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Inherent Stability Limits of Intramolecular Boron Nitrogen Lewis Acid–Base Pairs

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Abstract: The reaction of $(C_6F_5)_2BH$ (**1**) with *N*,*N*-dimethylallylamine (**2**), *N*,*N*-diethylallylamine (**3**) and 1-allylpiperidine (**4**) afforded the five-membered ring systems $(C_6F_5)_2B(CH_2)_3NR_2$ (R = Me (**5**), Et (**6**)) and $(C_6F_5)_2B(CH_2)_3N(CH_2)_5$ (**7**) with an intramolecular dative B−N bond. A different product was obtained from the reaction of $(C_6F_5)_2BH$ (**1**) with *N*,*N*-diisopropylallylamine (**8**), which afforded the seven-membered ring system $(C_6F_5)_2B(CH_2)_3N(i\mathrm{Pr})CH(Me)CH_2$ (**9**) under extrusion of dihydrogen. All compounds were characterised by elemental analysis, NMR spectroscopy and single-crystal X-ray diffraction experiments. Density functional theory (DFT) studies were performed to rationalise the different reaction mechanism for the formation of products **6** and **9**. The bonding situation of compound **9** was analysed in terms of its electron density topology to describe the delocalised nature of a borane–enamine adduct.

Keywords: boron · heterocycles · hydroboration · Lewis acids · nitrogen

Introduction

Initiated by the establishment of the concept of frustrated Lewis pairs (FLP),[1] recent developments have been directed towards molecules that contain Lewis acidic and basic sites at a distance, which establishes an electronic push–pull situation for substrates.[2] This is an intermolecular variant of the classical FLP concept, which requires steric overcrowding at the Lewis acidic and basic sites and prevents direct adduct formation. Thus an unquenched reaction potential is left to be exerted on substrates small enough to bind to both sites of contrasting reactivity. Particular interest was given to systems that reversibly activate dihydrogen,[3] because this sets the scene for metal-free hydrogenation catalysis. Due to toxicity concerns, the need to synthesise products free of traces of transition metals is of high interest to the pharmaceutical industry.[4] Whereas the first FLP systems tested were composed of separate Lewis acid and base molecules, later investigations also turned to molecules with Lewis acidic and basic sites that were connected by a covalent linker. Important contributions to this chemistry stem from Erker et al., who investigated cyclic, intramolecular ethylene-linked P−B species capable of easily activating dihydrogen.[5] Likewise, a linked boron−nitrogen system deduced from tetramethylpiperidine was applied by Rieger et al. for the catalytic hydrogenation of imines, enamines and silyl enol ethers.[6]

Recently, Lammertsma and co-workers presented an article on pre-organised FLPs in which $R_2PCH_2BR'_2$ systems—including fluorine-free $t\mathrm{Bu}_2PCH_2BPh_2$—with geminal donor and acceptor sites were shown to be capable of dihydrogen activation. The latter was attributed to an optimised alignment of the acceptor and donor site.[7]

We have recently investigated a BCN system previously established by Bürger and Pawelke et al.[8] with highly electronegative substituents, $(F_3C)_2BCH(SiMe_3)NMe_2$, but found that it did not activate dihydrogen. This is probably due to the fact that this compound as well as $(F_3C)_2BCH_2NMe_2$ adopts the form of three-membered BCN rings in solution and the solid state, with a B−N bond being too strong despite the ring strain involved in these systems. However, they show a highly unusual electron-density distribution. According to Bader's quantum theory of atoms in molecules (QTAIM),[9] its charge density topology is that of an open-chain system, as no bond critical point for the N−B interaction is found and accordingly no ring critical point. In this sense the system behaves similarly to compounds with SiON (X_3Si-O-NR_2),[10] SnON[11] and SiNN units (X_3Si-N(R′)-NR_2,[12] which show short Si−N/Sn−N distances and small Si-O-N, Sn-O-N and Si-N-N angles, respectively. We have studied such compounds intensely in the course of our investigations on the α effect in silicon chemistry.[13] The most extreme examples in this context are $F_3CSiF_2ONMe_2$ and $F_3SiONMe_2$. Both show neither a bond path nor an Si−N bond-critical point in the topology analysis of the electron

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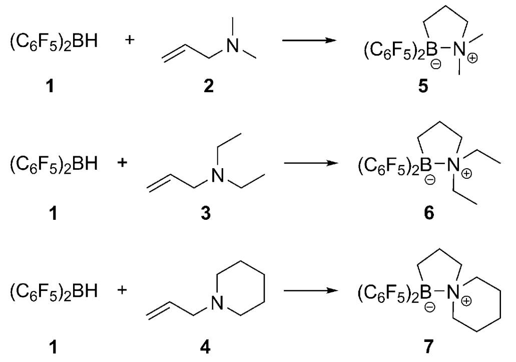
density according to QTAIM theory despite the observed short Si–N distances in the range of the sum of the covalent radii. By contrast, for the systems with SiCN and SiCO units (e.g., $F_3SiCH_2NMe_2$ or $F_3SiCH_2OCH_3$) no significant donor–acceptor interactions were found.[14]

Due to the fact that the chemistry of pentafluorophenyl[15] (C_6F_5)-substituted boron compounds is well developed and their easier accessibility relative to analogous trifluoromethyl (CF_3) compounds,[16] we set out to explore the syntheses and properties of compounds that contain $(C_6F_5)_2B$ and NR_2 groups linked by a C_3 chain. In this contribution we report the syntheses of five-membered ring systems with pentafluorophenyl-substituted boron atoms and varying alkyl groups at the nitrogen atom that yield the intended effects on the charge distribution in the B–N region of interest.

Results and Discussion

Reactions of $(C_6F_5)_2BH$ with allylamines with small N substituents: Piers' borane, $(C_6F_5)_2BH$ (**1**),[17] was treated with *N*,*N*-dimethylallylamine (**2**), *N*,*N*-diethylallylamine (**3**)[18] and 1-allylpiperidine (**4**), respectively, in toluene at 100 °C. Clean regioselective hydroboration resulted in the product **5**, **6** and **7** in 77–80 % yield as colourless powders (Scheme 1).



Scheme 1. Reactions of $(C_6F_5)_2BH$ (**1**) with allylamines **2**, **3** and **4**.

The new compounds were characterised by elemental analyses, single-crystal X-ray diffraction and NMR spectroscopy of the nuclei ^1H, ^{11}B, ^{13}C and ^{19}F. The ^1H NMR spectrum of compound **5** shows three multiplets at $\delta = 1.48$, 1.55 and 1.94 ppm caused by the six protons of the propylene bridge. The corresponding signals in the ^{13}C NMR spectrum are observed at $\delta = 66.9$, 20.0 and 17.5 ppm, the latter indicating by its broadness the formation of a B–C bond. In the ^{11}B NMR spectrum of **5** a single resonance at $\delta = 0.2$ ppm ($\nu_{1/2} = 97$ Hz) is observed. The ^{19}F NMR signals of the C_6F_5 groups are detected at $\delta = -128.6$ (o-C_6F_5), -157.3 (p-C_6F_5) and -163.7 ppm (m-C_6F_5). The small separation of the p- and m-C_6F_5 ^{19}F resonances is indicative of the presence of a tetra-coordinate boron atom.[19]

The ^1H and ^{13}C NMR spectra of compounds **6** and **7** exhibited characteristics similar to those of **5**. In the ^{11}B NMR spectra of **6** and **7** resonances are observed at $\delta = 2.2$ ($\nu_{1/2} = 141$ Hz) and 1.64 ppm ($\nu_{1/2} = 126$ Hz), respectively. The ^{19}F NMR spectra show signals similar to those of compound **5** with a $\Delta\delta[(m\text{-F})-(p\text{-F})]$ separation of 6.4 ppm for both compounds. The described NMR spectroscopic data are consistent with five-membered ring structures of **5**, **6** and **7**, that is, propylene-bridged B/N ring systems with dative B–N bonds. This was subsequently confirmed by X-ray diffraction.

