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Reactivity of a coordinated inorganic acetylene unit, HBNH, and the azidoborane cation $[HB(N_3)]^+$†

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A donor–acceptor complex of HBNH was prepared *via* thermolysis of a carbene-stabilized azidoborane. The reactivity of the fundamentally important HBNH unit (inorganic alkyne analogue) was explored in detail, including attempts to convert this species and related hydrido(azido)borane cations into molecular complexes of BN. This work provides added impetus for the development of molecular precursors that can release bulk boron nitride (a desirable insulator and thermal conductor) under mild conditions, and from solution.

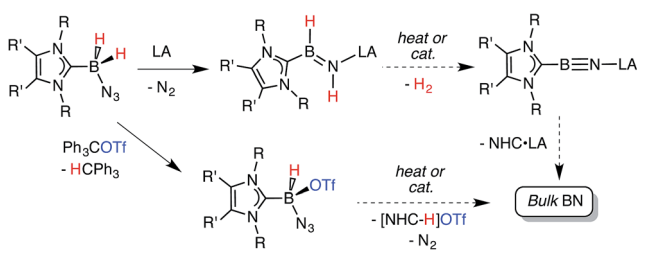
Introduction

Iminoboranes (RB≡NR′) are inorganic isoelectronic counterparts to alkynes however their isolation is challenging due to the highly polar nature of their core B–N triple bonds, making these species vulnerable to cyclooligomerization.[1,2] In seminal studies, Paetzold and coworkers used steric protection to obtain iminoboranes (*e.g.* ^{t}BuB≡N^{t}Bu) as stable entities, and demonstrated initial coordination chemistry.[2d] More recently, the Braunschweig, Bertrand and Stephan teams employed carbene-based donors to intercept reactive iminoboranes,[3] including the halosilyl analogue ClBNSiMe$_3$.[3a] Despite these excellent studies, the parent iminoborane, HBNH, remained only identifiable in cryogenic matrices (40 K) or as a fleeting species in the gas phase,[4,5] yet HBNH is of interest as a possible intermediate in the laser-induced dehydrogenative synthesis of boron nitride (BN) from $H_3N{\cdot}BH_3$.[6]

Recently our group was successful in intercepting the first example of a stable complex of HBNH by placing this unsaturated unit in between a sterically encumbered *N*-heterocyclic carbene (NHC) donor and a large triarylfluoroborane acceptor.[7,8] Unfortunately the use of these bulky substituents restricted access to the HBNH array by potential reagents/catalysts. In this Edge Article we introduce a more reactive HBNH adduct and describe our attempts to convert this species into LB·B≡N·LA complexes (LA = Lewis acid; LB = Lewis base; Scheme 1); in addition we investigate the reactivity of the donor-stabilized azidohydride boronium cation $[BH(N_3)]^+$.[9] The ultimate goal of our program would be to use these newly developed B–N species for the mild solution-based preparation of bulk boron nitride (Scheme 1). BN and its nanodimensional analogues are highly coveted in the context of advancing modern electronics due to their refractory nature, and desirable electronically insulating and heat dissipating properties.[10,11]

Results and discussion

Our initial donor–acceptor HBNH complex IPr·HB═NH·BAr$^F{}_3$ [IPr = [(HCNDipp)$_2$C:]; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$; Ar^F = 3,5-(F$_3$C)$_2$C$_6$H$_3$][7a] was generated by the Lewis acid (BAr$^F{}_3$) promoted loss of N_2 from the known boron azide IPr·BH$_2$N$_3$,[12] followed by an intramolecular 1,2 hydride shift from B to N (Scheme 1). The presence of both hydridic (B–H$^{\delta-}$) and acidic (N–H$^{\delta+}$) residues in the HBNH unit prompted us to explore the dehydrogenation of this iminoborane species as a possible route to a molecular adduct of boron nitride, IPr·B≡N·BAr$^F{}_3$. However IPr·HB═NH·BAr$^F{}_3$ was found to be unreactive in the presence of common dehydrogenation pre-catalysts[13] such as [Rh(COD)Cl]$_2$ (COD = 1,5-cyclooctadiene).[7a] The inertness of the iminoborane array was initially attributed to the presence of an extremely congested coordination environment. Thus we decided to generate an HBNH complex supported by the less hindered NHC, ImMe$_2$^{i}Pr$_2$ [ImMe$_2$^{i}Pr$_2$ = (MeCN^{i}Pr)$_2$C:].[14]



Scheme 1 Synthetic routes explored in this paper are each connected by a common goal of obtaining bulk BN under mild conditions.

