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Synthesis and structural studies on fluorophenylboron azides

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Abstract

The fluorophenyl substituted boron chlorides $(R_F)_2BCl$ (**3** and **4**) and dichlorides R_FBCl_2 (**6** and **7**) ($R_F = 2,6\text{-}F_2C_6H_3$, $2\text{-}FC_6H_4$) were prepared using the stannylated aryl transfer reagents $(R_F)_2SnMe_2$ (**1** and **2**). The boron azides $(R_F)_2BN_3$ (**8–9**), $[2,4,6\text{-}(CF_3)_3C_6H_2]_2BN_3$ (**10**) and diazides $R_FB(N_3)_2$ (**11** and **12**) were synthesized by the reaction of the corresponding boron chlorides $(R_F)_2BCl$ (**3** and **4**), $[(CF_3)_3C_6H_2]_2BCl$ (**5**) and R_FBCl_2 (**6** and **7**) with Me_3SiN_3. The influence of the electron withdrawing substituents on the molecular structure of these azides is discussed. The reactions were also performed in the presence of pyridine yielding the adducts $(R_F)_2BN_3\cdot py$ and $R_FB(N_3)_2\cdot py$ (**13–16**). All compounds were characterized by multinuclear NMR, vibrational (IR, Raman) spectroscopy; and the molecular structures of **1**, **3**, **8**, **10a** ($[(CF_3)_3C_6H_2]_2BN_3/[(CF_3)_3C_6H_2]_2BOH$) and **14** were established by single crystal X-ray crystallography.
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1. Introduction

It is well known that the electron deficient Lewis acidic character of the boron atom in boron azides R_2BN_3, or boron diazides $RB(N_3)_2$, is strongly depending on the nature of the substituent R [1]. While alkyl, aryl and alkoxy substituted boron azides are sufficiently Lewis acidic enough to form stable 1:1 pyridine adducts, amino boron azides $(R_2N)_{3-n}B(N_3)_n$ ($n = 1, 2$) are weak Lewis acids and form no pyridine adducts. Exceptional strong Lewis acidity is found for the boron atom in boron dihalide azides BX_2N_3 ($X = F$, Cl, Br), which causes the formation of trimers $(BX_2N_3)_3$ [2–4]. Oligomerization for Me_2BN_3 has been established by ^{11}B NMR spectroscopy [5].

Recently, we investigated such systems and reported on the synthesis and characterization of oligomeric pentafluorophenylboron azides [6,7]. Single crystal X-ray diffraction (XRD) studies revealed the dimeric structure of bis(pentafluorophenyl)boron azide $(C_6F_5)_2BN_3$ and the trimeric structure of pentafluorophenylboron diazide $C_6F_5B(N_3)_2$. It has been shown that vibrational (IR, Raman) spectroscopy is a useful tool for qualitatively determining the solid state structure of boron azides. For monomeric boron azides the characteristic antisymmetric stretching vibration of

the azide group ($v_{asym}N_3$) is typically found in the region of 2170–2100 cm^{-1}. In oligomeric boron azides, where the azide group acts as a bridging substituent, $v_{asym}N_3$ is shifted to higher wavenumbers (2240–2200 cm^{-1}) [8].

Although the chemistry of aryl substituted boron azides and diazides has been extensively discussed in the literature [9], the chemistry of boron azides containing fluorinated groups is limited to a few examples. To our knowledge, only $(C_6F_5)_2BN_3$ [6,10], $C_6F_5B(N_3)_2$ [7] and ($m\text{-}CF_3C_6H_4$)(Ph)- BN_3 [11] have been reported.

In this contribution, we report on the synthesis and characterization of 2,6-difluorophenyl and 2-fluorophenyl-boron azides and diazides and their pyridine adducts. Following the procedure for the preparation of pentafluorophenylboron azides [6,7,12,13], we synthesized these compounds via the hitherto unknown compounds $(R_F)_2$-$SnMe_2$ (**1** and **2**), $(R_F)_2BCl$ (**3** and **4**) and R_FBCl_2 (**6** and **7**) ($R_F = 2,6\text{-}F_2C_6H_3$, $2\text{-}FC_6H_4$). In addition, the synthesis of $2,4,6\text{-}[(CF_3)_3C_6H_2]_2BN_3$ (**10**), containing the sterically demanding, electron withdrawing nonafluoromesityl group is described. The molecular structures of some compounds were confirmed by single crystal XRD.
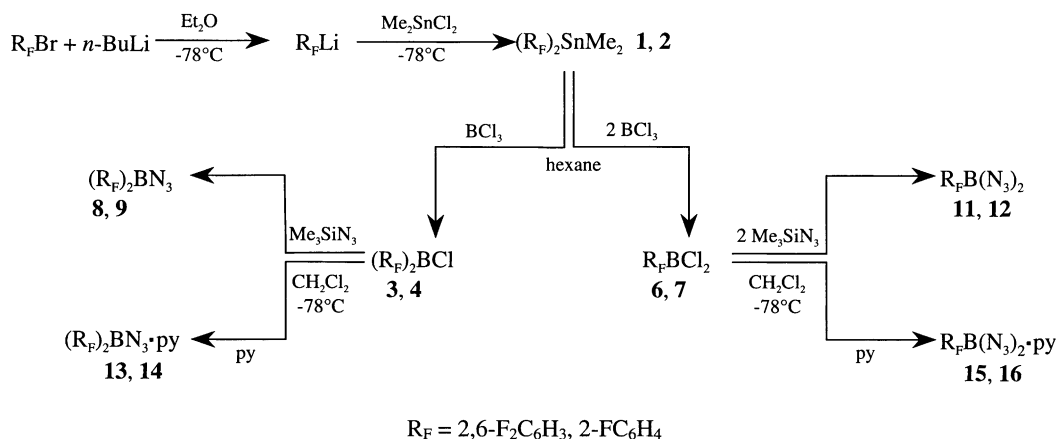
2. Results and discussion

