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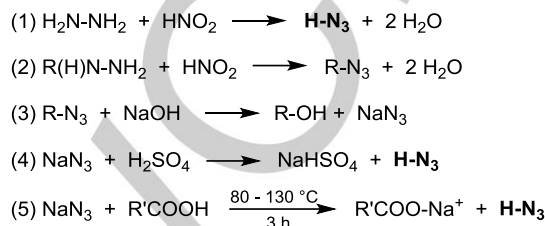
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Hydrazoic Acid and Organic Azide-Borane Adducts – Intermediates for the Formation of Aminoboranes

Kevin Bläsing,^[a] Jonas Bresien,^[a] René Labbow,^[a] Dirk Michalik,^[a,b] Axel Schulz,*^[a,b] Max Thomas,^[a] and Alexander Villinger^[a]

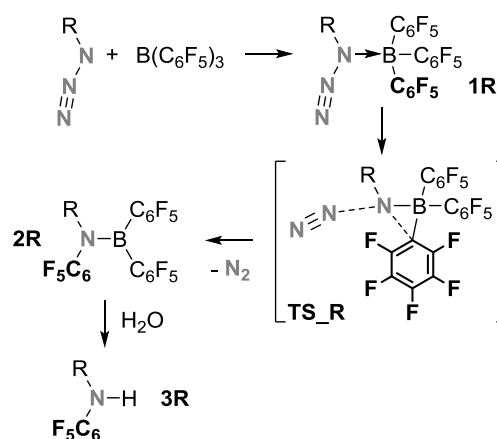
Abstract: The reaction of HN_3 with the strong Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ led to the formation of a very labile $\text{HN}_3 \cdot \text{B}(\text{C}_6\text{F}_5)_3$ adduct, which decomposed to an aminoborane, $\text{H}(\text{C}_6\text{F}_5)\text{NB}(\text{C}_6\text{F}_5)_2$, above -20°C with release of molecular nitrogen and simultaneous migration of a C_6F_5 group from boron to nitrogen. The intermediate formation of azide-borane adducts with $\text{B}(\text{C}_6\text{F}_5)_3$ was also demonstrated for a series of different organic azides, R-N_3 ($\text{R} = \text{Me}_3\text{Si} = \text{TMS}$, Ph, 3,5-(CF_3) $_2\text{C}_6\text{H}_3 = \text{Btp}$), as well as their Staudinger-like decomposition along with C_6F_5 -group migration. In accord with experiment, computations revealed highly labile azide adducts with rather small barriers to the release of nitrogen for all organic substituents except $\text{R} = \text{Me}_3\text{Si}$ (m. p. 120°C , $T_{\text{dec}} = 189^\circ\text{C}$). Hydrolysis of the aminoboranes provided C_6F_5 -substituted amines, $\text{HN}(\text{R})(\text{C}_6\text{F}_5)$, in good yields.

Published in 1857 by Griess,^[1,2] phenyl azide is probably the first synthesized azide compound, before Curtius reported on hydrogen azide (also known as hydrazoic acid or azoimide) in 1890 – a true milestone in chemistry.^[3] His azide syntheses are summarized in Scheme 1 (eq. 1 - 4). Although a series of further papers on HN_3 followed later,^[4-7] Curtius already described in great detail the properties of HN_3 and its salts (MN_3 ; $\text{M} = \text{alkali metal, Ag}$; $\text{M}'(\text{N}_3)_2$; $\text{M}' = \text{Ba, Hg, Cu, Fe}$) in his first report.^[3] He also noticed the extreme explosive properties of HN_3 and wrote: “It is only thanks to a happy coincidence that the writer of these lines was saved from harm.” At the beginning of azide chemistry, HN_3 was assumed to have a cyclic 1*H*-triazirine structure, i.e. a 3-membered N_3 ring attached to hydrogen. First hints of an acyclic HN_3 structure came from vibrational studies, until the characteristic *trans*-bent structure was established without doubt by electron diffraction in the gas phase.^[8,9] Only in 2011, the solid state structure of HN_3 proved unequivocally the presence of hydrogen-bonded tetramers of $(\text{HN}_3)_4$ in a nearly planar network of eight-membered rings featuring always *trans*-bent HN_3 molecules.^[10] The chemistry of organic and inorganic azides has been extensively studied, as summarized in a number of excellent review articles.^[6,11-19]



