Iminoborane Hot Paper

International Edition: DOI: 10.1002/anie.201504867
German Edition: DOI: 10.1002/ange.201504867

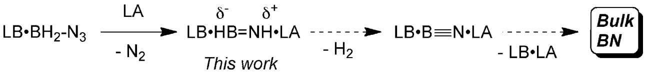
Encapsulating Inorganic Acetylene, HBNH, Using Flanking Coordinative Interactions

*Anindya K. Swarnakar, Christian Hering-Junghans, Koichi Nagata, Michael J. Ferguson, Robert McDonald, Norihiro Tokitoh, and Eric Rivard**

Abstract: *A stable donor–acceptor coordination complex of the elusive parent inorganic iminoborane HBNH (a structural analogue of acetylene) is reported. This species was generated via thermally induced N_2 elimination/1,2-H migration from a hydrido(azido)borane adduct $NHC{\cdot}BH_2N_3$ (NHC = N-heterocyclic carbene) in the presence of a fluorinated triarylborane. The mechanism of this process was also investigated by computational and isotopic labeling studies. This transformation represents a new and potentially modular route to unsaturated inorganic building blocks for advanced material synthesis.*

Iminoboranes (RB≡NR) are isoelectronic to alkynes; however, they display greatly enhanced reactivity due to the higher polarity of B–N bonds,[1,2] and thus self-oligomerize when smaller R groups are present.[3] This is typified by the parent iminoborane HB≡NH which only exists in the condensed phase as its iconic trimer, borazine $[HBNH]_3$ (also termed "inorganic benzene").[4] Despite these challenges, monomeric HBNH is of considerable fundamental interest and has only been isolated via matrix isolation below 40 K.[5,6] Furthermore HBNH is likely a key intermediate in the laser-induced preparation of nanodimensional boron nitride (BN) from $H_3N{\cdot}BH_3$ dehydrogenation;[7] boron nitride is of great value to the materials community due to its insulating properties and ability to withstand harsh external conditions.[8] Recent breakthroughs by the laboratories of Bertrand, Braunschweig, and Stephan have demonstrated that both N-heterocyclic carbene (NHC) and cyclic-(alkyl)amino carbene (CAAC) donors can bind functionalized iminoboranes such as $ClBNSiMe_3$ and *t*BuBN*t*Bu as 1:1 adducts LB·RB=NR′ (LB = Lewis base).[9]

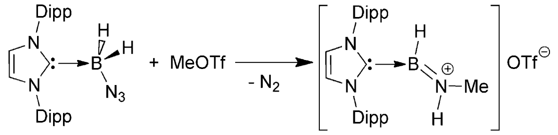
Herein we use a donor–acceptor approach[10] to isolate the first stable molecular adduct containing HBNH. Specifically this parent iminoborane is sandwiched between Lewis basic (LB) and Lewis acidic (LA) units to yield a stable complex of the form LB·HB=NH·LA, which could also be viewed as a formal frustrated Lewis pair (FLP)[11] interacting with HBNH. By judicious modification of the capping LB and LA groups it is expected that a solution-phase route to boron nitride would be possible via mild dehydrogenation of LB·HB=NH·LA,[12] followed by BN extrusion (Scheme 1); typically BN is prepared at temperatures exceeding 900 °C.[8] Herein we also introduce a general method to form B–N (and possibly other element–nitrogen) multiple bonds by the energetically favored loss of N_2 from inorganic hydridoazide precursors.[13] Key intermediates en route to our LB·HB=NH·LA complex were isolated and structurally characterized, and the mechanism of iminoborane adduct formation was probed by both computational and isotope-labeling studies.



Scheme 1. Potential route to bulk boron nitride via an HBNH adduct; LA = Lewis acid, LB = Lewis base.

The N_2 elimination process central to the current study was discovered in an attempt to form the electrophilic azidoborane adduct $IPr{\cdot}B(OTf)_2N_3$ from the addition of two equivalents of MeOTf[14] to the known azidoborane[15] $IPr{\cdot}BH_2N_3$ (**1**) (IPr = [(HCNDipp)$_2$C:], Dipp = 2,6-iPr$_2$C$_6$H$_3$; $OTf^- = OSO_2CF_3$). It was hoped that reducing $IPr{\cdot}B(OTf)_2N_3$ would afford an unstable boron(I) species that would yield oligomeric adducts of $[IPr{\cdot}(BN)]_x$ after loss of dinitrogen.[16] However, when $IPr{\cdot}BH_2N_3$ (**1**) was reacted with MeOTf, gas evolution was noted and a new product was formed that contained a nitrogen-bound methyl group. This product proved to be thermally unstable in solution at room temperature, yet at −35 °C colorless crystals suitable for X-ray crystallography were obtained, revealing the generation of the formal boraiminium adduct [IPr·HB=NH(Me)]OTf (**2**) (Scheme 2; Figure 1).