Synthetic procedures for the preparation of tris(fluoroaryl)boranes $(R_F)_3B$ ($R_F = C_6F_5$, $2\text{-}FC_6H_4$, $4\text{-}FC_6H_4$, $2,6\text{-}$

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$$R_FBr + n\text{-}BuLi \xrightarrow[-78°C]{Et_2O} R_FLi \xrightarrow[-78°C]{Me_2SnCl_2} (R_F)_2SnMe_2 \quad \textbf{1, 2}$$

Scheme 1.

$R_F = 2,6\text{-}F_2C_6H_3, 2\text{-}FC_6H_4$

$F_2C_6H_3$) have been reported in the literature. The boranes were directly accessible from the reaction of R_FMgBr with $BF_3 \cdot OEt_2$ [14,15]. Quite recently, the preparation of several fluorophenylboron difluorides have been described [16]. They were generated by treatment of trifluoroborate salts $K[R_FBF_3]$ with BF_3 in chlorocarbon solvents. In an alternative route, we prepared $2,6\text{-}F_2C_6H_3$ and $2\text{-}FC_6H_4$ substituted boron chlorides and dichlorides in a two-step synthesis using the stannylated aryl transfer agents $(R_F)_2SnMe_2$ (**1** and **2**). The boron azides were readily formed by reacting the boron chlorides $(R_F)_2BCl$ and R_FBCl_2 with Me_3SiN_3 (Scheme 1).

While $(C_6F_2H_3)_2SnMe_2$ (**1**) is almost quantitatively obtained from the reaction of $C_6F_2H_3Li$ with Me_2SnCl_2, the preparation of $(C_6FH_4)_2SnMe_2$ (**2**) is more difficult. The aryllithium reagent $2\text{-}FC_6H_4Li$ is known to undergo lithium fluoride elimination to form biphenyls at low temperature [17]. For the generation of $2\text{-}FC_6H_4Li$, it is therefore necessary to add bromo-2-fluorobenzene very slowly to a solution of n-BuLi in hexane at $-78°C$. Under these reaction conditions, it was possible to obtain pure **2** in 55% yield. Both compounds are soluble in common organic solvents and decompose only slowly on air.

For **1**, the ^{119}Sn NMR resonance is split into a quintet ($^3J_{SnF} = 53.2\,Hz$) at $-78.6\,ppm$ and for **2** into a triplet ($^3J_{SnF} = 68.2\,Hz$) at $-58.9\,ppm$ due to coupling with *ortho*-fluorine atoms. These values are shifted to higher field compared to the shifts observed for the corresponding trimethyltin derivatives R_FSnMe_3 [18]. The ^{19}F NMR resonances are found at $\delta = -92.7$ (**1**) and -94.4 (**2**). The ^{13}C NMR chemical shifts as well as the $^{13}C-^{19}F$ coupling constants are comparable with those found for R_FSnMe_3 [19]. The Raman spectra show the characteristic $Sn-CH_3$ stretching vibrations (νSnC) [20] at 552 and 533 cm^{-1} (**1**) and at 539 and 524 cm^{-1} (**2**); the IR bands appear at 543 and 527 cm^{-1} (**1**) and at 538 and 528 (**2**) cm^{-1}.

Slow sublimation of **1** at $35°C/10^{-2}$ mbar afforded crystals suitable for single crystal X-ray structure analysis (Fig. 1). Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$.

The geometry around the tin atom is essentially tetrahedral (average C–Sn–C: 109.6°). The Sn–C distances are on average of 2.14 Å, which compare with 2.14 Å observed in $(C_6H_5)_4Sn$ [21] and 2.13 Å in $(C_6F_5)_4Sn$ [22]. Additionally, compound **1** shows four weak tin–fluorine contacts (average $Sn \cdots F = 3.24$ Å) which are shorter than the Sn–F van der Waals distance of 3.640 Å [23].