Single crystals of **5**, **6** and **7** were obtained from concentrated hexane solutions. The ring structures of molecules of **5** and **7** are very similar and their parameters almost indistinguishable within experimental error. The structures of **5**, **6** and **7** are displayed in Figure 1, Figure 2, and Figure 3; selected structural parameters are listed in their captions.

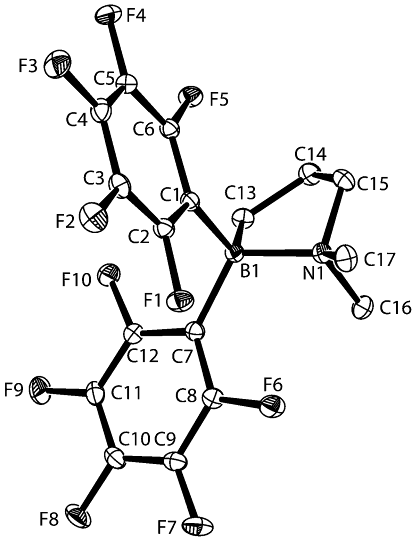


Figure 1. Molecular structure of **5** in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–B1 1.672(1), B1–C13 1.637(1), C13–C14 1.552(1), C14–C15 1.525(1), N1–C15 1.507(1), N1–C16 1.502(1), N1–C17 1.493(1), B1–C1 1.659(1), B1–C7 1.649(1); C17-N1-C16 108.6(1), C17-N1-C15 107.9(1), C16-N1-C15 107.4(1), C17-N1-B1 119.1(1), C16-N1-B1 112.3(1), C15-N1-B1 100.7(1), C13-B1-C7 111.2(1), C13-B1-C1 115.3(1), C7-B1-C1 108.4(1), C13-B1-N1 98.0(1), C7-B1-N1 116.5(1), C1-B1-N1 107.4(1), C14-C13-B1 107.0(1), C15-C14-C13 105.9(1), N1-C15-C14 106.9(1).

In the crystal structures of **5**, **6** and **7** the five-membered rings exhibit the typical envelope conformations. The three carbon atoms C13, C14 and C15 and the boron atom define an almost perfect plane, whereas the nitrogen atom is placed above this plane. The torsion angle C15-C14-C13-B1 is 1.1° for **5**, 0.2° for **6** and −1.5° for **7**. The dihedral angles between the (mean) planes B1-C13-C14-C15 and B1-N1-C15 measure 135.2 (**5**), 134.8 (**6**) and 133.4° (**7**). The lengths of the bonds created by the strong Lewis acidic boron atoms and the nitrogen atoms for compounds **5**–**7** are 1.672(2), 1.685(2) and 1.676(2) Å, respectively. This can be interpret-

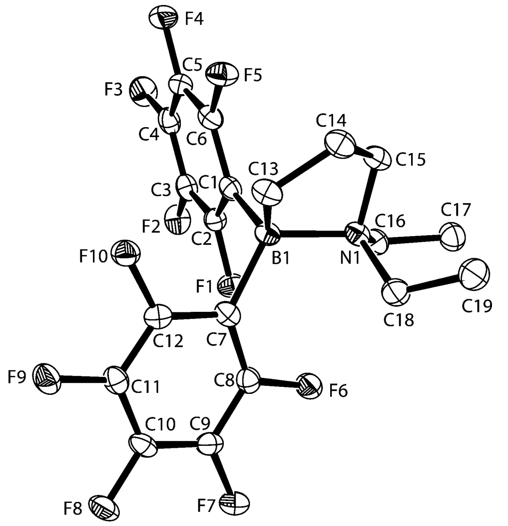


Figure 2. Molecular structure of **6** in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–B1 1.685(2), B1–C13 1.636(2), C13–C14 1.550(2), C14–C15 1.518(2), N1–C15 1.508(2), N1–C16 1.512(2), N1–C18 1.525(2), B1–C1 1.657(3), B1–C7 1.655(2), C16–C17 1.512(2), C18–C19 1.531(2); C15-N1-C16 109.3(1), C15-N1-C18 110.9(1), C16-N1-C18 111.2(1), C15-N1-B1 99.9(1), C16-N1-B1 115.1(1), C18-N1-B1 110.0(1), C13-B1-C7 110.6(1), C13-B1-C1 115.4(1), C7-B1-C1 107.9(1), C13-B1-N1 98.3(1), C7-B1-N1 116.6(1), C1-B1-N1 108.2(1), C14-C13-B1 106.5(1), C15-C14-C13 106.4(1), N1-C15-C14 106.8(1), N1-C16-C17 116.5(1), N1-C18-C19 118.0(2).

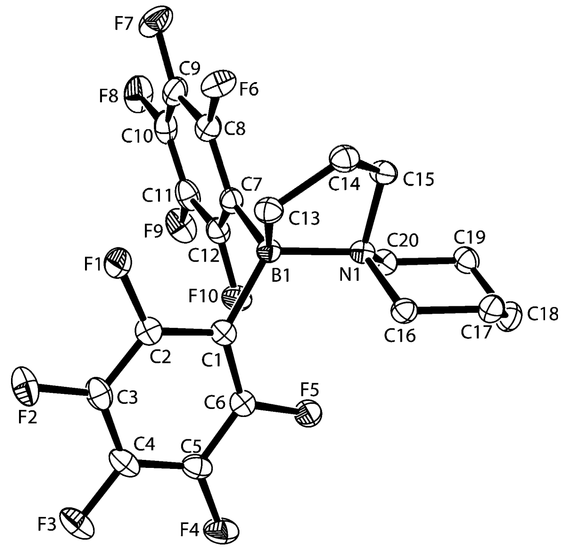


Figure 3. Molecular structure of **7** in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–B1 1.676(2), B1–C13 1.634(2), C13–C14 1.549(2), C14–C15 1.528(2), C16–C17 1.552(2), C17–C18 1.526(2), C18–C19 1.527(2), C19–C20 1.524(2), N1–C15 1.515(2), N1–C16 1.518(2), N1–C20 1.505(2), B1–C1 1.651(2), B1–C7 1.657(2); C20-N1-C15 110.3(1), C20-N1-C16 109.21, C15-N1-C16 108.9(2), C20-N1-B1 116.3(1), C15-N1-B1 99.7(1), C16-N1-B1 111.9(1), C13-B1-C7 115.5(1), C13-B1-C1 110.3(1), C7-B1-C1 107.3(1), C13-B1-N1 97.7(1), C7-B1-N1 108.0(1), C1-B1-N1 118.1(1), C14-C13-B1 106.9(1), C15-C14-C13 105.8(1), N1-C15-C14 106.4(1), N1-C16-C17 113.4(1), N1-C20-C19 113.5(1), C16-C17-C18 111.3(1), C17-C18-C1 110.8(1), C18-C19-C20 111.6(1).