Compound **2** adopts a *trans* HBNH configuration in the solid state with a B–N distance of 1.361(5) Å, a value that is slightly elongated with respect to the B=N bond lengths found



IPr•BH2N3 (**1**)

2

Scheme 2. Synthesis of **2** starting from **1** and MeOTf; adding extra equivalents of MeOTf to **1** led to the same products.

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[*] A. K. Swarnakar, Dr. C. Hering-Junghans, Dr. M. J. Ferguson, Dr. R. McDonald, Prof. Dr. E. Rivard
Department of Chemistry, University of Alberta
11227 Saskatchewan Drive, Edmonton, Alberta, T6G 2G2 (Canada)
E-mail: erivard@ualberta.ca
Homepage: http://www.chem.ualberta.ca/~erivard/
K. Nagata, Prof. Dr. N. Tokitoh
Institute for Chemical Research, Kyoto University
Uji, Kyoto, 611-0011 (Japan)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201504867.

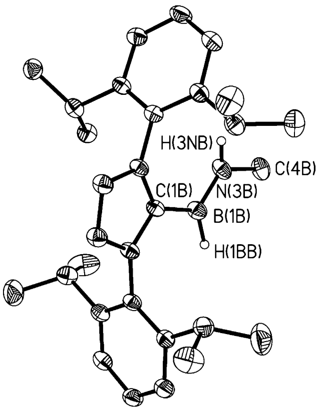


Figure 1. Molecular structure of [IPr·BH=NH(Me)]OTf (**2**) with thermal ellipsoids presented at a 30% probability level. All carbon-bound hydrogen atoms and OTf$^-$ counterion have been omitted for clarity. Selected bond lengths [Å] and angles [°] with parameters associated with a second molecule in the asymmetric unit listed in square brackets: C(1B)–B(1B) 1.574(5) [1.568(5)], B(1B)–N(3B) 1.366(5) [1.361(5)], N(3B)–C(4B) 1.478(5) [1.460(5)]; C(1B)-B(1B)-N(3B) 121.3(4) [122.1(4)].

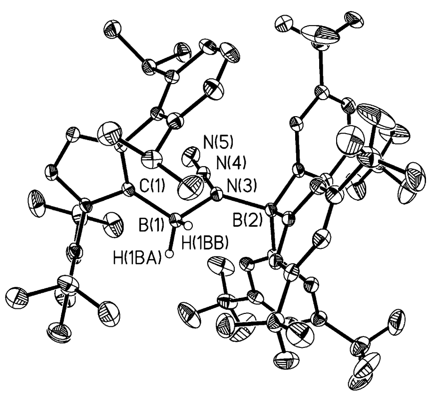
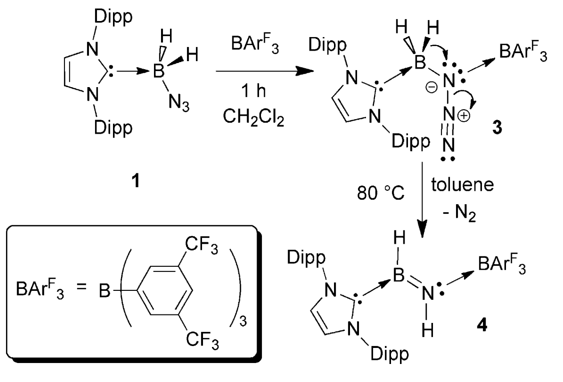


Figure 2. Molecular structure of IPr·BH$_2$N$_3$·BAr$^F_3$ (**3**) with thermal ellipsoids presented at a 30% probability level; all carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–B(1) 1.610(2), B(1)–N(3) 1.599(2), N(3)–N(4) 1.253(2), N(4)–N(5) 1.134(2), N(3)–B(2) 1.656(2); N(5)-N(4)-N(3) 177.68(18).

in the abovementioned CAAC and NHC iminoborane adducts LB·RBNR′ [1.300(3) to 1.340(5) Å] (LB = Lewis base).[9] The C$_{\mathrm{IPr}}$–B interaction in **2** [1.571(7) Å avg.] is nearly the same value within experimental error (3σ) as the related coordinative bond in CAAC·BrB=NSiMe$_3$ [1.606(4) Å],[9b] indicating that a similar C–B bonding environment is likely present in both species.