The boron chlorides $(R_F)_2BCl$ (**3** and **4**) were obtained in high yields ($\sim70\%$) from the 1:1 reactions of $(R_F)_2SnMe_2$ (**1** and **2**) with BCl_3 in hexane. The reaction of **1** and **2** with BCl_3 in a 1:2 ratio led to the formation of R_FBCl_2 (**6** and **7**). $[2,4,6\text{-}(CF_3)_3C_6H_2]_2BCl$ (**5**) was prepared according to the literature procedure from the reaction of $(CF_3)_3C_6H_2Li$ with BCl_3 [24]. In this case, the boron chloride (**5**) is directly available, because the bulky nonafluoromesityl substituents prevent a formation of the corresponding tris-substituted borane. All boron chlorides are moisture sensitive, soluble in organic solvents but decompose in chloroform. The ^{11}B NMR resonances are found in the typical region for phenyl substituted boron monochlorides and dichlorides at 60.5 (**3**),
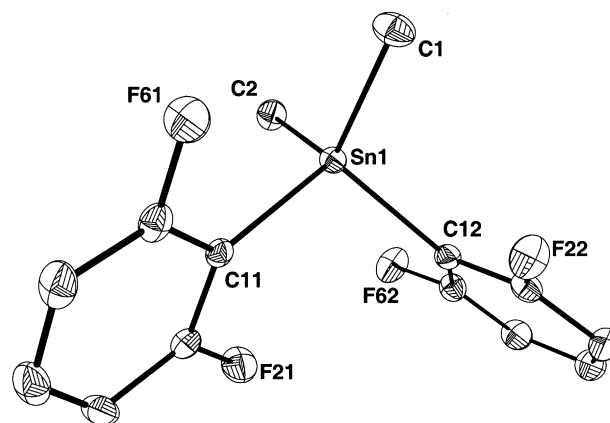

Fig. 1. ORTEP plot of **1** with selected bond lengths (Å) and angles (°) — Sn(1)–C(1): 2.123(4); Sn(1)–C(2): 2.130(4); Sn(1)–C(11): 2.150(3); Sn(1)–C(12): 2.153(3); C–F: 1.37; C(11)–Sn(1)–C(12): 105.9(1); C(11)–Sn(1)–C(1): 110.9(1); C(11)–Sn(1)–C(2): 108.2(1); C(1)–Sn(1)–C(2): 111.1(1).
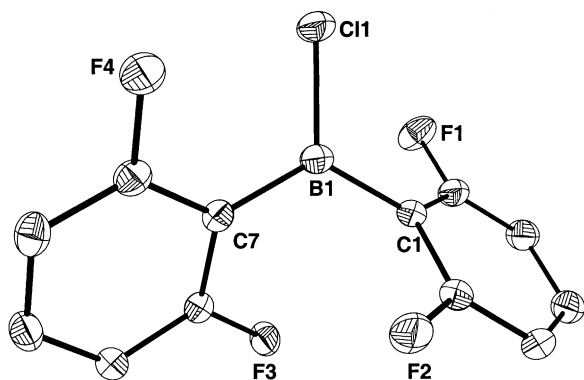
Fig. 2. ORTEP plot of **3** with selected bond lengths (Å) and angles (°) — B(1)–Cl(1): 1.755(2); B(1)–C(1): 1.561(3); B(1)–C(7): 1.556(3); C(1)–B(1)–Cl(1): 117.6(2); C(7)–B(1)–Cl(1): 119.4(2); C(1)–B(1)–C(7): 123.1(2).

61.0 (**4**), 54.0 (**6**) and 53.0 cm^{-1} (**7**) [25]. The ^{11}B NMR shift of **5** is found as a very broad signal at 46.0 ($\Delta\nu_{1/2} = 800$ Hz).

Single crystals of **3** were obtained by sublimation at 50°C/ 10^{-2} mbar (Fig. 2).

Compound **3** crystallizes in the space group $P2_1/c$ with $Z = 4$. The boron chlorine distance (1.755(2) Å) as well as the boron carbon distances (1.56 Å) are almost identical to those found for $(C_6F_5)_2BCl$ [26]. The planes of the C_6F_5 groups are twisted out of the C(1)–C(7)–B(1)–Cl(1) plane, probably due to steric repulsions between the F(2) and F(3) atoms (3.10 Å).