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The required azidoborane for our HBNH adduct synthesis, $ImMe_2{}^iPr_2{\cdot}BH_2N_3$ (**2**), was prepared from $ImMe_2{}^iPr_2{\cdot}BH_3$[15] in two high yielding steps (Scheme 2). $ImMe_2{}^iPr_2{\cdot}BH_2N_3$ (**2**) was then combined with a stoichiometric amount of the fluoroarylborane, $BAr^F{}_3$, followed by heating to 80 °C for 12 h in toluene to afford the target iminoborane adduct $ImMe_2{}^iPr_2{\cdot}HB{=}NH{\cdot}BAr^F{}_3$ (**3**) as a colorless solid in a 64% yield (mp = 142–146 °C). Based on prior studies[7a] this reaction is believed to proceed *via* initial N_2 elimination and trapping of the resulting nitrene adduct, $ImMe_2{}^iPr_2{\cdot}H_2B{-}N{\cdot}BAr^F{}_3$ by a 1,2-hydride migration from B to N (Scheme 2). It is salient to mention that the generation of transient nitrenes from boron azides is known in the literature.[1a,16]

As expected, the $^1H\{^{11}B\}$ NMR spectrum of $ImMe_2{}^iPr_2{\cdot}HB{=}NH{\cdot}BAr^F{}_3$ (**3**) gave discernable N–H and B–H resonances at 5.42 and 4.62 ppm, respectively (in C_6D_6), which are similar to the corresponding resonances found in $IPr{\cdot}HB{=}NH{\cdot}BAr^F{}_3$.[7a] X-ray crystallography later conclusively identified the presence of an HB=NH moiety in **3** (Fig. 1). The core iminoborane unit in **3** adopts a *trans* arrangement [C–B–N–B dihedral angle = 178.1(2)°] thereby minimizing intramolecular repulsion between the $ImMe_2{}^iPr_2$ and $BAr^F{}_3$ groups. The central B=N and $C_{(NHC)}$–B bond distances in **3** are 1.369(3) Å and 1.596(4) Å, which are the same within experimental error as in $IPr{\cdot}HB{=}NH{\cdot}BAr^F{}_3$.[7a] A slightly elongated B–N distance was reported in the iminoborane $(HC{\equiv}C)_2B{-}N{}^iPr_2$ (1.385(3) Å).[17]

$ImMe_2{}^iPr_2{\cdot}HB{=}NH{\cdot}BAr^F{}_3$ (**3**) was examined by computational methods and an overall charge of −0.13*e* was found for the central HB=NH moiety. As anticipated, the B=N linkage (Wiberg bond index, WBI = 1.33) has considerable polarization of the σ- and π-components towards N (*ca.* 80% located on N), according to NBO analysis. The LUMO shows B–N π* and B–C π-character, while contributions to the B–N π-manifold appear in HOMO−2 and HOMO−6 (Fig. 2).[18] The computed HOMO–LUMO gap is 173 kcal mol^{-1} and is in agreement with the observed inertness of **3** (*vide infra*).

With the less hindered HBNH complex **3** in hand, we attempted to promote its dehydrogenation to afford the BN adduct $ImMe_2{}^iPr_2{\cdot}B{\equiv}N{\cdot}BAr^F{}_3$. When compound **3** was treated with the well-known dehydrogenation pre-catalyst $[Rh(COD)Cl]_2$ (2–5 mol%) in toluene, no reaction occurred at room temperature. When the same dehydrogenation reaction was attempted at 90 °C for 7 days, only partial decomposition of **3** (<10%; $[ImMe_2{}^iPr_2{-}H]^+$ salt) was noted. Moreover, compound **3** was also combined with the potential dehydrogenation catalyst $CpFe(CO)_2OTf$ and the Frustrated Lewis Pair (FLP), $^tBu_3P$ and $BAr^F{}_3$, (both known to promote H_2 loss from amine-boranes) however in each case no reaction with **3** transpired. Likewise attempted H_2 release from **3** by photolysis (300 W Hg lamp in Et_2O) gave no reaction.