Scheme 1. Equations 1 - 4: Curtius's original synthesis of HN_3 ($\text{R} = \text{acyl group}$, e.g. benzoyl);^[3] eq. 5: best synthesis for pure HN_3 applied in this work $\text{R}' = \text{CH}_3\text{-(CH}_2\text{)}_{16}\text{-}$.^[20,21]

The first report on the reaction of organic azides with borane (Et_3B) was published by Brown et al. in 1971.^[22] Similarly to Scheme 2, they observed the release of molecular nitrogen and the migration of one organic substituent (ethyl group) from the boron to the remaining nitrogen atom affording an aminoborane (**2R**). Moreover, they already speculated on the in-situ formation of an azide-borane adduct (**1R**) and introduced the hydrolysis of **2R** as new route to secondary amines (**3R**). Ever since, just one additional paper by the same group was published extending the scope of this process regarding the substituents at the azide and the borane.^[23] In related work, formation of diborylamines in the thermal decomposition of diarylazidoboranes with Et_3B was described by Paetzold and Maier,^[24] while Rivard et al. were able to generate a $\text{HB}=\text{NH}$ adduct in the reaction of $\text{LB} \cdot \text{BH}_2\text{N}_3$ with a Lewis acid (LA) upon release of nitrogen ($\text{LB} = \text{Lewis base}$).^[25]



Scheme 2. Reaction of RN_3 ($\text{R} = \text{H, Me}_3\text{Si} = \text{TMS, Ph, 3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3 = \text{Btp}$; $\text{TS} = \text{transition state}$) with $\text{B}(\text{C}_6\text{F}_5)_3$ to give intermediate **1R** as well as upon release of N_2 and C_6F_5 migration aminoborane **2R**. **2R** can be hydrolysed affording amines of the type $\text{H}(\text{R})\text{N}(\text{C}_6\text{F}_5)$ (**3R**).

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To the best of our knowledge, neutral HN_3 adducts of the type HN_3 -LA have not been isolated yet. There is one report by Schmidt investigating the reaction of HN_3 with SbCl_5 ,^[26] which was proposed to form the $\text{HN}_3\cdot\text{SbCl}_5$ adduct in a first reaction step, yielding $\text{NH}_4[\text{SbCl}_6]$ and $[\text{SbCl}_4(\text{N}_3)]_2$ in a decomposition process. Closely related to HN_3 adducts are the cationic species $[\text{H}_2\text{N}_3]^+$ and $[(\text{MeSi}_3)_2\text{N}_3]^+$, which could be isolated and fully characterized as salts.^[27,28] Hydrogen-bonded $\text{N}_3\text{-H}\cdots\text{LB}$ complexes (LB = pyridine, diethyl ether, propylene oxide, acetonitrile) were studied in solution by means of ^1H NMR experiments,^[29] while complexes of the type $\text{R}_3\text{E-N}_3\text{-LA}$ (R = Ph, Me; E = Si - Sn; LA = BBr_3 , SnCl_4 , SbCl_5) were investigated by IR spectroscopy and elemental analysis.^[30] Following of our interests in azide and adduct chemistry, we were intrigued by the idea of stabilizing HN_3 by a strong Lewis acid such as $\text{B}(\text{C}_6\text{F}_5)_3$, thereby significantly increasing the acidity of HN_3 .^[28,31,32]

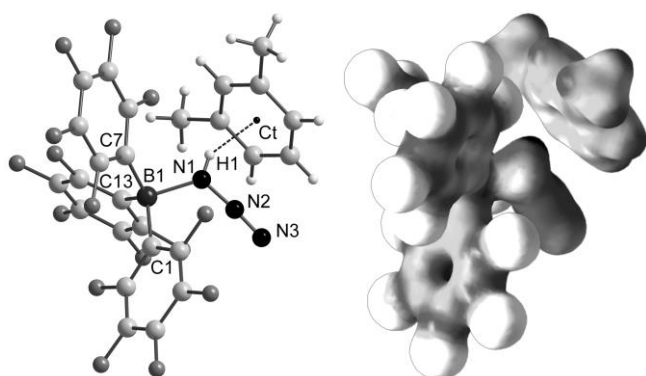


Figure 1. Left: Ball-and-stick representation of the molecular structure of **1H·xyl** in the crystal. Selected bond lengths in [Å] and angles in [°]: N1-N2 1.271(2), N2-N3 1.112(2), N1-B1 1.664(2), N1...Ct = 3.241(1); N1-N2-N3 174.2(1), B1-N1-N2 120.2(1). Right: Computed charge density isosurface plot for **1H·xyl**. The isosurface has been shaded according to the electrostatic potential ESP (white: most negative regions; black: most positive regions).