The boron azides **8**, **9** and diazides **11**, **12** are prepared from the reaction of the corresponding boron chlorides with Me$_3$SiN$_3$. Long reaction time required for the conversion of **5** into **10** (14 days, monitored by ^{19}F NMR) is most likely due to the bulky nonafluoromesityl substituents. The azides were obtained as non-explosive, moisture sensitive solids (**8** and **10**) or distillable liquids (**9**, **11** and **12**), soluble in benzene, toluene and CH$_2$Cl$_2$. The ^{11}B NMR resonances for all azides were found in the region of three-coordinated boron. A difference is observed in the solid state structure of the compounds shown by Raman spectroscopy. The vibrational spectra (IR, Raman) (25 to −100°C) of the azides **9**, **10** and **12** show the antisymmetric stretching vibrations of the azide groups (ν_{asym}N$_3$) in the typical region for terminal boron azide groups (2168–2138 cm^{-1}). For **8**, this vibration is shifted to a higher wavenumber (IR: 2202 cm^{-1}/Raman: 2207 cm^{-1}), which indicates the presence of an oligomeric solid state structure with bridging azides. Monomeric **8** could not be detected by Raman spectroscopy, because of its decomposition at the melting point (104–107°C). A temperature dependent oligomerization was detected for **11** by low temperature Raman spectroscopy. At 25°C (liquid **11**), ν_{asym}N$_3$ was found at 2168, 2157 and 2145 cm^{-1}; at 0°C (solid **11**) it was found at 2208, 2166 and 2146 cm^{-1}.

In order to confirm the oligomeric structure of **8**, a single crystal X-ray structure analysis was carried out proving **8** as the second dimeric boron azide (Fig. 3).
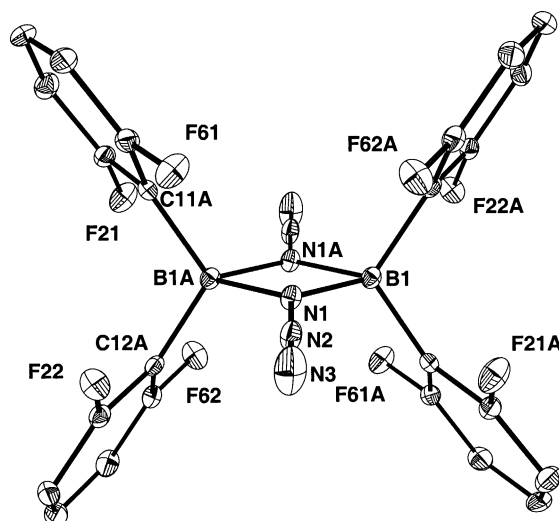

Fig. 3. ORTEP plot of **8** with selected bond lengths (Å) and angles (°) — B(1)–N(1): 1.592(3); B(1a)–N(1): 1.600(2); N(1)–N(2): 1.242(2); N(2)–N(3): 1.112(3); B(1)–C(11): 1.608(3); N(1)–N(2)–N(3): 178.0(2); N(2)–N(1)–B(1): 130.3(2); N(1)–B(1)–N(1a): 82.1(1).

Compound **8** crystallizes in the space group $P\bar{1}$. It is a dimer in the solid state with one dimeric unit in the unit cell. Therefore, the molecule is centersymmetric having C_i symmetry. The B$_2$N$_2$ ring is planar with a B–N–B angle of 97.9(1)° and a N–B–N angle of 82.1(1)°. The azide groups are slightly bent (178.0(2)°), the N(1)–N(2) distance is 1.242(2) Å and the N(2)–N(3) distance is 1.112(3) Å, the latter having considerable triple bond character. The data are almost identical to those found for $[(C_6F_5)_2BN_3]_2$ [6].

For an investigation of the influence of electron withdrawing groups on bond lengths and angles of a terminal azide group, attempts were made to determine the molecular structure of **10**, but only succeeded in the crystallization of partially hydrolyzed **10a**, as shown in Fig. 4. Further attempts to obtain single crystals of **10** under strictly anhydrous conditions resulted in microcrystalline powders which were not suitable for X-ray.