Undaunted by the lack of thermally- or catalytically-instigated H_2 release from **3**, we decided to see if the core HBNH unit underwent chemical transformations one would expect for a polarized B=N linkage.[19] When $ImMe_2{}^iPr_2{\cdot}HB{=}NH{\cdot}BAr^F{}_3$ (**3**) was combined with one equivalent of HCl in Et_2O, the resulting ^{11}B NMR spectrum was consistent with the presence

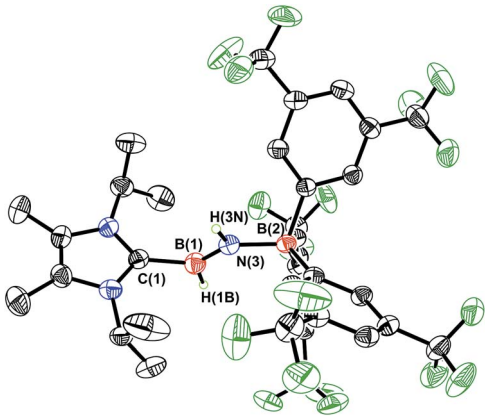
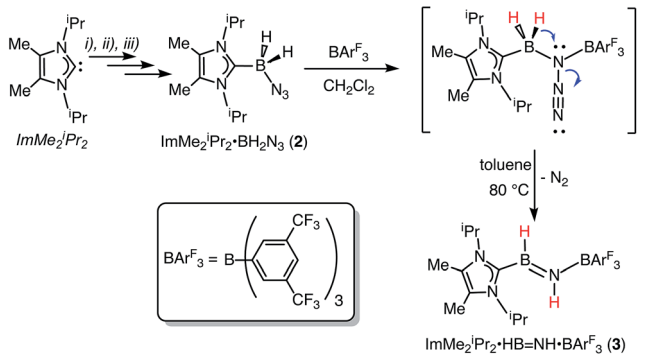


Fig. 1 Molecular structure of $ImMe_2{}^iPr_2{\cdot}HB{=}NH{\cdot}BAr^F{}_3$ (**3**) with thermal ellipsoids presented at a 30% probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–B(1) 1.596(2), B(1)–N(3) 1.369(3), N(3)–B(2) 1.572(2); C(1)–B(1)–N(3) 121.8(2), B(1)–N(3)–B(2) 130.5(2), N(3)–B(1)–H(1B) 125.2(16), B(1)–N(3)–H(3N) 115.8(19).



Scheme 2 Synthesis of $ImMe_2{}^iPr_2{\cdot}HB{=}NH{\cdot}BAr^F{}_3$ (**3**) starting from the azidoborane adduct $ImMe_2{}^iPr_2{\cdot}BH_2N_3$ (**2**). Reagents: (i) $THF{\cdot}BH_3$, THF, rt (95% yield); (ii) 0.5 equiv. I_2, benzene, rt (90% yield); (iii) NaN_3, DMSO, rt (68% yield).

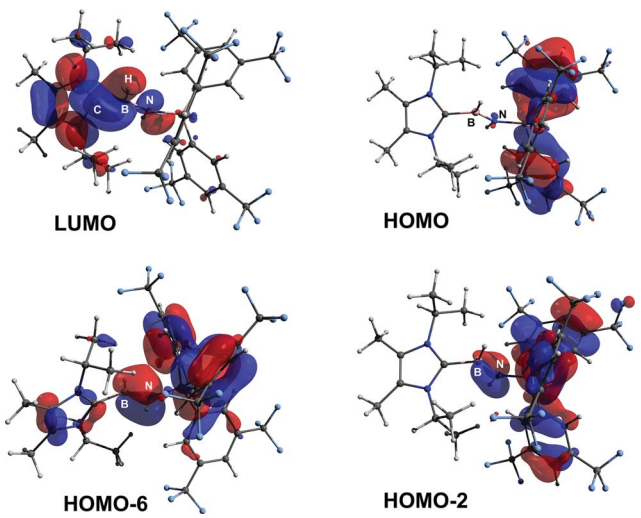


Fig. 2 POV-ray depiction of selected Kohn–Sham orbitals of **3**.