HN_3 is readily synthesized on the preparative scale by the reaction of stearic acid with sodium azide at 80 - 130 °C in the melt (Scheme 1, eq. 5).^[20,21] To avoid longer handling of highly explosive pure HN_3 , it was always condensed directly onto a frozen suspension of $\text{B}(\text{C}_6\text{F}_5)_3$ in *m*-xylene at -196 °C. After warming this reaction mixture up to -20 °C to dissolve all solids, colourless crystals suitable for single crystal X-ray diffraction were obtained by cooling down again to -40 °C. Structure elucidation proved the existence of an $\text{HN}_3\cdot\text{B}(\text{C}_6\text{F}_5)_3$ adduct (**1H**, Figure 1) that is further stabilized by η^6 type $\text{N}_3\text{-H}\cdots\text{aryl}$ hydrogen bonding with the aromatic ring system of one molecule of *m*-xylene (**1H·xyl**). **1H·xyl** is extremely sensitive and releases molecular nitrogen at once upon thermal treatment. As shown by variable temperature ^1H and ^{19}F NMR studies in solution (Figure S7, see SI), the release of molecular nitrogen occurred almost simultaneously with the formation of the adduct **1H** at temperatures > -20 °C, so that a mixture of adduct and a new BN species (**2H**, Scheme 2) was always observed (**1H**: 5.07 ppm, cf. free HN_3 : 5.43, new BN species **2H**: 6.00 ppm, see below). In situ adduct formation of **1H** was also proven by ^{11}B NMR spectroscopy which is particularly well suited to distinguish between free, three-

coordinate and the four-coordinate boron (see Table S1) found in the Lewis acid-base adduct **1H**, for which the ^{11}B resonance was significantly shifted to lower frequency with respect to free $\text{B}(\text{C}_6\text{F}_5)_3$ (**1H**: -4.2, cf. $\text{HCN}\cdot\text{B}(\text{C}_6\text{F}_5)_3$: -7.8 and free $\text{B}(\text{C}_6\text{F}_5)_3$: 59.1 ppm in CD_2Cl_2).^[31,33-37] Once the release of N_2 had stopped upon warming to 20 °C, the solvent was removed, affording aminoborane $[\text{H}(\text{C}_6\text{F}_5)\text{N-B}(\text{C}_6\text{F}_5)_2]$ (**2H**). Sublimation (at 100 °C, 10^{-3} atm) of the colourless raw material **2H** led to the formation of pure aminoborane that could be isolated in 58% yield (Figure 3 top left, Scheme 2). X-ray diffraction experiments revealed the migration of one C_6F_5 group from the boron to the nitrogen atom upon release of N_2 , in accord with solution NMR studies (see Figure S7 and Table S1). Migration of a C_6F_5 group from $\text{B}(\text{C}_6\text{F}_5)_3$ adducts was reported before, for example, in $\text{Me}_3\text{Si}(\text{Ph})\text{N}=\text{N}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ to give $\text{Me}_3\text{Si}(\text{Ph})\text{N}=\text{N}(\text{C}_6\text{F}_5)\text{-B}(\text{C}_6\text{F}_5)_2$ ^[35] or in diazomethane adducts such as $(\text{C}_6\text{F}_5)(\text{H})\text{C}=\text{N}=\text{N}\cdot\text{B}(\text{C}_6\text{F}_5)_3$ affording $(\text{C}_6\text{F}_5)_2(\text{H})\text{C-B}(\text{C}_6\text{F}_5)_2$ on N_2 release.^[38] The transfer of a C_6F_5 group from boron to another main group element was also observed in the decomposition of the adduct formed between a bis(amino)silylene and $\text{B}(\text{C}_6\text{F}_5)_3$ within one month.^[39] Such a migration is also known in transition metal chemistry when $\text{B}(\text{C}_6\text{F}_5)_3$ was used e.g. as catalyst.^[40]