Compound **10a** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. There are no interactions between the $[(CF_3)_3C_6H_2]_2BN_3$ (molecule 1) and the $[(CF_3)_3C_6H_2]_2$-BOH (molecule 2) units. The B(1)–N(1) distance of 1.404(6) Å in molecule 1 is shorter than the distance found for catecholboron azide (1.433(3) Å) [27]. The N(1)–N(2) [1.251(2) Å] and the N(2)–N(3) [1.126(5) Å] distances are in accord with the structures of other three-coordinated boron azides previously determined [27–29]. The azide group is slightly bent [N(1)–N(2)–N(3): 172.9(5)°] and the B(1)–N(1)–N(2) angle is 122.3(4)°. In the boronic acid (molecule 2), the B(2)–O(1) distance is 1.350(6) Å and the average B–C distances (1.60 Å) are slightly shorter than those found for molecule 1 (1.62 Å); the C(12A)–B(2)–O(1) and the C(12B)–B(2)–O(1) angles are 113.8(4) and 121.1(4)°, respectively. An intramolecular OH⋯F hydrogen bridge is found for the hydrogen atom of the OH group
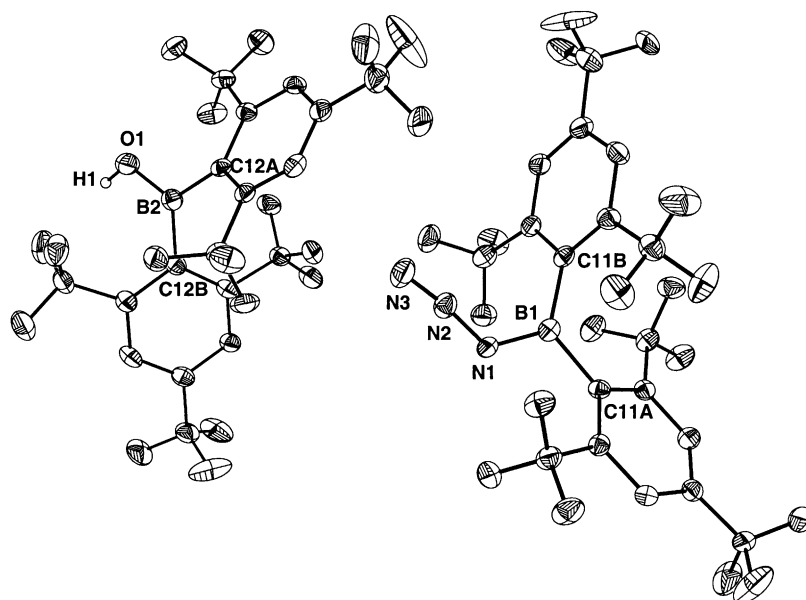
Fig. 4. ORTEP plot of **10a** with selected bond lengths (Å) and angles (°) — B(1)–N(1): 1.404(6); B(1)–C(11A); 1.620(6); N(1)–N(2): 1.251(2); N(2)–N(3): 1.126(5); N(1)–N(2)–N(3): 172.9(5); B(1)–N(1)–N(2): 122.3(4); C(11A)–B(1)–N(1): 115.0(4); B(2)–O(1); 1.350(6); B(2)–C(12A): 1.599(7); C(12A)–B(2)–O(1): 113.8(4).

to one fluorine atom of a CF_3 group. The O–H distance is 0.84 Å, the H···F(82B) contact 2.09 Å and the O(1)–H···F(82B) angle is 147°.

The reactions of the boron chlorides **3**, **4** and dichlorides **6**, **7** with Me_3SiN_3 were also performed in the presence of pyridine yielding the 1:1 adducts **13**−**16**. Due to the bulky nonafluoromesityl substituents, no reaction to form an adduct was found in the case of **10**. All compounds were obtained as colorless, crystalline, slightly moisture sensitive solids soluble in aromatics and chlorocarbon solvents. The
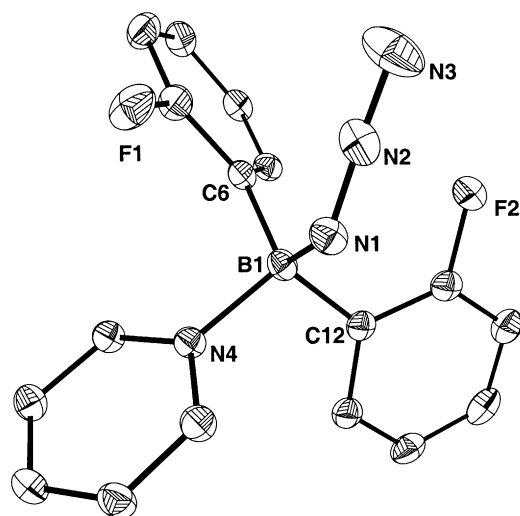

Fig. 5. ORTEP plot of **14** with selected bond lengths (Å) and angles (°) — B(1)–N(1): 1.558(3); B(1)–N(4): 1.621(3); N(1)–N(2): 1.208(3); N(2)–N(3): 1.146(3); B(1)–C(6): 1.615(4); N(1)–N(2–N(3): 175.5(3); B(1)–N(1)–N(2): 123.0(2); N(4)–B(1)–N(1): 102.7(2); C(6)–B(1)–C(12): 113.5(2); N(1)–B(1)–C(12): 108.8(2).

^{11}B NMR resonances are found in the expected region of four-coordinated boron atoms. In the IR spectra, $v_{asym}N_3$ was found as a very strong absorption, in the Raman spectra as a peak of weak intensity in the typical area for terminal azide groups (2120 cm^{-1}). These data are in good agreement with the data observed for Ph_2BN_3·py [1] and $PhB(N_3)_2$·py [30]. The molecular structure of the adduct **14** was confirmed by single crystal structure analysis (Fig. 5).

Compound **14** crystallizes monoclinically in the space group $P2_1/n$ with $Z = 4$. The boron atom is surrounded by the four substituents in a tetrahedral fashion. While the B(1)–N(1) distance (1.558(3) Å) has the length of a typical B–N $sp^3−sp^3$ single bond, the B(1)–N(4) distance (1.621(3) Å) is considerably longer as expected for a typical B–N donor−acceptor bond. The azide group is slightly bent [N(1)–N(2)–N(3) 175.5(3)°] and the N(2)–N(3) [1.146(3) Å] distance is, as expected, shorter than that of N(1)–N(2) [1.208(3) Å].