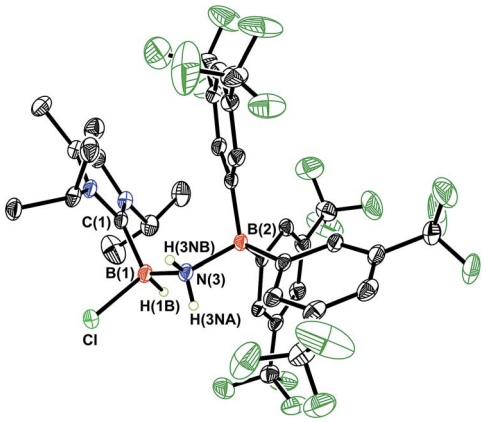


Fig. 3 Molecular structure of $ImMe_2^iPr_2{\cdot}H(Cl)B{-}NH_2{\cdot}BAr^F{}_3$ (**4**) with thermal ellipsoids presented at a 30% probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–B(1) 1.616(5), B(1)–N(3) 1.585(4), N(3)–B(2) 1.632(4), B(1)–Cl 1.906(4); C(1)–B(1)–N(3) 115.7(3), B(1)–N(3)–B(2) 124.4(2), N(3)–B(1)–Cl 107.2(2), B(1)–N(3)–H(3NA) 105(2).

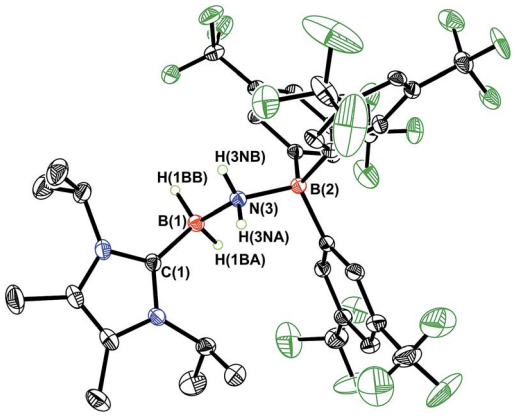
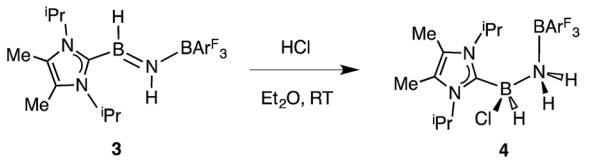


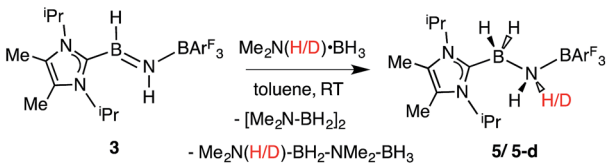
Fig. 4 Molecular structure of $ImMe_2^iPr_2{\cdot}H_2B{-}NH_2{\cdot}BAr^F{}_3$ (**5**) with thermal ellipsoids presented at a 30% probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–B(1) 1.627(3), B(1)–N(3) 1.613(3), N(3)–B(2) 1.622(2); C(1)–B(1)–N(3) 110.23(15), B(1)–N(3)–B(2) 120.11(14), N(3)–B(1)–H(1BB) 109.0(12), B(1)–N(3)–H(3NA) 106.8(15).

of two four-coordinate boron centers ($\delta = -3.7$ and -9.5 ppm in C_6D_6). X-ray crystallography confirmed the successful addition of HCl across the B=N bond to form $ImMe_2^iPr_2{\cdot}H(Cl)$-$B{-}NH_2{\cdot}BAr^F{}_3$ (**4**) as a racemic mixture due to the presence of a chiral boron atom (Fig. 3; eqn (1)). The addition of chloride at the boron center in **4** illustrates the Lewis acidic nature of the boron atom in coordinated HB=NH in **3**. The central B–N bond distance in **4** is 1.585(4) Å and is comparable to the B–N bond lengths found in structurally related amine-boranes, such as $IPr{\cdot}BH_2NH_2BH_3$.[20] The $C_{(NHC)}$–B bond distance in **4** is 1.616(5) Å which, somewhat to our surprise, is similar in length as the corresponding $C_{(NHC)}$–B bond distance of 1.596(4) Å in **3**, despite the change in hybridization at boron to sp^3 in **4**; however, the capping $N{-}BAr^F{}_3$ interaction in **4** (1.632(4) Å) is longer than in the HBNH adduct **3** (1.572(2) Å). Addition of HCl also leads to a substantial canting of the relative arrangement of the capping NHC and borane groups (*vs.* in **3**), as evidenced by the C–B–N–B dihedral angle of 65.3(3)°.