Compound **2** can be viewed as an NHC adduct of methylated HBNH, and accordingly we thought that the N$_2$ elimination/1,2-H migration protocol in Scheme 1 could be extended to include other Lewis acidic entities.[17] Given our prior successes using W(CO)$_5$ as a Lewis acid,[10c,d,h] IPr·BH$_2$N$_3$ (**1**) was combined with THF·W(CO)$_5$; however, no reaction occurred. Fortunately the sterically demanding fluoroarylborane BAr$^F_3$ (Ar^F = 3,5-C$_6$H$_3$(CF$_3$)$_2$)[18] binds to the azide moiety in **1** to yield IPr·BH$_2$N$_3$·BAr$^F_3$ (**3**) as a colorless solid (Scheme 3, Figure 2).

The most notable structural feature of IPr·BH$_2$N$_3$·BAr$^F_3$ (**3**) is the substantial shortening of the terminal N(4)–N(5) bond [1.134(2) Å] in relation to the internal N(3)–N(4) linkage [1.253(2) Å], consistent with the accumulation of triple bond character. Interestingly, the bond lengths and the overall geometry of the H$_2$B–N$_3$ unit in **3** remain unperturbed in relation to those found in the precursor IPr·BH$_2$N$_3$ (**1**).[15] In addition to the B–H stretching mode at 2467 cm^{-1}, a diagnostic azide IR ν(N$_3$) band at 2134 cm^{-1} was noted for **3**, which matches well the related stretches at 2189 and 2175 cm^{-1} found in the bis-silylated azide [(Me$_3$Si)$_2$NNN]B(C$_6$F$_5$)$_4$.[19] IPr·BH$_2$N$_3$·BArF$_3$ (**3**) slowly decomposes at room temperature, both in solution (within 24 h) and in the solid state (4 days). As a result we decided to explore the thermolysis of **3** in more detail.



Scheme 3. Preparation of the azidoborane **3** and its conversion into the iminoborane complex **4**; for related ^{15}N and ^{2}H labeling studies, see the Supporting Information.

The clean conversion of IPr·BH$_2$N$_3$·BAr$^F_3$ (**3**) to a new carbene-containing product was accomplished by heating a solution of **3** in toluene to 80 °C for 12 h.[20] The resulting highly lipophilic colorless solid afforded an IR spectrum devoid of an azide band, suggesting that N$_2$ loss occurred. Furthermore weak ν(N–H) and ν(B–H) vibrations emerged at 3370 and 2511 cm^{-1}, respectively, while the corresponding N–H and B–H resonances were located at 5.44 and 4.00 ppm in the ^{1}H{^{11}B} NMR spectrum of the product with an integration ratio of 1:1. The N–H group yields a doublet resonance due to $^{3}J_{\mathrm{HH}}$ coupling with an adjacent B–H group, supporting the formation of an iminoborane HBNH array. X-ray crystallography conclusively identified the product as the donor–acceptor iminoborane complex IPr·HB=NH·BAr$^F_3$ (**4**) (Scheme 3, Figure 3). The central iminoborane B–N distance in **4** is 1.364(2) Å and is in line with the presence of a double bond (Σr_{cov}(B=N) = 1.38 Å).[21] The capping IPr and BAr$^F_3$ units in **4** form a steric sheath about the central HB=NH unit and help enforce a *trans* core geometry [C(1)-B(1)-N(3)-B(2) torsion angle = 179.26(12)°] which minimizes the IPr···BAr$^F_3$ intramolecular repulsions. The C$_{\mathrm{IPr}}$–B distance in **4** is 1.596(2) Å and is shorter than the dative C–B interaction in Im*i*Pr$_2$·*t*BuB=N*t*Bu [1.648(2) Å; Im*i*Pr$_2$ = (HCN*i*Pr)$_2$C:],[9c] illustrating the lower steric demand of the HBNH unit in **4**. The terminal N–BAr$^F_3$ bond in **4** is 1.5708(18) Å and lies in the range of B–N single bonds noted in IPr·BH$_2$NH$_2$BH$_3$