3. Conclusion

The boron chlorides (**3** and **4**) and dichlorides (**6** and **7**) were obtained by treatment of the stannylated aryl transfer reagents $(R_F)_2SnMe_2$ with BCl_3. These boron chlorides were readily converted into the azides **8**, **9**, **11** and **12** by reaction with Me_3SiN_3. The conversion time of **5** into the azide **10** is significantly extended due to the bulky nonafluoromesityl substituents. ^{11}B NMR spectroscopy showed that all azides are monomeric in solution, which is in contrast to the solid state structures of the boron azides containing the stronger electron withdrawing $C_6F_2H_3$ substituent. $[(C_6F_2H_3)_2BN_3]_2$ (**8**) is dimeric as shown by X-ray crystallography, and also an

oligomeric structure is predicted for solid $C_6F_2H_3B(N_3)_2$ (**11**) suggested by low temperature Raman spectroscopy.

4. Experimental

4.1. General experimental procedures

All manipulations of air and moisture sensitive materials were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried and degassed by standard methods. Raman spectra were recorded on a Perkin-Elmer 2000 NIR FT-Raman spectrometer fitted with a Nd-YAG laser (1064 nm), infrared spectra on Perkin-Elmer 983 G IR spectrometer between KBr plates or as Nujol mulls. The elemental analyses were performed with a C-, H-, N-Analysator Elementar Vario EL. NMR spectra were recorded on a JEOL Eclipse400 instrument, and chemical shifts are with respect to $(CH_3)_4Si$ (^1H, 400.2 MHz, $^{13}C\{^1H\}$, 100.6 MHz), $BF_3 \cdot OEt_2$ (^{11}B, 128.3 MHz), $CFCl_3$ (^{19}F, 376.5 MHz), CH_3NO_2 (^{14}N, 28.9 MHz), and Me_4Sn ($^{119}Sn\{^1H\}$, 149.2 MHz). Melting points were determined in capillaries using a Büchi B540 instrument. Commercially available chemicals were used as received (Aldrich, FluoroChem). Higher deviations from the theoretical values of the elemental analyses are common for fluorine containing boron azides [31]; elemental analyses of the diazides **11** and **12** were not satisfactory and omitted. The ^{13}C NMR signal of C-1 (CB) atom is only visible in some cases [30].

Caution: *Covalent azides are potentially explosive; appropriate safety precautions must be taken!*

($C_6F_2H_3$)$_2$SnMe$_2$ (**1**): 8.0 ml n-butyllithium (2.5 M in hexane, 20.0 mmol) were added dropwise to a stirred solution of 3.86 g (20.0 mmol) $C_6F_2H_3Br$ in 30 ml ether at $-78°C$ and additionally stirred for 3 h. Into this solution, 2.20 g (10.0 mmol) Me_2SnCl_2 were added and the mixture was allowed to warm up slowly. After additional stirring at ambient temperature for 3 h, the mixture was filtered and the solvent was removed under vacuum leaving a yellow oil. Distillation afforded a colorless liquid which solidified on standing. Single crystals were obtained by slow sublimation at $35°C/10^{-2}$ mbar. Yield: 3.56 g (95%); mp: $39–42°C$; bp: $48°C/10^{-2}$ mbar.

Raman (400 mW): $v = 3081$ (10), 3021 (3), 2926 (4), 1606 (2), 1591 (1), 1571 (1), 1244 (6), 1196 (2), 1148 (2), 1085 (2), 1041 (3), 750 (1), 650 (2), 552/533 (3/7, v_{SnCH_3}), 376 (2), 244 (3), 194 (3), 167 (4), 137 (4), 109 (4) cm^{-1}. IR: $v = 3077$ vw, 3004 vw, 1606 vs, 1590 s, 1574 vs, 1449 vs, 1288 m, 1244 m, 1219 vs, 1085 m, 973 vs, 780 vs, 751 m, 697 m, 543 s/527 s (v_{SnCH_3}), 500 m cm^{-1}. ^1H NMR (CDCl$_3$): $\delta = 7.31$ (m, 1H, 4-H), 6.85 (m, 2H, 3-H), 0.80 (s, 3H, CH$_3$, $^2J_{HSn} = 62.9$ Hz). ^{13}C NMR (CDCl$_3$): $\delta = 167.4$ (dd, C-2, $^1J_{CF} = 239.8$ Hz, $^3J_{CF} = 18.7$ Hz), 132.2 (t, C-4, $^3J_{CF} = 9.3$ Hz), 112.5 (t, C-1, $^2J_{CF} = 45.7$ Hz), 111.0 (dm, C-3, $^2J_{CF} = 30.5$ Hz), -6.3 (quin, CH$_3$, $^4J_{CF} = 2.5$ Hz, $^1J_{C^{119}Sn}$

$= 427.2$ Hz, $^1J_{C^{117}Sn} = 408.0$ Hz). ^{19}F NMR (CDCl$_3$): $\delta = -92.7$ (m, $^3J_{FSn} = 53.2$ Hz). ^{119}Sn NMR (CDCl$_3$): $\delta = -78.6$ (quin, $^3J_{SnF} = 53.2$ Hz). Anal. Calcd. for $C_{14}H_{12}F_4Sn$ (374.95): C, 44.9; H, 3.2. Found: C, 44.7; H, 3.5.