3 **4** (1)

While the polarized B=N linkage in $ImMe_2^iPr_2{\cdot}HB{=}NH{\cdot}BAr^F{}_3$ (**3**) did not exhibit Frustrated Lewis Pair (FLP) type reactivity with H_2, CO or CO_2,[21] effective transfer hydrogenation[22] occurred between the amine-borane $Me_2NH{\cdot}BH_3$ and **3** (eqn (2)). The resulting hydrogenated product $ImMe_2^iPr_2{\cdot}H_2$-$B{-}NH_2{\cdot}BAr^F{}_3$ (**5**) formed after 12 h at room temperature; the expected dehydrogenated by-products $[Me_2N{-}BH_2]_2$ and $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ were also detected by NMR spectroscopy. To probe the mechanism of this transformation in more detail, compound **3** was combined with $Me_2ND{\cdot}BH_3$; the resulting product $ImMe_2^iPr_2{\cdot}H_2B{-}N(H)D{\cdot}BAr^F{}_3$ (**5-d**)[18] suggested direct H/D atom transfer from B to B and N to N.[22a] The molecular structure of **5** (Fig. 4) has similar overall structural features as the HCl addition product $ImMe_2^iPr_2{\cdot}H(Cl)B{-}$ $NH_2{\cdot}BAr^F{}_3$ (**4**) with an elongated C_{NHC}–B distance of 1.627(3) Å in accordance with the decreased electrophilicity of the $BH_2{-}NH_2{-}BAr^F{}_3$ unit in **5**.



3 **5/ 5-d** (2)

Despite the presence of both hydridic and acidic H atoms in $ImMe_2^iPr_2{\cdot}H_2B{-}NH_2{\cdot}BAr^F{}_3$ (**5**), our efforts to induce dehydrogenation (and reform the HBNH adduct **3**) by heating up to 100 °C in the presence of known dehydrogenation pre-catalysts $[Rh(COD)Cl]_2$ or $CpFe(CO)_2OTf$ led to no discernable reaction. Furthermore, **5** remained unreactive towards the possible H_2 acceptors, PhN=NPh and the FLP ($^tBu_3P/BAr^F{}_3$), and did not yield **3** upon attempted photolysis (300 W Hg lamp). Accordingly, the calculated NPA charges for **5** show less hydridic character for the B–H array (−0.009 and −0.020*e*) compared to the reactive amine-borane $MeNH_2{\cdot}BH_3$ (B–H charges of −0.030 to −0.034*e*), thus partially explaining the higher reactivity for the latter species. The computed positive charges for N-bound hydrogen atoms in **5** (0.429 and 0.437*e*) are similar to those in $MeNH_2{\cdot}BH_3$.[18]

In order to directly probe the Lewis acidity of the HBNH unit in **3**,[23] an additional equivalent of the carbene donor $ImMe_2^iPr_2$ was combined with $ImMe_2^iPr_2{\cdot}HB{=}NH{\cdot}BAr^F{}_3$ (**3**). While the expected bis adduct $(ImMe_2^iPr_2)_2HBNH{\cdot}BAr^F{}_3$ (**6**) could be isolated in the solid state as a yellow solid (88% yield)

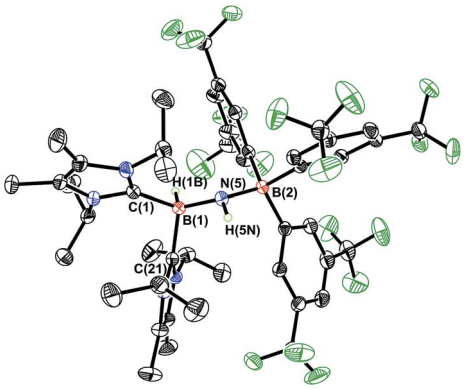
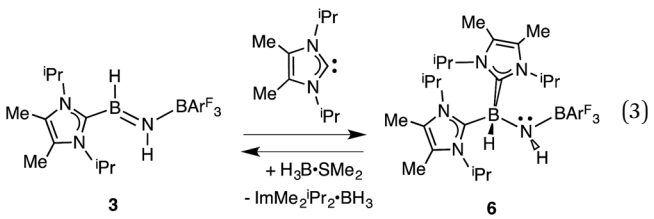


Fig. 5 Molecular structure of $[ImMe_2{}^iPr_2]_2{\cdot}HB\text{-}NH{\cdot}BAr^F{}_3$ (**6**) with thermal ellipsoids presented at a 30% probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)–B(1) 1.684(3), C(21)–B(1) 1.660(2), B(1)–N(5) 1.512(2), N(5)–B(2) 1.539(2); C(1)–B(1)–N(5) 117.28(14), B(1)–N(5)–B(2) 125.03(14), N(5)–B(1)–C(21) 112.26(14), N(5)–B(1)–H(1B) 113.4(11), B(1)–N(5)–H(5N) 112.5(14).