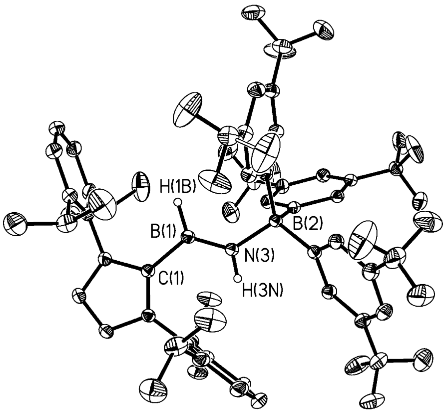


Figure 3. Molecular structure of IPr·HB=NH·BAr$^{F}_{3}$ (**4**) with thermal ellipsoids presented at a 30% probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C(1)–B(1) 1.596(2), B(1)–N(3) 1.364(2), N(3)–B(2) 1.5708(18); C(1)-B(1)-N(3) 123.45(13), B(1)-N(3)-B(2) 130.72(12), N(3)-B(1)-H(1B) 122.3(10), B(1)-N(3)-H(3N) 117.3(12).

[1.540(3)–1.605(2) Å];[22] of note, the capping N–BAr$^{F}_{3}$ interaction in IPr·BH$_2$N$_3$·BAr$^{F}_{3}$ (**3**) is 1.599(2) Å.[23]

As outlined in Scheme 3, the formation of **4** is postulated to occur via N$_2$ loss from **3** followed by a 1,2-hydride shift from boron to nitrogen (vide infra). A related process has been observed by Paetzold,[1a] who prepared iminoboranes via alkyl-group migration (R$_2$N–B(R′)-N → R$_2$N-B≡N–R′) involving a transient boranitrene.[24] Cummins and Fox also observed nitrogen extrusion from the azidoborate salt nBu$_4$N-[(N$_3$)B(C$_6$F$_5$)$_3$] in the presence of (THF)U[N(tBu)Ar]$_3$ (Ar = 3,5-Me$_2$C$_6$H$_3$) to yield the uranium(V) nitride nBu$_4$N-[(F$_5$C$_6$)$_3$B·N=U{N(tBu)Ar}]$_3$.[25]

To gain insight into the mechanism by which IPr·HB=NH·BAr$^{F}_{3}$ (**4**) is formed, the deuterium-labeled analogue IPr·BD$_2$N$_3$·BAr$^{F}_{3}$ (**3-d**) was synthesized (Scheme 3). Subsequent thermolysis of **3-d** at 80 °C yielded the isotopomer IPr·DB=ND·BAr$^{F}_{3}$ (**4-d**) as confirmed by NMR and IR spectroscopy, supporting a 1,2-H migration process. The rate of conversion of **3** to **4** was monitored by NMR spectroscopy (75 °C, C$_6$D$_6$) and displayed a first-order dependence on the concentration of IPr·BH$_2$N$_3$·BAr$^{F}_{3}$ (**3**). Notably thermolysis of the deutero analogue **3d** did not yield any discernable H/D kinetic isotope effect (Figure S4),[26] suggesting that N$_2$ loss and formation of a transient nitrene is the rate-determining step.

In order to facilitate the recording of an ^{15}N{^{1}H} NMR spectrum, the ^{15}N-labeled adduct IPr·HB=^{15}NH·BAr$^{F}_{3}$ was prepared as a 1:1 mixture with unlabeled **4** (Scheme S2).[26] Interestingly the ^{15}N–H group in IPr·HB=^{15}NH·BAr$^{F}_{3}$ gave rise to a doublet of doublet resonance in its ^{1}H NMR spectrum (Figure 4) with a $^{1}J_{\mathrm{H-^{15}N}}$ value of 69.6 Hz; for comparison, the -NH$_2$ group in 4-nitroaniline yields a $^{1}J_{\mathrm{H-^{15}N}}$ of 86.3 Hz.[27] An ^{15}N{^{1}H} NMR resonance for **4-N15** was located at 155.4 ppm, and is downfield in relation to the ^{15}N NMR resonance in borazine [HBNH]$_3$ (−278 ppm).[28]