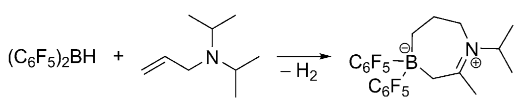
ed as a strong dative bond, especially considering the ring strain of the five-membered ring system. Due to the increase of Lewis acidity of the boron atom by C_6F_5 substituents, the B–N bond lengths in these compounds are shorter compared to the known related ring system [9-(2-dimethylaminomethyl)phenyl]-9-borabicyclo[3.3.1]nonane (1.746(3) Å)[20] and similar to $(CH_2)_5B(CH_2)_3NMe_2$ (1.682(4) Å).[21] The B–N bond lengths in compounds **5**–**7** are nearly the same as in the comparable five-membered BC_3N ring of $(C_6F_5)_2BC_6H_4(Me)NMe_2$ with 1.666(3) Å.[22]

The endocyclic B–C bond lengths (B1–C13) have values of 1.637(2) (**5**), 1.636(2) (**6**) and 1.634(2) Å (**7**). This is in the range of related five-membered ring systems with a C_6F_5-substituted boron atom (1.646 Å in $(C_6F_5)_2B(CH_2)_3P(tBu)_2$).[2b]

The coordination geometry around the boron and nitrogen atoms in compounds **5**, **6** and **7** is distorted tetrahedral. The angles around the boron atom lie in the ranges 98.0(1)–116.5(1)° for **5**, 98.3(2)–116.6(2)° for **6** and 97.7(1)–118.1(1)° for **7**. The values around the nitrogen atom are in the ranges 100.7(1)–119.1(1)° for **5**, 99.9(1)–115.1(1)° for **6** and 99.7(1)–116.3(1)° for **7**. For a detailed comparison of structural parameter values, refer to Figures 1–3.

It should be mentioned that we have attempted reactions of **5**, **6** and **7** with dihydrogen to evaluate their potential in the sense of frustrated Lewis base pairs (although a "frustration" is not present in the ring structures determined in the solid state); however, we did not observe such reactions.

Reactions of $(C_6F_5)_2BH$ with *N,N*-diisopropylallylamine: The reactions described above of $(C_6F_5)_2BH$ with allylamines with different nitrogen alkyl substituents led to the ring systems **5**, **6** and **7** with dative B–N bonds. By contrast, reaction of $(C_6F_5)_2BH$ (**1**) with *N,N*-diisopropylallylamine (**8**)[18] at 100 °C in toluene afforded a product with a seven-membered ring system under extrusion of hydrogen (Scheme 2). The product could be isolated as a colourless powder in 75 % yield.



1 **8** **9**

Scheme 2. Reaction of $(C_6F_5)_2BH$ (**1**) with *N,N*-diisopropylallylamine (**8**).

Compound **9** was characterised by elemental analyses, by single-crystal X-ray diffraction and by ^1H, ^{11}B, ^{13}C and ^{19}F NMR spectroscopy. The ^1H NMR spectrum of **9** shows three broad signals with the same integral at $\delta = 2.86$, 1.61 and 1.34 ppm. They can be assigned to the six protons of the propylene bridge. The B-CH_2-CH(Me) moiety is observed as a broad signal at $\delta = 2.90$ ppm. The signals at $\delta = 3.02$ (sept) and 0.41 ppm (d) result from the isopropyl group. A singlet for the methyl group is observed at $\delta = 1.06$ ppm. Corresponding signals can be detected in the ^{13}C NMR spectrum of **9**. Due to the quadrupole broadening by the boron nuclei, both aliphatic carbon atoms directly bonded to boron give broad signals at $\delta = 42.7$ and 24.3 ppm, respectively. The resonance for the quaternary carbon atom is detected at $\delta = 197.4$ ppm. $^1H/^1H$-COSY, $^1H/^{13}C$-HMQC and $^1H/^{13}C$-HMBC data confirm this assignment. The ^{11}B NMR spectroscopic data show a single resonance at $\delta = -14.4$ ppm ($\nu_{1/2} = 52$ Hz). ^{19}F NMR spectroscopic signals can be observed at $\delta = -133.5$ (*o*-), -161.0 (*p*-) and -164.8 (*m*-C_6F_5). The small $\Delta\delta[(m\text{-F})-(p\text{-F})]$ separation of approximately $\Delta\delta = 4$ ppm is indicative of a tetra-coordinate boron atom.

The molecular structure of compound **9** was determined by single-crystal X-ray crystallography (single crystals were obtained from a concentrated solution in toluene). Compound **9** crystallises in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The structure is displayed in Figure 4; selected structural parameters are listed in the caption.

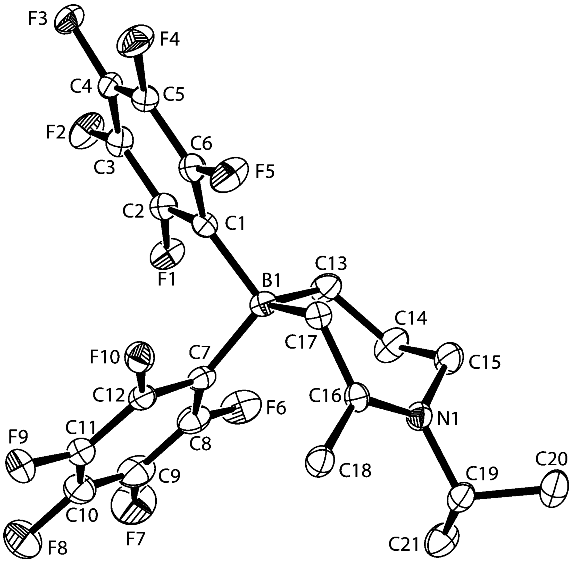
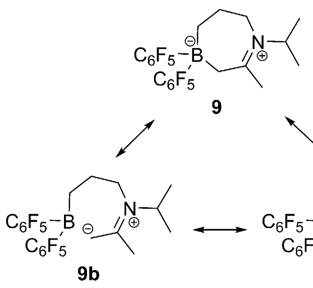


Figure 4. Molecular structure of **9** in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C16 1.304(2), N1–C15 1.486(2), N1–C19 1.496(2), B1–C13 1.630(2), B1–C17 1.689(2), C13–C14 1.537(2), C14–C15 1.522(2), C16–C17 1.467(2), C16–C18 1.499(2), B1–C1 1.665(2), B1–C7 1.661(2); C16-N1-C15 120.6(2), C16-N1-C19 123.3(1), C15-N1-C19 116.1(1), C13-B1-C7 117.2(1), C13-B1-C1 106.7(1), C7-B1-C1 103.9(1), C13-B1-C17 106.6(1), C7-B1-C17 110.8(1), C1-B1-C17 111.7(1), C14-C13-B1 118.4(1), C15-C14-C13 115.5(1), N1-C15-C14 113.4(1), N1-C16-C17 122.4(1), N1-C16-C18 120.5(1), C17-C16-C18 117.1(1), C16-C17-B1 113.0(1), N1-C19-C21 110.3(1), N1-C19-C20 111.1(1), C21-C19-C20 113.0(1).