and characterized by X-ray crystallography (Fig. 5, *vide infra*), the NMR spectra of this product in solution exhibited dynamic behavior, consistent with partial dissociation of one NHC ligand. Addition of the Lewis acid acceptor BH_3 (delivered in the form of $Me_2S{\cdot}BH_3$) led to the quantitative removal of one equiv. of $ImMe_2{}^iPr_2$ from **6** to reform **3** (eqn (3)). Consistent with weaker overall C_{NHC}–B interactions in **6** relative to in the HBNH adduct **3**, elongated distances of 1.684(3) and 1.660(2) Å were found in **6** (by *ca.* 0.06–0.08 Å). For comparison, the C–B distances in Bertrand's mixed NHC/CAAC complex [CAAC·B(L)H(OTf)]BPh_4 [CAAC = cyclic alkyl(amino) carbene; L = benzimidazolylidene] were slightly shorter (1.645(2) and 1.627(2) Å).[24] Coordination of two NHCs at boron in **6** resulted in substantial lengthening of the core B–N distance from a value of 1.369(3) in **3** to 1.512(2) Å, suggesting a lack of a B–N π-bond interaction in **6**. Our computational studies on **6** support this postulate with a computed B–N Wiberg bond index (WBI) of 0.85 (*vs.* 1.33 in **3**). Moreover, interaction of the Lewis base $ImMe_2{}^iPr_2$ with the LUMO in **3** populates an orbital with B–N π*-character (Fig. 2).[18]

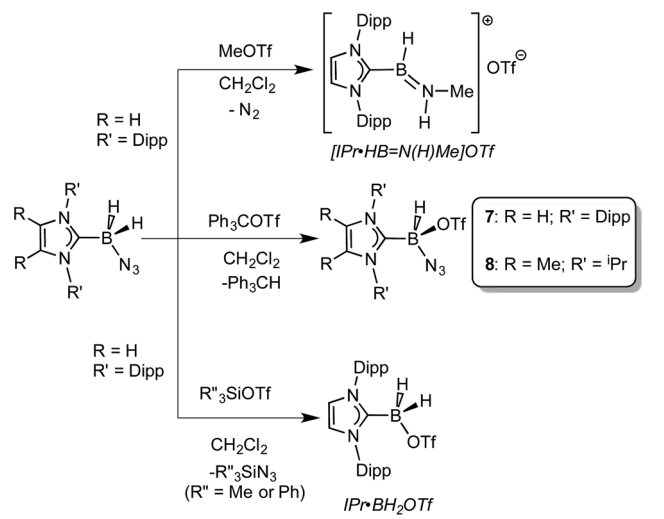


(3)

Prior work in our group showed that N_2 loss/1,2-hydride migration in $IPr{\cdot}BH_2N_3$ could also be instigated with the methylating agent MeOTf (Scheme 3), eventually leading to the formation of [IPr·HB═N(Me)H]OTf.[7a] Accordingly we wanted to expand the range of known electrophiles that could trigger this potentially general transformation. However, with Ph_3COTf and R_3SiOTf (R = Me and Ph), divergent reactivity was uncovered (Scheme 3). Specifically, when $IPr{\cdot}BH_2N_3$ or the less hindered analogue $ImMe_2{}^iPr_2{\cdot}BH_2N_3$ (**2**) was combined with Ph_3COTf in CH_2Cl_2, hydride abstraction occurred to yield triphenylmethane (Ph_3CH) and the new azido(hydrido)borane adducts IPr·B-H(OTf)N_3 (**7**) and $ImMe_2{}^iPr_2{\cdot}BH(OTf)N_3$ (**8**) in isolated yields of 95 and 66%, respectively (see Fig. 6 and S1† for the corresponding X-ray structures).[18] The ^{19}F NMR spectra of **7** and **8** show the retention of strong B-OTf contacts in solution (*e.g.* $\delta = -76.9$ ppm for **7** in C_6D_6), while intense azide IR stretches were present at 2117 and 2116 cm^{-1} for compounds **7** and **8**, respectively; these values compare well with the $\nu(N_3)$ of 2117 cm^{-1} reported for Cummins' azido borate salt $[^nBu_4N][(N_3)B(C_6F_5)_3]$.[25] Thus by simply replacing MeOTf with Ph_3COTf, H/OTf exchange chemistry can transpire in place of N_2 loss.