(C_6FH_4)$_2$SnMe$_2$ (**2**): Into a solution of 13.7 ml n-butyllithium (2.5 M, 34.2 mmol) in 30 ml ether 6.00 g (34.2 mmol) C_6FH_4Br were added at $-78°C$ during a period of 2 h. After additional stirring for 1 h, 3.75 g Me_2SnCl_2 (17.1 mmol) were added and the solution was allowed to warm up slowly.

For further work up, see **1**. Yield: 3.18 g (55%); bp: $47–50°C/10^{-2}$ mbar.

Raman (150 mW): $v = 3050$ (4), 2997 (1), 2926 (2), 1593 (2), 1575 (1), 1466 (1), 1436 (1), 1282 (1), 1257 (1), 1206 (3), 1155 (1), 1106 (1), 1055 (2), 1024 (5), 815 (2), 643 (3), 539/524 (4/10, v_{SnCH_3}), 457 (2), 260 (1), 224 (3), 155 (5), 110 (3) cm^{-1}. IR: $v = 3067$ s, 3004 m, 2921 m, 1593 vs, 1574 vs, 1465 vs, 1435 vs, 1286 m, 1256 vs, 1204 vs, 1155 m, 1106 vs, 1055 vs, 1023 m, 941 m, 857 m, 814 vs, 757 vs, 703 s, 538 vs/528 s (v_{SnCH_3}) cm^{-1}. ^1H NMR (CDCl$_3$): $\delta = 7.40$ (m, 2H), 7.18 (m, 1H), 7.07 (m, 1H), 0.68 (s, 3H, CH$_3$, $^2J_{HSn} = 59.6$ Hz). ^{13}C NMR (CDCl$_3$): $\delta = 167.3$ (d, C-2, $^1J_{CF} = 235.2$ Hz), 137.2 (d, C-6, $^3J_{CF} = 13.8$ Hz), 131.0 (d, C-4, $^3J_{CF} = 8.5$ Hz), 125.3 (d, C-1, $^2J_{CF} = 42.3$ Hz), 124.4 (d, C-5, $^4J_{CF} = 3.1$ Hz), 114.4 (d, C-3, $^2J_{CF} = 27.7$ Hz), -8.9 (t, CH$_3$, $^4J_{CF} = 1.9$ Hz, $^1J_{C^{119}Sn} = 402.0$ Hz, $^1J_{C^{117}Sn} = 384.3$ Hz). ^{19}F NMR (CDCl$_3$): $\delta = -94.4$ (m, $^3J_{SnF} = 68.2$ Hz). ^{119}Sn NMR (CDCl$_3$): $\delta = -58.9$ (t, $^3J_{SnF} = 68.2$ Hz). Anal. Calcd. for $C_{14}H_{14}F_2Sn$ (338.97): C, 49.6; H, 4.2. Found: C, 49.4; H, 3.8.

($C_6F_2H_3$)$_2$BCl (**3**): 5.0 ml BCl$_3$ (1.0 M in hexane, 5.0 mmol) were added into a solution of 1.89 g (5.0 mmol) **1** in 20 ml hexane at $-78°C$. The solution was allowed to warm up and was heated to reflux for 8 days. The formed Me_2SnCl_2 crystals were filtered and the solvent removed under vacuum. Distillation afforded **3** as a colorless liquid which solidified on standing. Single crystals were obtained by slow sublimation at $50°C/10^{-2}$ mbar. Yield: 1.02 g (74%); mp: $58–61°C$; bp: $60°C/10^{-2}$ mbar. Raman (200 mW): $v = 3098$ (2), 3066 (2), 1619 (10), 1455 (2), 1267 (4), 1239 (2), 1160 (3), 1065 (3), 754 (1), 605 (2), 569 (3), 548 (2), 514 (2), 329 (2), 250 (3), 108 (6) cm^{-1}. IR (Nujol): $v = 3100$ vw, 3070 w, 1562 s, 1480 m, 1343 m, 1265 s, 1239 s, 1229 sh, 1160 m, 1152 m, 989 s, 910 s, 789 s, 732 m, 715 m, 645 w, 598 m, 566 m, 545 m, 512 s, 495 m, 442 m, 353 m cm^{-1}. ^1H NMR (C$_6$D$_6$): $\delta = 6.64$ (m, 1H, 4-H), 6.38 (m, 2H, 3-H). ^{13}C NMR (C$_6$D$_6$): $\delta = 164.9$ (dd, C-2, $^1J_{CF} = 253.3$ Hz, $^3J_{CF} = 10.9$ Hz), 135.1 (t, C-4, $^3J_{CF} = 11.4$ Hz), 116 (br, C-1), 111.3 (dm, C-3, $^2J_{CF} = 26.5$ Hz). ^{11}B NMR (C$_6$D$_6$): $\delta = 60.5$ (s). ^{19}F NMR (C$_6$D$_6$): $\delta = -99.9$ (m). Anal. Calcd. for $C_{12}H_6BClF_4$ (272.43): C, 52.9; H, 2.2. Found: C, 53.1; H, 2.5.