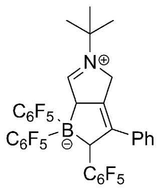
Three meaningful mesomeric structures have to be taken into consideration for compound **9**: besides the seven-membered ring system, two open forms—an enamine and an iminium ion form—can contribute to bonding in the Lewis structure formula picture.

The structure exhibits a seven-membered *cyclo*-BC_3NC_2 ring system. No structure of another heterocyclic system of this ring size that contains one boron and one nitrogen atom has been reported in the literature. However, Stephan and co-workers described a system with a related N=C-C-B moiety, [*t*BuNC$_4$H$_3$(3-PhC=C(H)(C$_6$F$_5$)B(C$_6$F$_5$)$_2$)] (**10**) (Scheme 4).[23]

The B1–C13 bond of compound **9** at 1.630(2) Å is of similar length to the boron carbon bond in the five-membered ring systems **5**–**7**. The B1–C17 distance, which is the one described as partially bonded in the mesomeric Lewis formulae in Scheme 3, is nearly 0.06 Å longer (1.688(2) Å) than the latter B–C bonds and also longer than the B–C bond of Stephan's compound **10** (1.671(5) Å).[23] Due to this fact, this boron–carbon bond can be assigned a (partial) dative character. The coordination around the boron atom is distorted tetrahedral with the largest angle between C13-B1-C7 at 117.2(1)°. Consequently, the angle C13-B1-C17 adopts a smaller value of 106.6(1)°.



Scheme 3. Mesomeric structures of product **9**.



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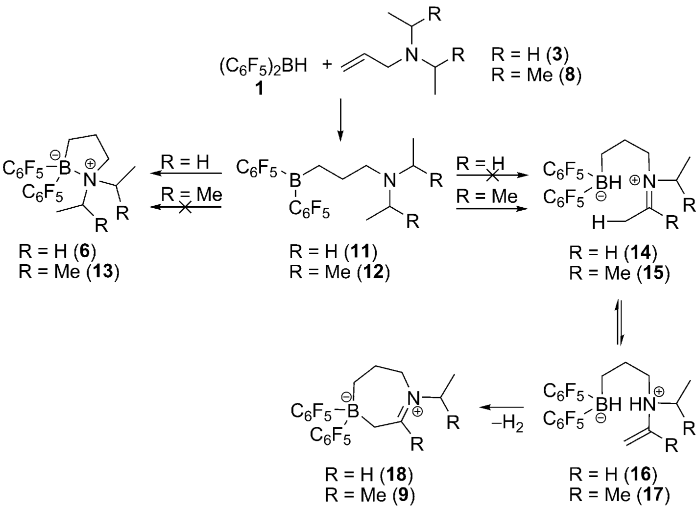
Scheme 4. *t*BuNC$_4$H$_3$[3-PhC=C(H)(C$_6$F$_5$)B(C$_6$F$_5$)$_2$] (**10**) with a N=C-C-B moiety.[23]

The N1–C15 and N1–C19 bonds exhibit lengths of 1.486(2) and 1.495(2) Å, respectively. This is slightly larger than normal N–C bonds (1.47 Å).[24] By contrast, the N1–C16 bond has a length of 1.304(2) Å and is therefore slightly longer than a nitrogen–carbon double bond (1.22 Å).[24] It is also longer than the corresponding N–C bond in **10** (1.295(4) Å).[23] The C16–C17 distance (1.467(2) Å) is remarkably shorter than the carbon single bonds of the propylene bridge, C13–C14 at 1.537(2) and C14–C15 at 1.522(2) Å, which represent standard C–C bond lengths (1.54 Å).[24] However, C16–C17 is also longer than a typical double bond (1.33 Å).[24] The related carbon C–C bond in **10** has a length of 1.470(5) Å.[23] The mesomeric enamine structure contribution to the bonding situation of **9** explains the length of the single bond C16–C17 and the notably shortened length of the C16–C18 bond with a value of 1.499(2) Å is a result of the almost planar coordination geometry of C16. Consequently, the nitrogen atom features a nearly perfect trigonal planar coordination with bond angles of 120.6(1) (C16-N1-C15), 123.3(1)° (C16-N1-C19) and 116.1(1)° (C15-N1-C19).

Proposed mechanism of formation for 6 and 9: It is obvious that the first step of the reactions of *N*,*N*-diethylallylamine (**3**) and *N*,*N*-diisopropylallylamine (**8**) with $(C_6F_5)_2BH$ is hydroboration. The product in the case of **3** cyclises to give **6**, but in the case of **8** dihydrogen is extruded and **9** is formed. To rationalise differences in the mechanisms behind these reactions, we present some mechanistic considerations in Scheme 5. A full evaluation of all possible intermediates would require extensive work, because numerous conformational possibilities would have to be considered. Moreover, due to the fact that many dative bonds and highly polar species are involved, neglecting solvent polarity and concentration effects would lead to a rather incomplete description. Consequently, we have restricted a computational exploration to some key species.



Scheme 5. Proposed mechanism for the formation of **6** and **9**.

The first question to be answered was whether the formation of a ring with a B–N bond following the hydroboration reaction would be hindered in the case of the more bulky isopropyl substituents in **8**.

DFT (RI-BP86/def2-SVP) calculations show that in the case of the ethyl-substituted compound the five-membered ring (**6**) is 10.3 kcal mol^{-1} lower in energy than the open-chain form with three-coordinate boron and nitrogen atoms (**11**). However, the situation is reversed for the isopropyl-substituted compound, in which the open form (**12**) is 10.7 kcal mol^{-1} lower in energy than the closed ring (**13**). This is consistent with the known fact that isopropyl groups lead to a steric overcrowding at nitrogen as is well established in Hünig's base ($i\text{Pr}_2\text{EtN}$) and the planarised nitrogen atom in triisopropylamine.[25]

This indicates that **6** has found a resting state in this cyclised form, whereas for **12** the unquenched reaction potential of free Lewis acid and base remains. This seems to initiate an alternative reactive pathway. The $-B(C_6F_5)_2$ moiety of the open intermediate **12** can react by means of an α-hydride abstraction from one of the isopropyl groups at nitrogen by to yield an iminium cation (**15**). Hydride abstractions from bulky amines with $B(C_6F_5)_3$ have already been reported.[26] Calculations for the isolated molecules predict an increasing energy when transforming **12** into **15** by +23.7 kcal mol^{-1}, whereas the corresponding process **11**→**14** is more endothermic at +30.9 kcal mol^{-1}. A conceivable 1,3-hydrogen shift of the iminium ion **15** can then lead to the formation of a vinyl ammonium salt (**17**); this process is also predicted to be endothermic by +3.0 kcal mol^{-1} (whereas the corresponding step for R = H: **14**→**16** is slightly exothermic and yields −3.1 kcal mol^{-1}).