To better understand the bonding and reactivity trends observed, computations were carried out (pbe0/cc-pVDZ level).[26] Natural bond orbital analysis (NBO) of IPr·BH$_2$N$_3$ (**1**) shows a high negative partial charge of −0.54 on the internal N$_{\mathrm{azide}}$ atom, thus explaining the electrophilic attack at this site by MeOTf and BAr$^{F}_{3}$. Within IPr·BH$_2$N$_3$·BAr$^{F}_{3}$ (**3**) the borane-bound nitrogen [N(3) in Figure 2] has significant lone pair character, in line with the mesoionic form drawn in Scheme 3. The computed energies for the conversion of **3** into IPr·HB=NH·BAr$^{F}_{3}$ (**4**) are −64.5 kcal mol^{-1} ($\Delta_r H°$(298 K)) and −75.6 kcal mol^{-1} ($\Delta_r G°$(298 K)), while the estimated activation barrier for N$_2$ loss from **3** is 31.3 kcal mol^{-1}.[26,29] NBO analysis gives rise to a charge of the central HB=NH fragment in **4** of −0.13. The B–N linkage in **4** can be formulated as a double bond, with significant polarization of the σ and π components towards N (78% for each). Moreover, the Wiberg bond index (WBI) for this linkage (1.32) supports the presence of multiple-bond character; accordingly, the Kohn–Sham orbitals reveal a LUMO having B–N π* character, while contributions to the BN double bond appear in the HOMO−7 (Figure S6).[26]

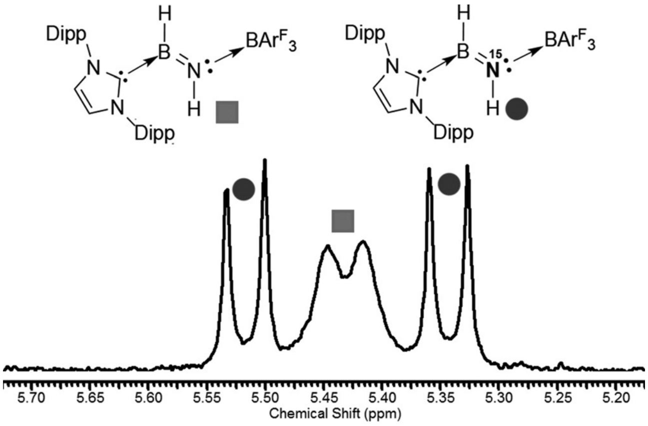


Figure 4. ^{1}H{^{11}B} NMR N–H resonances from a 1:1 mixture of IPr·HB=^{15}NH·BAr$^{F}_{3}$ and **4**.

Given the presence of hydridic (B–H) and acidic (N–H) residues within the parent iminoborane adduct IPr·HB=NH·BAr$^{F}_{3}$ (**4**), we attempted the dehydrogenation[12] of this species to yield the first molecular adduct of boron nitride IPr·B≡N·BAr$^{F}_{3}$. However, when **4** was treated with 2 mol% of the active aminoborane dehydrogenation catalyst [(cod)RhCl]$_2$ (cod = 1,5-cyclooctadiene) at room temperature and later at 90 °C, only the starting material could be recovered. Increasing the catalyst loading to 20 mol%, and prolonged heating to 140 °C (for 96 h) led to decomposition of **4** into an unidentifiable mixture of products. The lower reactivity of **4** in relation to other unsaturated B–N systems can be traced to the high degree of steric protection about the HB=NH unit (Figure S10)[26] due to the bulky flanking IPr and BAr$^{F}_{3}$ groups; in fact **4** can be handled in air (but decomposes in water) and remains unchanged in the presence of nBuLi, K[N(SiMe$_3$)$_2$], Ph$_3$C[B(C$_6$F$_5$)$_4$], MeOTf, and even elemental I$_2$.

In conclusion, we have discovered a novel Lewis acid induced N$_2$ elimination/hydride-shift process to yield the first stable adduct of the parent iminoborane HBNH. By lowering the steric bulk of the capping groups within LB·HB=NH·LA complexes we hope to encourage H$_2$ loss and the subsequent formation of bulk boron nitride in a solution-based approach. The generality of this method will also be explored across the main group to obtain new unsaturated species of potential use in controlled, low-temperature, advanced material syntheses.[30]

Acknowledgements

This work was supported by the NSERC of Canada (Discovery Grant for E.R) and the Canada Foundation for Innovation (CFI). C.H.-J. acknowledges the Alexander von Humboldt Foundation for a Feodor Lynen Postdoctoral Fellowship, while K.N. thanks the Japan Society for the Promotion of Science (JSPS) for a PhD fellowship. We also thank Dr. Tapas Purkait, Olena Shynkaruk, and William Torres Delgado for experimental assistance, Compute Canada for providing computational resources, and Prof. Alex Brown and Dr. Urmi Bhusan Bhakta for helpful discussions.

Keywords: boron · carbenes · donor–acceptor systems · multiple bonds · nitrogen

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 10666–10669
Angew. Chem. **2015**, *127*, 10812–10816

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[26] For full details, see the Supporting Information. CCDC 1403519 (**2**), 1403520 (**3**) and 1403521 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
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Received: May 28, 2015