As expected hydrolysis of **2H** with a water/acetonitrile mixture led to the formation of the free amine $\text{H}_2\text{N}(\text{C}_6\text{F}_5)$ (**3H**, Figure S21, Scheme 2), besides HC_6F_5 and $\text{B}(\text{OH})_3$ in good yields (yield of isolated substance = 72%, m. p. 35 °C). Interestingly, when hydrolysis is stopped shortly after addition of water by adding MgSO_4 to the mixture, the formation of a puckered six-membered ring species (**4**· CH_3CN) was observed (Figure 2), indirectly proving the intermediate formation of $\text{HO}(\text{C}_6\text{F}_5)_2$ in the first hydrolysis step. Compound **4** is probably formed by the addition of free $\text{HO-B}(\text{C}_6\text{F}_5)_2$ to the triple bond of an acetonitrile adduct of the type $\text{HO}(\text{C}_6\text{F}_5)_2\text{-N}\equiv\text{C-CH}_3$ followed by ring closure. The solvate free species has already been reported.^[41]

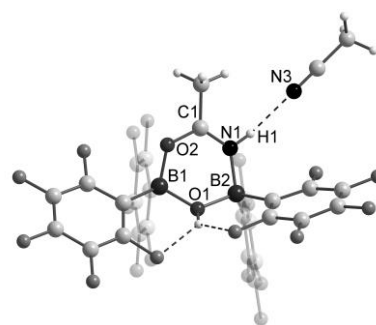


Figure 2. Ball-and-stick representation of the molecular structure of **4** in the crystal. Selected distances in [Å] and angles in [°]: B1-O2 1.486(2), B1-O1 1.525(2), B1-O1 1.528(2), B2-N1 1.552(2), C1-O2 1.305(2), C1-N1 1.298(2).

To gain further insight into the stability of azide-borane adducts, the reaction of $\text{B}(\text{C}_6\text{F}_5)_3$ with a series of different covalently bound azides R-N_3 (R = TMS, Ph, and Btp) was investigated (Table 1). Only in case of Ph-N_3 and TMS-N_3 , it was possible to isolate the adducts **1R** (Figure 4), while in case of Btp-N_3 immediate decomposition into **2Btp** and N_2 was observed (Table 1). Interestingly, **1TMS** is by far the most stable adduct of all studied species (m. p. 120 °C, $T_{\text{dec.}}$ = 189 °C, vide infra), all

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other are only of fleeting existence and tend to release N_2 even in the solid state and at low temperature. Hydrolysis of aminoboranes **2R** led to the desired secondary amines of type $HN(C_6F_5)R$, except for hydrolysis of **2TMS** which led to the formation of an unidentified product mixture. Different syntheses, bonding and application of aminoboranes in general have already been reported in a series of publications.^[42–47]

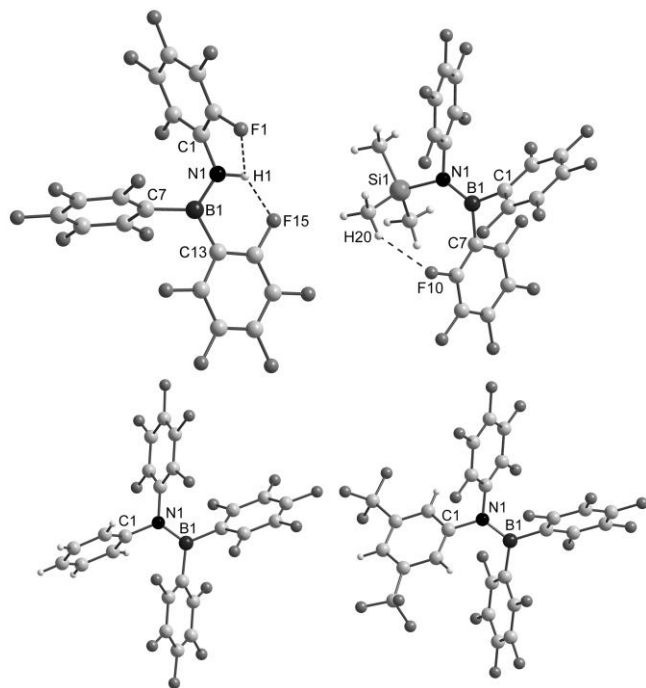


Figure 3. Ball-and-stick representation of the molecular structure of **2H** (top left), **2TMS** (top right), **2Ph** (bottom left) and **2Btp** (bottom right) in the crystal. Selected distances in [Å] and angles in [°]: **2H**: N1-B1 1.393(2); N1-B1-C7 121.2(1), B1-N1-C1 126.4(1); **2TMS**: N1-B1 1.398(2), N1-B1-C1 121.4(1), N1-B1-C7 122.6(1). **2Ph**: N1-B1 1.395(3), C1-B1-N1 121.2(1); **2Btp**: N1-B1 1.408(2), C1-B1-N1 123.4(1).