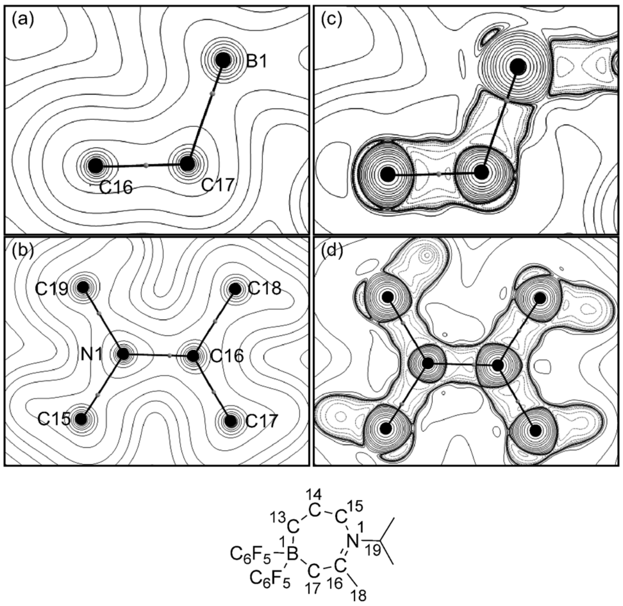
Note that a structure related to **17** in the sense that N–H and B–H functions come close together and form a BH···HN interaction between inversely polarised hydrogen atoms (dihydrogen bonding) has recently been structurally characterised in the form of 1-*N*-TMPH-CH_2-2-[HB-$(C_6F_5)_2$]C_6H_4 by neutron diffraction; the H···H separation in this compound is 1.674(8) Å.[27]

Our DFT calculations of the structure of **17** result in a related structure and give a more unusual value of 1.383 Å for a contact of two formally unbound hydrogen atoms, but still underline the similarity in bonding. Either the intermediate **15**—or more likely **17**—eliminates dihydrogen to yield the seven-membered heterocycle **9**. These processes are predicted to be exothermic by −11.4 or −14.4 kcal mol^{-1}, respectively (similar to **16**→**18** by −12.3 kcal mol^{-1}). The enamine structure **9a** can thereby serve as an intermediate of slightly different structure geometrically that relaxes into **9** (where it serves as description of one possible resonance form). The whole process of H_2 elimination starting from **12** and ending at **9** is accompanied by an increase in energy by +12.3 kcal mol^{-1} (and +15.5 kcal mol^{-1} for **11**→**18**).

These considerations do not take into account reaction barriers; this is due to the complicated conformational behaviour, which makes a search for the reaction pathway extremely costly. Furthermore, the proposed intermediates, and consequently transition states, involve betaine structures, dative bonds and even BH···HN hydrogen interactions, which make a further rigorous quantumchemical treatment a worthwhile goal and indicate that solvent and concentration effects might play a very significant role. In this sense, the energies discussed above should not be overinterpreted.

However, we may conclude that the crucial difference between the behaviour of the two systems is the hindrance of B–N bond formation for **13**. This helps to rationalise why no further reaction is observed and **6** is isolated as the product.

On the other hand, the proposed intermediate **14** is higher in energy than **15**, which provides some indication of why this process might be disfavoured for R = H. In this context it should be mentioned that **6** (as well as **5** and **7**) have been heated with the intention to convert them into seven-membered ring products analogous to **9**, but these experimental attempts remained fruitless.



9

Figure 5. Electron-density plots of **9** obtained at the MP2/TZVPP level of theory in the planes a) C16-C17-B1 and b) C17-C16-N1 with atom positions, atomic interaction lines and bond-critical points and corresponding Laplacian plots (c and d; negative values as dotted lines). The labelling scheme is shown below.

Electron-density topologies of 9 and 17: To get a better description of the nature of the chemical bonding in the seven-membered ring system **9** we calculated the electron density of this molecule at the MP2/TZVPP level of theory (see the Experimental Section) and analysed the charge density by means of QTAIM.[8] The electron density and the Laplacian maps are displayed in Figure 5; selected results are listed in Table 1.

The calculations show the highest values for the electron densities within the seven-membered ring for the bonds N1–C16 ($\rho(\mathrm{BCP}) = 2.25\,\mathrm{e\,Å^{-3}}$; BCP = bond critical point) and C16–C17 ($\rho(\mathrm{BCP}) = 1.86\,\mathrm{e\,Å^{-3}}$). The Laplacian of these bonds adopts values typical for covalent bonds: $-\nabla^2\rho(\mathrm{BCP}) = 18.8\,\mathrm{e\,Å^{-5}}$ (N1–C16) and $-\nabla^2\rho(\mathrm{BCP}) = 15.7\,\mathrm{e\,Å^{-5}}$ (C16–C17). This is consistent with the interpretation as a partial doubly bonded system and supported by the ellipticities of these bonds (0.09 and 0.14), which do not reach the values of isolated double bonds such as in ethene (0.45) or even benzene (0.23).

Table 1. Parameters of the electron-density topology for selected bonds in **9** in the calculated ground state: Electron densities $\rho(\mathrm{BCP})$ [$\mathrm{e\,Å^{-3}}$], Laplacians $-\nabla^2\rho(\mathrm{BCP})$ [$\mathrm{e\,Å^{-5}}$] and ellipticities ε at the BCP.

Atoms	$\rho(\mathrm{BCP})$	$-\nabla^2\rho(\mathrm{BCP})$	ε
B1–C17	0.77	0.41	0.09
B1–C7	0.94	0.14	0.08
B1–C1	0.96	0.51	0.11
B1–C13	1.06	3.28	0.03
N1–C16	2.25	18.8	0.09
N1–C15	1.64	14.0	0.03
N1–C19	1.64	13.9	0.02
C16–C17	1.86	15.7	0.14
C15–C14	1.61	12.6	0.02
C14–C13	1.57	11.9	0.02

By contrast, the B1–C17 bond has the lowest electron density within the seven-membered ring with a value of $\rho(\mathrm{BCP}) = 0.77\,\mathrm{e\,Å^{-3}}$, which is in the region of a dative bond.[28] This assumption is confirmed by the Laplacian value, which is $-\nabla^2\rho(\mathrm{BCP}) = 0.41\,\mathrm{e\,Å^{-5}}$. The other three carbon boron bonds all have higher values for the electron density ($\rho(\mathrm{BCP}) = 1.06$, 0.96 and $0.94\,\mathrm{e\,Å^{-3}}$ for B1–C13, B1–C1 and B1–C7, respectively) and their Laplacian values are always positive ($-\nabla^2\rho(\mathrm{BCP}) = 3.28$, 0.14 and $0.51\,\mathrm{e\,Å^{-5}}$ for B1–C13, B1–C1 and B1–C7, respectively), thus indicating their covalent nature. Likewise, the remaining bonds of the methylene bridge within the seven-membered ring exhibit electron-density values of $\rho(\mathrm{BCP}) = 1.57$, 1.61 and $1.64\,\mathrm{e\,Å^{-3}}$ for C13–C14, C14–C15 and N1–C15. The Laplacian parameters of these bonds are higher than the values of the previous described boron–carbon bonds with $-\nabla^2\rho(\mathrm{BCP}) = 11.91$, 12.60 and $14.03\,\mathrm{e\,Å^{-5}}$, respectively, which is in the region of a typical covalent bond.

The ellipticity at the BCP of the bond B1–C17 bond has a value of 0.09, which indicates a deformation along the dative bond. This also reflects the partial enamine resonance structure in the Lewis formula description.