Yet another reaction pathway occurred when $IPr{\cdot}BH_2N_3$ was combined with the silyltriflates Me_3SiOTf and Ph_3SiOTf (Scheme 3). In each case, complete OTf/azide exchange transpired to form the corresponding silylazides (Me_3SiN_3 and Ph_3SiN_3; identified by NMR spectroscopy) and the known borane adduct $IPr{\cdot}BH_2OTf$.[12] It appears that N_3/OTf exchange is driven by the relatively strong Si–N bonds (*ca.* 355 kJ mol^{-1})[26] in relation to the C–N linkages (*ca.* 305 kJ mol^{-1}), thus azide abstraction by Ph_3C^+ sources is not as favorable. To recap, $NHC{\cdot}BH_2N_3$ shows three distinct possible reactivity pathways in the presence of electrophiles: (a) HBNH formation *via* N_2 loss/1,2-H shift; (b) hydride abstraction; (c) azide abstraction.

The accidentally uncovered high yield syntheses of the $NHC{\cdot}BH(OTf)N_3$ adducts **7** and **8** (Scheme 3) opened another possible path to boron nitride (BN). Motivated by the balanced equation ($NHC{\cdot}BH(OTf)N_3 \rightarrow BN + N_2 +$ [NHC–H]OTf; Scheme 1) we decided to investigate the reactivity of both **7** and **8** in more detail. Initially we explored the direct thermolysis of **7** and **8** in solution at temperatures approaching 100 °C (**Caution!**) but these adducts proved to be stable under these conditions. Treatment of **8** with potassium as a reducing agent (in order to



Scheme 3 Divergent reactivity of $NHC{\cdot}BH_2N_3$ adducts with MeOTf, R''_3SiOTf (R″ = Me or Ph), and Ph_3COTf.

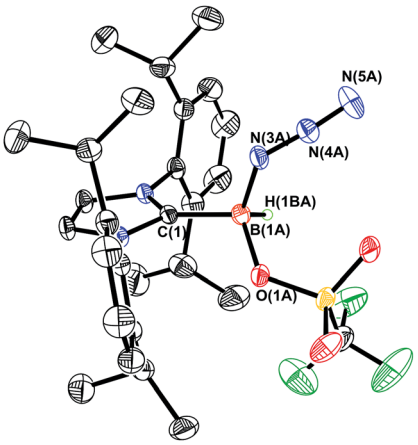


Fig. 6 Molecular structure of IPr·BHN$_3$(OTf) (**7**) with thermal ellipsoids presented at a 30% probability level. All carbon-bound hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) with parameters associated with a second molecule in the asymmetric unit listed in square brackets: C(1)–B(1A) 1.590(11) [1.652(10)], B(1A)–N(3A) 1.542(8) [1.482(12)], N(3A)–N(4A) 1.223(7) [1.211(8)], N(4A)–N(5A) 1.168(9) [1.145(11)], B(1A)–O(1A) 1.552(11) [1.562(11)]; N(3A)–N(4A)–N(5A) 175.0(11) [178.2(11)].

promote the possible reaction: **8** + K → $\frac{1}{2}$H$_2$ + N$_2$ + KOTf + BN + NHC) produced the free carbene ImMe$_2$^{i}Pr$_2$ as the only soluble product by NMR spectroscopy. Whereas the reaction of **8** with KC$_8$ produced three different carbene containing products: free carbene ImMe$_2$^{i}Pr$_2$, ImMe$_2$^{i}Pr$_2$·BH$_2$N$_3$ and ImMe$_2$^{i}Pr$_2$·BH$_3$.[27] Analysis of the insoluble fractions from both of the reactions by IR identified the presence of K[N$_3$] and K[OTf], indicating that B–N(azide) bond scission transpired in place of H$_2$ loss and boron nitride formation; in support of this reaction path, no IR bands for bulk BN could be found in the product mixture. Furthermore, the LUMO computed for the model species ImMe$_2$·B(H)N$_3$(OTf) (ImMe$_2$ = (HCNMe)$_2$C:) revealed B–N σ*-character, thus explaining the preferential B–N bond scission noted upon reduction.[18]

