₂B=NR₂ (R = ⁱPr, Cy) by *ca.* 6 kcal·mol⁻¹ [65.9 kcal·mol⁻¹ for [2]⁺, 66.8 kcal·mol⁻¹ for [3]⁺; cf. 72.6 and 72.3 kcal·mol⁻¹ for H₂B=NⁱPr₂ and H₂B=NCy₂ respectively]. Consistent with nitrogen planarity for [2]⁺ and [3]⁺, 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]⁺ and [3]⁺ than in the free aminoboranes [0.57e cf. 0.36 e], which we attribute to Ir-H(2)(σ) \rightarrow B(*p*) donation and modest B-O π character.

Having established the structure for these systems, the potential energy surfaces (PES) for B-N bond rotation were subsequently determined for [2]⁺ and [3]⁺ (representative PES for [3]⁺ shown in Figure 4). The surfaces obtained were found to be asymmetric due to the orientation ⁱPr 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 ¹H NMR spectroscopy [$\Delta E^{\ddagger}_{rot} \sim 12.4$ and 11.1 kcal·mol⁻¹ cf. $\Delta G^{\ddagger}_{rot} = 14.3 \pm 0.3$ and 15.5 ± 0.3 kcal·mol⁻¹ for [2]⁺ and [3]⁺]. Similar calculations were performed on the free aminoboranes, H₂B=NR₂ (R = ⁱPr, Cy) and show significant barriers to rotation ($\Delta E^{\ddagger}_{rot}$) of 37.3 kcal·mol⁻¹ (R = ⁱPr) and 37.1 kcal·mol⁻¹ (R = Cy); *ca.* 26 kcal·mol⁻¹ higher than in [2]⁺ and [3]⁺.

Careful examination of the PESs for B-N bond rotation in [3]⁺ resulted in the identification of a high-energy intermediate^[19] [3-rot]⁺ existing in a shallow well near the local maximum for rotation by 180° (Figure 5). For this intermediate, the NR₂ and H₂B

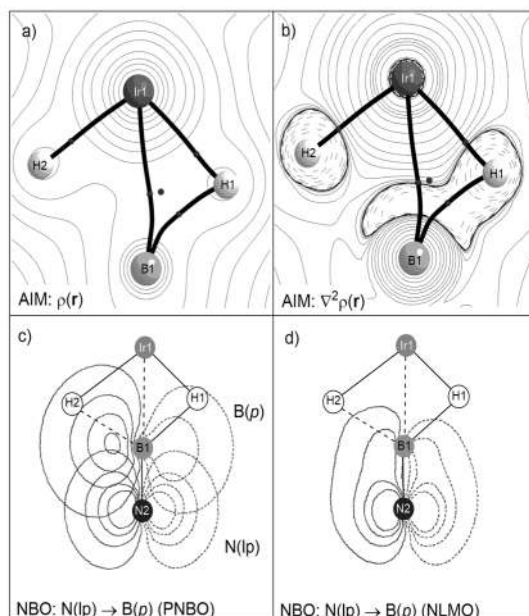


Figure 3. AIM and NBO analysis of [3]⁺: a) contour plot of $\rho(r)$ with bond paths shown as black tubes, bcps as red points and rcps as purple points. b) contour plot of $\nabla^2\rho(r)$ with positive contours shown as solid black lines, negative contours shown as dashed red lines [3]⁺ c) PNBO overlap N(2)-B(1)-H(2) plane d) N-B π 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 H₂B=NCy₂ (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]⁺ [1.481 Å cf. 1.449 Å] suggests that [3-rot]⁺ retains some B-N π character, which we suggest results from N(*lp*) \rightarrow B-O(σ^*) donation. This notion is also supported by only a small degree of nitrogen pyramidalization in [3-rot]⁺ [Σ (\angle RNR): 354° cf. 345° for H₂B=NCy₂]. Consistent with this proposal, NBO analysis of [3-rot]⁺ shows significant N(*lp*) \rightarrow B-O(σ^*) donation [$E^{(2)} = 14.5$ kcal·mol⁻¹]. As the N(*lp*) \rightarrow B(*p*) stabilization energy of the aminoborane only decreases by *ca.* 6 kcal·mol⁻¹ 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 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.

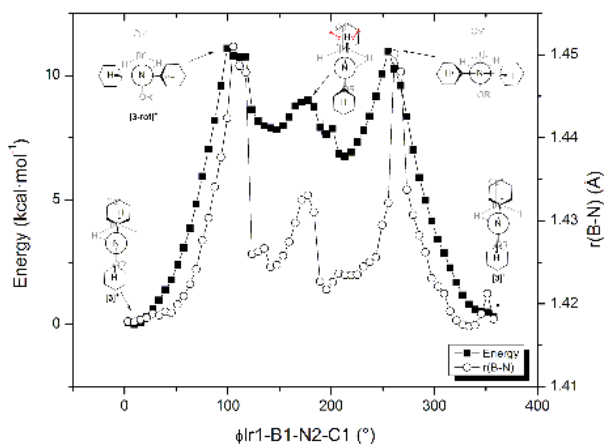


Figure 4. DFT-calculated potential energy surface and change in B(1)-N(2) bond length for rotation about the B-N bond in $[3]^+$.

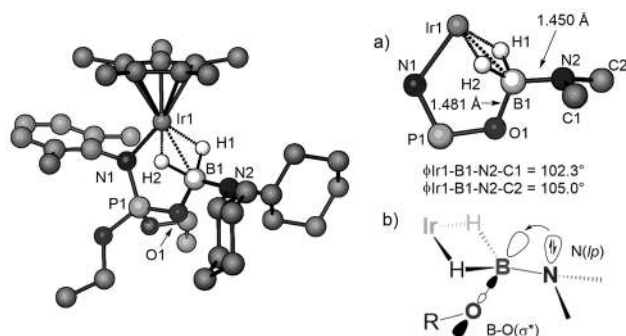


Figure 5. DFT-calculated structure of $[3\text{-rot}]^+$ with non-coordinating hydrogen atoms omitted for clarity. a) view of the geometry about boron b) $\text{N}(lp) \rightarrow \text{B-O}(\sigma^*)$ donation.

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 ^1H 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

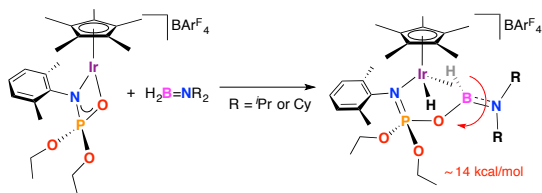
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Keywords: B-H activation • hemilability • aminoborane • dehydropolymerization • DFT

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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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