Both compounds **1H-xyl** and **2H** crystallized in the triclinic space group $P1$, while **3H** crystallized in the monoclinic space group Cc . Structure elucidation for **1H-xyl** unequivocally revealed the formation of a 1,1-azide-borane adduct, which is, according to computations (vide infra), favored by 13.6 kcal/mol over the 1,3-substituted $(C_6F_5)_3B-NNN-H$ species. This adduct could be regarded as a formal aminodiazonium derivative, considering that the N1-N2 bond length (1.271(2) Å) is significantly longer than the N2-N3 bond (1.112(2) Å), which is almost in the range of a triple bond (cf. $\Sigma r_{cov}(N\equiv N) = 1.08$ Å).^[48] The *trans*-bent (170.7°) HN_3 molecule is linked to the $B(C_6F_5)_3$ group by a strong B–N donor acceptor bond (1.664(2) Å; cf. 1.616(3) Å in $CH_3CN \cdot B(C_6F_5)_3$).^[49] Similar structural features were found for **1TMS** and **1Ph** (Figure 4 and see SI). The structure of **1H-xyl** consists of separated $xyl \cdots NNN(H)-B(C_6F_5)_3$ units with no significant interactions between them. The most prominent structural feature is the η^6 -coordinating *m*-xylene molecule as shown in Figure 1 ($d(Ct \cdots H1) = 2.50(2)$ Å, Ct = centroid; cf. 2.41 in $C_6H_6 \cdots HCN(g)$).^[50,51] A closer look reveals that the aryl ring is strongly tilted (Ct-H1-N1 147.3°) and there are three shorter (2.611 - 2.752 Å) and three longer $H1 \cdots C_{aryl}$ distances (2.971 - 3.075 Å; cf. $\Sigma r_{vdW}(H \cdots C) = 2.90$ Å),^[52]

which is in agreement with computed structural data (see SI). Since the potential for the Ct-H-N angle is very flat, lattice effects have a great influence on this structural parameter. A similar situation was found for a series of $aryl \cdots HCN-B(C_6F_5)_3$ adducts.^[31] The electrostatic potential (ESP) mapped onto the electron density of **1H-xyl** nicely illustrates the electrostatically favorable arrangement of the *m*-xylene molecule, allowing strong van der Waals interaction between the $H^{\delta+}(-N_3)$ center and C_{aryl} atoms (Figure 1 right).

Bulky **1TMS** and **1Ph** also exhibit 1,1-adducts as shown in Figure 4 with B–N bond lengths (1.648(2) and 1.678(2) Å) in the same range found for **1H** (1.664(2) Å). While **1Ph** is also *trans*-bent with respect to the Ph- N_3 moiety ($\angle(R-N-N-N) = 173.4^\circ$), a *cis*-bent structure was found for the Me_3Si-N_3 molecule (24.8°) in **1TMS**. Probably the most interesting structural features of **2H** are the relatively short B–N bond with 1.393(2) Å (cf. **2TMS** 1.398(2), **2Ph** 1.395(3), and **2Btp** 1.408(2); Figure 3) and two intramolecular N–H \cdots F- C_6F_4 hydrogen bonds (Figure 3 top left).

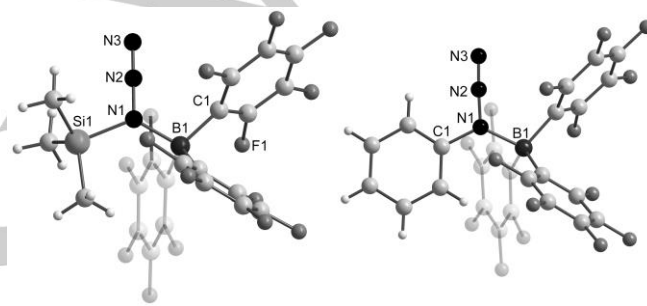


Figure 4. Ball-and-stick representation of the molecular structure of **1TMS** (left) and **1Ph** (right) in the crystal. Selected distances in [Å] and angles in [°]: **1TMS**: Si1-N1 1.874(1), B1-N1 1.648(2), N1-N2 1.259(1), N2-N3 1.117(2); N1-N2-N3 179.6(1). **1Ph**: B1-N1 1.678(2), N1-N2 1.266(2), N2-N3 1.118(2); N1-N2-N3 177.4(1).