In a related sense, the electron-density topology of **17** (Figure 6) is interesting because it contains an N–H···H–B interaction. We discuss here only this part of the molecule. A bond path between the two hydrogen atoms is found, with an considerable electron-density value at the bond critical point ($\rho(\mathrm{BCP}) = 0.35\,\mathrm{e\,Å^{-3}}$). The Laplacian at this point adopts a value of $-\nabla^2\rho(\mathrm{BCP}) = -1.30\,\mathrm{e\,Å^{-5}}$. This is a value for a typical closed-shell interaction. These values compare with those for the aminoborane dimer, $(H_3BNH_3)_2$, in which the H···H interactions are associated with distances between 1.9 and 2.4 Å and with electron-density values at their BCPs

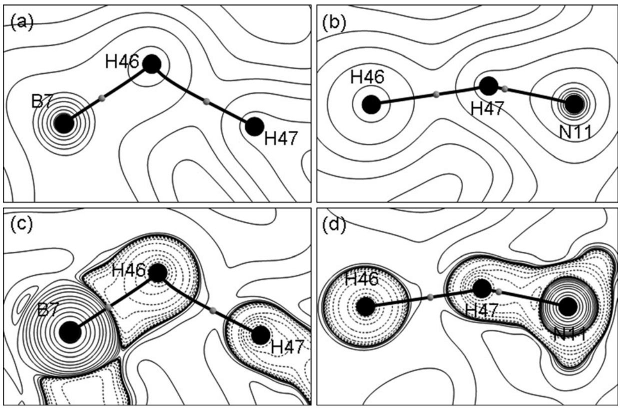


Figure 6. Electron density plots of **17** obtained at the RI-BP86/def2-SVP level of theory in the planes a) B-H-H and b) N-H-H with atom positions, atomic interaction lines and bond-critical points and corresponding Laplacian plots (c and d; negative values of $\nabla^2\rho$ as dotted lines).

between 0.05 and 0.12 e Å^{-3} and Laplacian values between $-\nabla^2\rho(\mathrm{BCP}) = 0.60$ and 1.11 e Å^{-5}.[29]

The H···H interaction energy for $(\mathrm{H_3BNH_3})_2$ has been estimated to be 3.0 kcal mol^{-1} in the solid state for each of the twelve H···H (bifurcated) interactions to other molecules.[30] Our estimate for the H···H interaction energy in **17** is 16.1 kcal mol^{-1}; this value is based on the comparison of the cyclic molecule with a H···H dihydrogen bond (**17**) and an open-chain conformation without a short H···H contact (neglecting conformational contributions).

The characteristics of the B–H and N–H bonds are as follows: B–H $\rho(\mathrm{BCP}) = 0.94$ e Å^{-3}, $-\nabla^2\rho(\mathrm{BCP}) = 0.48$ e Å^{-5} and N–H $\rho(\mathrm{BCP}) = 1.82$ e Å^{-3}, $-\nabla^2\rho(\mathrm{BCP}) = 28.7$ e Å^{-5}, which compares well with Popelier's values for the dimer of $\mathrm{H_3BNH_2}$: B–H $\rho(\mathrm{BCP}) = 1.07$ e Å^{-3}, $-\nabla^2\rho(\mathrm{BCP}) = 1.7$ e Å^{-5} and N–H $\rho(\mathrm{BCP}) = 2.42$ e Å^{-3}, $-\nabla^2\rho(\mathrm{BCP}) = 48.7$ e Å^{-5}.[29]

Conclusion

Hydroboration of a series of allylamines with Piers' borane, $(\mathrm{C_6F_5})_2\mathrm{BH}$, resulted in the formation of five-membered ring systems with intramolecular dative B–N bonds (**5**, **6** and **7**). In contrast to the ethyl-substituted amine, the reaction of *N,N*-diisopropylallylamine with $(\mathrm{C_6F_5})_2\mathrm{BH}$ led to a seven-membered ring system $(\mathrm{F_5C_6})_2\mathrm{B(CH_2)_3N}(i\mathrm{Pr})\mathrm{CMeCH_2}$ (**9**) under dihydrogen formation. In the proposed mechanism, an α-hydride abstraction from one isopropyl group at N by the $\mathrm{B(C_6F_5)_2}$ moiety takes place, thus forming an iminium cation, which eliminates dihydrogen to yield the product by means of an enamine. The different reactivities obviously depend on the steric demand of the nitrogen substituents. Calculations confirm that two isopropyl groups prevent the formation of a B–N bond such as in **5**, **6** and **7**. In a proposed mechanism, the unquenched reaction potential leads then to α-hydride abstraction and follow-up reactions that finally lead to **9**. A key step is possibly the formation of a hydridoboranate–ammonium species with a relatively strong B–H···H–N dihydrogen bond.

On the basis of the structural results from single-crystal X-ray diffraction but also an electron-density topology analysis based on calculated charge-density distribution, this compound (**9**) can be described as an electronically delocalised system with a partially dative nature of the newly formed boron–carbon bond (B1–C17) and the double-bond character of C16–C17 within the seven-membered ring system.

Experimental Section

General methods: All manipulations were performed under a rigorously dry inert atmosphere of argon using standard Schlenk and glovebox techniques. Toluene was dried with potassium and hexane was dried with $\mathrm{LiAlH_4}$ before being employed in reactions. [D$_8$]Toluene was dried with Na/K alloy and degassed. Piers' borane $(\mathrm{C_6F_5})_2\mathrm{BH}$,[17] *N,N*-diethylallylamine and *N,N*-diisopropylallylamine were synthesised according to literature procedures.[18] *N,N*-Dimethylallylamine and 1-allylpiperidine were purchased from ABCR. All amines were dried over BaO and freshly condensed from 4 Å molecular sieves. NMR spectroscopic measurements were undertaken using Bruker DRX 500, Bruker Avance 500 and Bruker Avance 600 instruments. NMR spectroscopic chemical shifts were referenced to the residual peaks of the protons of the used solvents (^{1}H, ^{13}C) or externally (^{11}B, $\mathrm{BF_3{\cdot}OEt_2}$; ^{19}F, $\mathrm{CFCl_3}$). Elemental analyses were performed using a Leco CHNS 932 instrument.

General procedure for the synthesis of 5, 6, 7, and 9: $(\mathrm{C_6F_5})_2\mathrm{BH}$ (**1**) (200 mg, 0.58 mmol) was suspended in toluene (3 mL) and the corresponding allylamine (*N,N*-dimethylallylamine (**2**) (51 mg, 0.58 mmol), *N,N*-diethylallylamine (**3**) (66 mg, 0.58 mmol), 1-allylpiperidine (72 mg, 0.58 mmol), or *N,N*-diisopropylallylamine (82 mg, 0.58 mmol)) was condensed onto it. After warming to room temperature, the clear solution was heated to 100 °C overnight and the volatiles removed under reduced pressure to dryness. The residue was washed with pentane (2 mL) and the solvent was removed under vacuum until dryness was achieved. In all cases a colourless solid was obtained. Single crystals suitable for single-crystal X-ray diffraction were obtained from a concentrated toluene or hexanes solution, respectively, at −35 °C after several days.