In order to induce 1,2-H transfer in the NHC·BHN$_3$(OTf) species **7** and **8** the donor ImMe$_2$^{i}Pr$_2$ (ref. 28) was added to form the respective bis(carbene) boronium salts [IPr(ImMe$_2$-^{i}Pr$_2$)·BH(N$_3$)]OTf (**9**) and [(ImMe$_2$^{i}Pr$_2$)$_2$·BH(N$_3$)]OTf (**10**) (eqn (4)). The spectral parameters of these salts were consistent with free OTf$^-$ counteranions (*e.g.* ^{19}F resonance at −78.1 ppm for **10** in CDCl$_3$) and the retention of boron-bound azide and hydride substituents (*e.g.* IR stretches at *ca.* 2107 and 2400 cm^{-1} for **9**). Structural confirmation of the proposed bonding environment was provided by an X-ray structure of the tetraarylfluoroborate salt [(ImMe$_2$^{i}Pr$_2$)$_2$·BH(N$_3$)]BAr^F$_4$ (**11**) (eqn (5); Fig. 7). With the goal of taking advantage of possibly higher nucleophilic character of the azide group in **11** in relation to the mono-carbene congener **8**, we combined **11** with one equivalent of BAr^F$_3$. In place of observing Lewis acid-assisted N$_2$ elimination/H-migration to give the "trapped" BNH adduct [(ImMe$_2$^{i}Pr$_2$)$_2$·B═NH·BAr^F$_3$]OTf, no reaction transpired. Likewise no conversion of **11** was noted upon heating this species with BAr^F$_3$ at 90–100 °C or under UV irradiation.

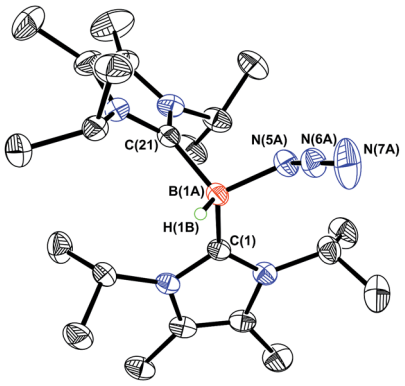
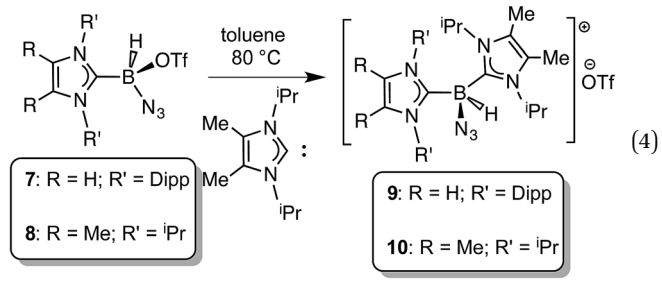
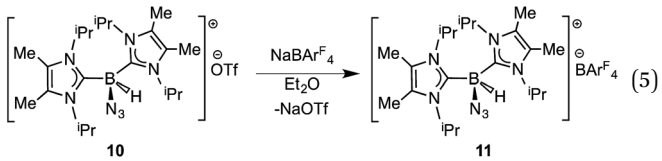


Fig. 7 Molecular structure of [(ImMe$_2$^{i}Pr$_2$)$_2$·BHN$_3$][B{C$_6$H$_3$(*m*-CF$_3$)$_2$}$_4$] (**11**) with thermal ellipsoids presented at a 30% probability level. All carbon-bound hydrogen atoms and BAr^F$_4$ anion have been omitted for clarity. Selected bond lengths (Å) and angles (deg) with parameters associated with a second molecule in the asymmetric unit listed in square brackets: C(1)–B(1A) 1.642(9) [1.71(3)], C(21)–B(1A) 1.650(9) [1.59(3)], B(1A)–N(5A) 1.553(7) [1.514(13)], N(5A)–N(6A) 1.202(6) [1.206(11)], N(6A)–N(7A) 1.147(10) [1.159(14)]; N(5A)–N(6A)–N(7A) 173.7(6) [158(2)].



(4)



(5)

Conclusion

In this article we present efficient methods to prepare complexes of HBNH and [HB(N$_3$)]$^+$, starting from readily available carbene–azidoborane adducts. In addition, this study provides key insights into the reactivity of the fundamentally important HBNH unit, an inorganic analogue of acetylene. While our detailed investigations aimed at forming bulk boron nitride (BN) from these species under mild conditions were not directly successful, we hope that this work inspires others to seek low temperature (<200 °C) routes to this inorganic wide band gap material. By suitable modification of the capping stabilizing groups, related B–N sources could be potentially used as building blocks for the rational construction of boron nitride materials and π-extended structures.[29]

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