Table 1. Melting points (in °C) for **1R** and **2R** along with yields (η) for the generation of **2R** (in %). Computed thermodynamic data ($\Delta_R G_{298}^\ominus$ in kcal/mol) for the formation of **1R** and **2R** as well as the activation enthalpy for the N_2 release for **1R** \rightarrow **TS_R** \rightarrow **2R** and the isomerisation from the 1,1- to the 1,3-isomer of **1R** (in kcal/mol, Scheme 2) at the DLPNO-CCSD(T)/def2-TZVPP//PBE0-D3BJ/def2-TZVP level. The overall charge transfer Q_{CT} (e) from the azide to the $B(C_6F_5)_3$.

	H	TMS	Ph	Btp
m. p. 1R	>–40 ^[a,d]	120 ^[d]	>–40 ^[a,d]	[b,c]
m. p. 2R	105 ^[d]	131 ^[d]	126 ^[d]	158 ^[d]
η (2R)	58	70	55	43
A + B \rightarrow 1R ^[e]	–4.3	–4.4	–3.0	4.3
1R \rightarrow 2R	–87.1	–78.4	–88.1	–93.1
1R \rightarrow TS_R	21.6	36.4	22.2	19.1
1,1 \rightarrow 1,3	13.6	8.7	14.2	12.0
Q_{CT}	0.366	0.379	0.355	0.346

^[a] There was no clear decomposition point, since also below –40°C always a small release of N_2 was observed even in the solid state. However, above –40°C a rather fast decomposition was detected. ^[b] Species could not be isolated due to immediate decomposition into **2R** and N_2 . ^[c] Azo coupling as side reaction was observed; ^[d] Compound was isolated and characterized by single crystal structure elucidation (see SI). ^[e] A = azide, B = borane.

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To better understand the formation and decay of adduct **1H**, calculations were performed at the DLPNO-CCSD(T)/def2-TZVPP//PBE0-D3BJ/def2-TZVP level of theory (Table 1, see SI). The formation of **1H** (1,1-isomer) is a slightly exergonic process (−4.3 kcal/mol, Scheme 2), while the release of N₂, which leads to **2H**, is strongly exergonic (−87.1 kcal/mol). The activation barrier to be overcome is 21.6 kcal/mol in accord with experimental observation. The structure of the transition state (**TS_H**, Scheme 2) is characterized by elongated N1-N2 and B1-C1 bonds. The imaginary frequency describes a movement of the N2-N3 group away from N1 and a movement of N1 towards C1. Thus, the formation of N₂ and the migration of one C₆F₅ group from the boron atom to the N1 atom is a concerted mechanism.

The 1,1-isomers of all adducts are significantly more stable than the 1,3-isomers ($\Delta_{\text{rel}}G^\circ$ between 8.7 and 14.3 kcal/mol, Table 1). The calculated activation barriers for the release of molecular nitrogen in **1R** increase along the series Btp (19.1) < H (21.6) < Ph (22.2) < TMS (36.7 kcal/mol) in agreement with experiment, that is, **1TMS** is most stable and **1Btp** and **1H** are most labile. Consistent with this sequence, the calculated charge transfer from azide to borane increases exactly along this series (cf. **1Btp**: 0.346 vs. **1TMS**: 0.379 e), i.e. higher charge transfer leads to more stable azide-borane adducts **1R**. The release of molecular nitrogen, yielding **2R**, is a highly exothermic process for all considered **1R** species (**1TMS**: −78.4 - **1Btp**: −93.1 kcal/mol). It is worthy to note that the computed Gibbs energy for the solvate formation **1H** + **xyl** → **1H·xyl** is 0.2 kcal/mol and therefore an equilibrium. As pointed out before, the adduct formation of **1H** is associated with a charge transfer of 0.37 e from the HN₃ to the B(C₆F₅)₃ molecule. This, in turn, results in a significantly increased Brønsted acidity of **1H** ($pK_{\text{a,H}_2\text{O}} = -7.3$, $pK_{\text{a,MeCN}} = 3.7$, see SI Table S20) compared to “naked” HN₃ ($pK_{\text{a,H}_2\text{O}} = 6.8$, $pK_{\text{a,MeCN}} = 18.4$), now being even more acidic than HCl ($pK_{\text{a,H}_2\text{O}} = -3.9$, $pK_{\text{a,MeCN}} = 7.2$, see SI), an effect that has already been reported for water and other weak acids by Beckmann et al.^[53]