$(\mathrm{C_6F_5})_2\mathrm{B(CH_2)_3NMe_2}$ (5): Yield: 195 mg (78 %); ^{1}H NMR (500.1 MHz, [D$_8$]toluene, 298 K): $\delta = 1.94$ (m, 2 H; $\mathrm{NC}H_2$), 1.88 (s, 6 H; $\mathrm{NC}H_3$), 1.55 (m, 2 H; $\mathrm{BCH_2{-}C}H_2$), 1.48 ppm (br, 2 H; $\mathrm{B{-}C}H_2$); ^{11}B{^{1}H} NMR (160.4 MHz, [D$_8$]toluene, 298 K): $\delta = 0.2$ ppm ($\nu_{1/2} = 97$ Hz); ^{13}C{^{1}H} NMR (125.7 MHz, [D$_8$]toluene, 298 K): $\delta = 148.5$ (dm, $^1J(\mathrm{C,F}) = 239.8$ Hz; $\mathrm{C_6F_5}$), 140.1 (dm, $^1J(\mathrm{C,F}) = 250.3$ Hz; $\mathrm{C_6F_5}$), 137.7 (dm, $^1J(\mathrm{C,F}) = 251.5$ Hz; $\mathrm{C_6F_5}$), 119.5 (br; *i*-$\mathrm{C_6F_5}$), 66.9 ($\mathrm{N}C\mathrm{H_2}$), 45.3 ($\mathrm{N}C\mathrm{H_3}$), 20.0 ($\mathrm{BCH_2{-}}C\mathrm{H_2}$), 17.5 ppm (br; $\mathrm{B}C\mathrm{H_2}$); ^{19}F NMR (470.5 MHz, [D$_8$]toluene, 298 K): $\delta = -163.7$ (m, 4 F; *m*-$\mathrm{C_6F_5}$), −157.3 (t, $^3J(\mathrm{F,F}) = 20.6$ Hz, 2 F; *p*-$\mathrm{C_6F_5}$), −128.6 ppm (m, 4 F; *o*-$\mathrm{C_6F_5}$); elemental analysis calcd (%) for $\mathrm{C_{17}H_{12}BF_{10}N}$ (431.08): C 47.37, H 2.81, N 3.25; found: C 47.45, H 2.73, N 3.26.

$(\mathrm{C_6F_5})_2\mathrm{B(CH_2)_3NEt_2}$ (6): Yield: 162 mg (77 %); ^{1}H NMR (500.1 MHz, [D$_8$]toluene, 298 K): $\delta = 3.15$ (dq, $^3J(\mathrm{H,H}) = 7.4$ Hz, $^2J(\mathrm{H,H}) = 14.5$ Hz, 2 H; $\mathrm{NC}H_2\mathrm{CH_3}$), $\delta = 2.34$ (dq, $^3J(\mathrm{H,H}) = 7.4$ Hz, $^2J(\mathrm{H,H}) = 14.5$ Hz, 2 H; $\mathrm{NC}H_2\mathrm{CH_3}$), 2.19 (m, 2 H; $\mathrm{NC}H_2$), 1.55 (m, 2 H; $\mathrm{BCH_2{-}C}H_2$), 1.48 (br, 2 H; $\mathrm{B{-}C}H_2$) 0.48 ppm (t, $^3J(\mathrm{H,H}) = 7.4$ Hz, 6 H; $\mathrm{NCH_2C}H_3$); ^{11}B{^{1}H} NMR (160.4 MHz, [D$_8$]toluene, 298 K): $\delta = 2.2$ ppm ($\nu_{1/2} = 141$ Hz); ^{13}C{^{1}H} NMR (125.7 MHz, [D$_8$]toluene, 298 K): $\delta = 148.6$ (dm, $^1J(\mathrm{C,F}) = 237.2$ Hz; $\mathrm{C_6F_5}$), 140.1 (dm, $^1J(\mathrm{C,F}) = 250.1$ Hz; $\mathrm{C_6F_5}$), 137.7 (dm, $^1J(\mathrm{C,F}) = 248.4$ Hz; $\mathrm{C_6F_5}$), 120.5 (br; *i*-$\mathrm{C_6F_5}$), 53.5 ($\mathrm{N}C\mathrm{H_2}$), 50.0 ($\mathrm{N}C\mathrm{H_2CH_3}$), 21.1 ($\mathrm{BCH_2{-}}C\mathrm{H_2}$), 17.6 (br; $\mathrm{B}C\mathrm{H_2}$), 11.0 ppm ($C\mathrm{H_3}$); ^{19}F NMR (470.5 MHz, [D$_8$]toluene, 298 K): $\delta = -163.6$ (m, 4 F; *m*-$\mathrm{C_6F_5}$), −157.2 (t, $^3J(\mathrm{F,F}) = 20.6$ Hz, 2 F, *p*-$\mathrm{C_6F_5}$), −127.3 ppm (m, 4 F; *o*-$\mathrm{C_6F_5}$); elemental analysis calcd (%) for $\mathrm{C_{19}H_{16}BF_{10}N}$ (459.14): C 49.70, H 3.51, N 3.05; found: C 49.59, H 3.81, N 3.04.

$(\mathrm{C_6F_5})_2\mathrm{B(CH_2)_3N(CH_2)_5}$ (7): Yield: 219 mg (80 %); ^{1}H NMR (500.1 MHz, [D$_8$]toluene, 298 K): $\delta = 3.18$ (mt, $^3J(\mathrm{H,H}) = 12.2$ Hz, 2 H; $\mathrm{NC}H_2$(ax)pip), 2.26 (m, 2 H; $\mathrm{NC}H_2$(B)), 2.09 (d, $^3J(\mathrm{H,H}) = 13.4$ Hz, 2 H; $\mathrm{NC}H_2$(eq)pip), 1.56 (m, 2 H; $\mathrm{BC}H_2\mathrm{{-}C}H_2$), 1.50 (m, 2 H; $\mathrm{BC}H_2\mathrm{{-}C}H_2$), 1.22–1.20 (m, 1 H; $(\mathrm{N(CH_2C}H_2)_2\mathrm{C}H_2)$), 1.02–0.85 ppm (m, 5 H; $(\mathrm{N(CH_2C}H_2)_2\mathrm{C}H_2)$); ^{11}B{^{1}H} NMR (160.4 MHz, [D$_8$]toluene, 298 K): $\delta = 1.6$ ppm ($\nu_{1/2} = 120$ Hz); ^{13}C{^{1}H} NMR (125.7 MHz, [D$_8$]toluene, 298 K): $\delta = 148.6$ (dm, $^1J(\mathrm{C,F}) = 243.3$ Hz; $\mathrm{C_6F_5}$), 140.0 (dm, $^1J(\mathrm{C,F}) = 250.3$ Hz; $\mathrm{C_6F_5}$), 137.6 (dm, $^1J(\mathrm{C,F}) = 249.0$ Hz; $\mathrm{C_6F_5}$), 119.8 (br; *i*-$\mathrm{C_6F_5}$), 53.7 ($\mathrm{N}C\mathrm{H_2}$(B)), 50.0 ($\mathrm{N}C\mathrm{H_2}$(pip), 22.3 ($\mathrm{N(CH_2}C\mathrm{H_2)_2CH_2}$), 20.5 ($\mathrm{N(CH_2CH_2)_2}C\mathrm{H_2}$) 19.5 ($\mathrm{BCH_2{-}}C\mathrm{H_2}$), 16.2 ppm (br; $\mathrm{B}C\mathrm{H_2}$); ^{19}F NMR (470.5 MHz, [D$_8$]toluene, 298 K): $\delta = -163.6$ (m, 4 F; *m*-$\mathrm{C_6F_5}$), −157.2 (m, 2 F; *p*-$\mathrm{C_6F_5}$), −126.9 ppm (m, 4 F; *o*-$\mathrm{C_6F_5}$); elemental analysis calcd (%) for $\mathrm{C_{20}H_{16}BF_{10}N}$ (471.14): C 50.99, H 3.42, N 2.97; found: C 50.96, H 3.23, N 2.94.