In summary, we succeeded in isolating highly labile azide adducts such as HN₃-B(C₆F₅)₃. Other organic azide adducts were also shown to be only of fleeting existence. These intermediates, in turn, readily release N₂ in a strongly exergonic process, parallel to the migration of a C₆F₅ group from boron to the remaining nitrogen atom, affording aminoboranes of the type R(C₆F₅)N-B(C₆F₅)₂. Hydrolysis of these aminoboranes leads to difficult-to-access H(R)N(C₆F₅) amines. The azide-borane reaction (ABR) resembles the Staudinger reaction,^[54–56] however, in the Staudinger reaction, a phosphorus(III) is oxidized to a phosphorus(V) species with simultaneous P-N bond formation and N₂ release, while in the ABR the valency of boron is maintained, since a C₆F₅ substituent migrates at the same time to the nitrogen atom. In contrast to the ABR, the Staudinger reaction begins with the nucleophilic attack of the phosphane (e.g. Ph₃P) on the terminal N atom of the covalently bound azide, RN₃. The resulting phosphazide now cyclizes to a transient 4-membered ring, yielding a phosphazene, R₃P=NR', by releasing molecular nitrogen.^[57–59] On the contrary, the ABR begins with 1,1-azide-borane-adduct formation, from which N₂ is liberated, featuring an acyclic transition state (Scheme 2 **TS_R**), however with an already shortened N⋯C₆F₅ distance (ca. 2.1 Å) and an elongated N1-N2

bond length (ca. 1.75 Å), in a concerted mechanism. With this work, we want to close a gap in modern boron-nitrogen chemistry, which maybe began with the synthesis of borazole by Stock and Pohland^[60] followed by the studies of boron azides by Paetzold^[61,62] and later by Klapötke et al.,^[14,63–65] and culminated with metal-free N₂ fixation in a borylene dinitrogen compound by the Braunschweig group last year.^[66]

Experimental Section

Caution! HN₃ is highly toxic and can decompose explosively under various conditions! Appropriate safety precautions (protection shield, face shield, ear protection, Kevlar gloves, low temperatures, small amounts) should be taken.

Experimental and computational details including all spectra and ORTEP representations of all experimentally studied species are given in the supporting information.

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Keywords: Adduct • Azide • Aminoborane • Amine synthesis • Hydrazoic acid

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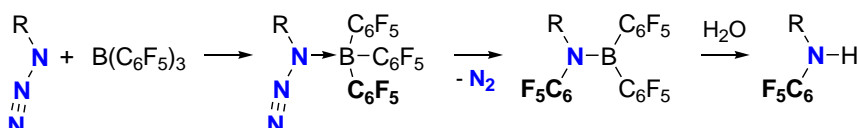
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Max Thomas, and Alexander Villingier

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**Hydrazoic Acid and Organic Azide
Borane Adducts – Intermediates for
the Formation of Aminoboranes**

Boron on a Staudinger trip. Pure HN_3 reacts with the strong Lewis acid $\text{B(C}_6\text{F}_5)_3$ to give a highly labile $\text{HN}_3 \cdot \text{B(C}_6\text{F}_5)_3$ adduct, which readily decomposes above -20°C to an aminoborane, $\text{H(C}_6\text{F}_5\text{)NB(C}_6\text{F}_5)_2$, and N_2 . This Staudinger-like reaction, which involves a C_6F_5 group migration from boron to the attached nitrogen, could be transferred to a variety of organic azides, RN_3 , enabling the synthesis of C_6F_5 -substituted aminoboranes and by hydrolysis amines of the type $\text{H(R)N(C}_6\text{F}_5)$.