$(\mathrm{C_6F_5})_2\mathrm{B(CH_2)_3N}(i\mathrm{Pr})\mathrm{C(Me)CH_2}$ (9): Yield: 210 mg (75 %); ^{1}H NMR (500.1 MHz, [D$_8$]toluene, 298 K): $\delta = 3.02$ (sept, $^3J(\mathrm{H,H}) = 6.65$ Hz, 1 H; $\mathrm{NC}H$), 2.90 (br s, 2 H; $\mathrm{BC}H_2\mathrm{{-}C}_q$), 2.86 (br m, 2 H; $\mathrm{NC}H_2$), 1.61 (br m, 2 H; $\mathrm{BCH_2{-}C}H_2$), 1.34 (br s, 2 H; $\mathrm{BC}H_2$), 1.06 (s, 3 H; $\mathrm{C}_q\mathrm{C}H_3$), 0.41 ppm (d, $^3J(\mathrm{H,H}) = 6.65$ Hz, 6 H; $\mathrm{C}H_3$); ^{11}B{^{1}H} NMR (160.4 MHz, [D$_8$]toluene, 298 K): $\delta = -14.4$ ppm ($\nu_{1/2} = 52$ Hz); ^{13}C{^{1}H} NMR (125.7 MHz, [D$_8$]toluene, 298 K): $\delta = 197.4$ (C_q), 148.1 (dm, $^1J(\mathrm{C,F}) = 236.6$ Hz; $C_6\mathrm{F_5}$), 138.6 (dm, $^1J(\mathrm{C,F}) = 246.7$ Hz; $C_6\mathrm{F_5}$), 137.1 (dm, $^1J(\mathrm{C,F}) = 241.8$ Hz; $C_6\mathrm{F_5}$), 53.9 ($\mathrm{N}C\mathrm{H}$), 47.4 ($\mathrm{N}C\mathrm{H_2}$), 42.7 (br; $\mathrm{BCH_2{-}C}_q$), 24.4 (br and s;

Table 2. Crystallographic data for compounds **5**, **6**, **7** and **9**.

	5	**6**	**7**	**9**
formula	$C_{17}H_{12}BF_{10}N$	$C_{19}H_{16}BF_{10}N$	$C_{20}H_{16}BF_{10}N$	$C_{21}H_{18}BF_{10}N$
M_r	431.09	459.14	471.15	485.17
T [K]	100(2)	100(2)	100(2)	100(2)
crystal size [mm]	0.30×0.29×0.20	0.30×0.24×0.08	0.30×0.28×0.26	0.16×0.14×0.14
crystal system	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	$Pbca$	$P2_1/c$	$P2_1/c$
a [Å]	7.4523(3)	8.9409(3)	11.4389(2)	14.7644(6)
b [Å]	7.6260(3)	17.0929(7)	16.4885(3)	10.9518(4)
c [Å]	16.6484(6)	24.8217(8)	19.9068(4)	13.4735(5)
α [°]	91.9844(15)	90	90	90
β [°]	96.0757(14)	90	90.421(1)	111.586(1)
γ [°]	118.9928(15)	90	90	90
V [Å^3]	818.90(5)	3793.4(2)	3754.5(1)	2025.8(1)
Z	2	8	8	4
ρ_{calcd} [g cm^{-3}]	1.748	1.608	1.667	1.591
μ [mm^{-1}]	0.182	0.162	0.166	1.401
$F(000)$	432	1856	1904	984
θ range [°]	3.4–30.0	3.1–27.5	3.0–30.0	3.2–72.0
index range	$-10 \leq h \leq 10$ $-10 \leq k \leq 10$ $-23 \leq l \leq 23$	$-11 \leq h \leq 11$ $-22 \leq k \leq 22$ $-32 \leq l \leq 32$	$0 \leq h \leq 16$ $0 \leq k \leq 23$ $-27 \leq l \leq 28$	$-18 \leq h \leq 17$ $-13 \leq k \leq 13$ $-16 \leq l \leq 16$
reflns collected	7614	21893	90771	26213
unique reflns	4673	4315	10901	3951
observd reflns (2σ)	4404	3217	9140	3820
R_{int}	0.0251	0.055	0.043	0.0277
data/restraints/params	4673/0/264	4315/0/282	10901/0/578	3951/0/301
GoF (F^2)	1.052	1.014	1.027	1.050
R_1, wR_2 ($I > 2\sigma(I)$)	0.0354, 0.0995	0.0386, 0.0879	0.0422, 0.1058	0.0327, 0.0851
R_1, wR_2 (all data)	0.0373, 0.1014	0.0594, 0.0974	0.0549, 0.1147	0.0336, 0.0859
$\Delta\rho_{(max/min)}$ [e Å^{-3}]	0.44/−0.21	0.27/−0.24	0.32/−0.26	0.31/−0.33

BCH_2 and BCH$_2$–CH_2), 23.1 (C$_q$$CH_3$), 18.3 ppm ($CH_3$), quaternary carbon of C_6F_5 ring was not observed; ^{19}F NMR (470.5 MHz, [D$_8$]toluene, 298 K): $\delta = -164.8$ (m, 4F; m-C_6F_5), −161.0 (m, 2F; p-C_6F_5), −133.5 ppm (m, 4F; o-C_6F_5); elemental analysis calcd (%) for $C_{21}H_{18}BF_{10}N$ (485.17): C 51.99, H 3.74, N 2.89; found: C 52.25, H 3.71, N 2.94.

Crystallographic structure determinations: Single crystals of compounds **5**, **6**, **7** and **9** suitable for X-ray diffraction measurement were chosen inside a glovebox, suspended in a paratone-N/paraffin oil mixture, mounted on a glass fibre and transferred onto the goniometer of the diffractometer. The measurements were carried out with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) for **5**, **6** and **7** and with Cu$_{K\alpha}$ radiation ($\lambda = 1.54178$ Å) for **9**. Crystallographic data of compounds **5**, **6**, **7** and **9** are listed in Table 2. The structures were solved by direct methods and refined by full-matrix least-squares cycles (program SHELX-97[31]). CCDC-865379 (**5**), 865380 (**6**), 865381 (**7**) and 865382 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: All calculations were performed using the TURBOMOLE program package (version 6.2)[32] at the RI-DFT(BP86) level[33] using the def2-SVP basis sets, the multipole accelerated rij and default settings (except mgrid 4 and $denconv 0.1d-06). The electron-density calculation of **9** was performed (at an optimised geometry) at the RI-MP2/def2-TZVPP level of theory as it is implemented in TURBOMOLE using the default settings. The topology analysis was done using the AIMALL program package.[34]

Acknowledgements

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Hydroboration

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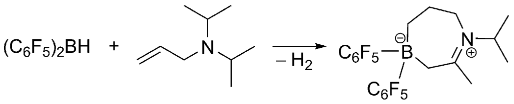
Inherent Stability Limits of Intramolecular Boron Nitrogen Lewis Acid–Base Pairs



Two roads diverged: Two different reaction pathways in the hydroboration of allylamines $R_2NCH_2CHCH_2$ with $(C_6F_5)_2BH$ lead to the expected heterocycles with B–N bonds for small R substituents, but to hydride abstraction and evolution of dihydrogen for R = *i*Pr (see scheme).