(C_6FH_4)$_2$BCl (**4**): 2.03 g (6.0 mmol) **2** were dissolved in 25 ml hexane. 6.0 ml of BCl$_3$ (1.0 M in hexane, 6.0 mmol) were added at $-78°C$ and the solution was stirred for 2 days

at ambient temperature. The formed Me_2SnCl_2 crystals were filtered off, the solvent was removed under vacuum and the residue was distilled yielding **4** as a colorless liquid. Yield: 0.98 g (69%); bp: 56–59°C/10^{-2} mbar.

Raman (200 mW): ν = 3074 (2), 1608 (10), 1479 (1), 1300 (1), 1218 (2), 1171 (2), 1153 (2), 1036 (4), 808 (1), 650 (2), 549 (1), 485 (1), 308 (1), 269 (1), 234 (1), 206 (1), 162 (3), 108 (4) cm^{-1}. IR: ν = 3077 m, 3027 w, 1607 vs, 1568 s, 1478 vs, 1442 vs, 1301 vs, 1281 vs, 1237 s, 1209 vs, 1173 m, 1151 m, 1098 m, 1032 w, 980 w, 950 m, 905 s, 864 m, 824 m, 811 m, 795 m, 759 vs, 721 m, 698 w, 648 m, 636 m, 610 m cm^{-1}. ^{1}H NMR (C_6D_6): δ = 7.68 (m, 1H), 7.03 (m, 1H), 6.83 (m, 1H), 6.72 (m, 1H). ^{13}C NMR (C_6D_6): δ = 166.6 (d, C-2, $^1J_{CF}$ = 253.9 Hz), 137.4 (d, C-6, $^3J_{CF}$ = 3.7 Hz), 135.5 (d, C-4, $^3J_{CF}$ = 11.2 Hz), 124.0 (d, C-5, $^4J_{CF}$ = 3.4 Hz), 115.5 (d, C-3, $^2J_{CF}$ = 24.8 Hz). ^{11}B NMR (C_6D_6): δ = 61.0 (s). ^{19}F NMR (C_6D_6): δ = −99.8 (m). Anal. Calcd. for $C_{12}H_8BClF_2$ (236.45): C, 61.0; H, 3.4. Found: C, 60.1; H, 3.9.

[$(CF_3)_3C_6H_2]_2BCl$ (**5**): Compound **5** was prepared according to [24]. Yield: 45%; mp: 62–65°C.

Raman (200 mW): ν = 3112 (3), 3075 (1), 1633 (8), 1462 (2), 1321 (1), 1150 (2), 1062 (5), 741 (10), 671 (2), 330 (1), 297 (3), 263 (7), 196 (3), 155 (7), 121 (2), 85 (1) cm^{-1}. IR: ν = 3110 m, 3049 vw, 1633 m, 1576 m, 1469 m, 1360 w, 1321 m, 1285 vs, 1279 vs, 1187 vs, 1130 vs, 1153 m, 1113 m, 1035 w, 953 m, 907 s, 842 m, 825 m, 776 m, 738 w, 686 m, 667 w, 605 w, 578 vw cm^{-1}. ^{1}H NMR (C_6D_6): δ = 7.77 (s). ^{13}C NMR (CD_2Cl_2): δ = 137.5 (q, C-4, $^2J_{CF}$ = 34.3 Hz), 135.0 (q, C-2, $^2J_{CF}$ = 34.6 Hz), 127.3 (s, C-3), 123.3 (q, o-CF_3, $^1J_{CF}$ = 273.5 Hz), 122.7 (q, p-CF_3, $^1J_{CF}$ = 271.5 Hz). ^{11}B NMR (C_6D_6): δ = 46.0 (s). ^{19}F NMR (C_6D_6): δ = −57.35, −57.40 (s, o-CF_3), −64.1 (s, p-CF_3). Anal. Calcd. for $C_{18}H_4BClF_{18}$ (608.46): C, 35.5; H, 0.7. Found: C, 34.8; H, 1.0.

$C_6F_2H_3BCl_2$ (**6**): Into a solution of 2.20 g (5.9 mmol) **1** in 30 ml hexane, 13.0 ml BCl_3 (1.0 M in hexane, 13.0 mmol) were added dropwise at −78°C. The solution was allowed to warm up slowly and was stirred for 2 days at ambient temperature. The formed Me_2SnCl_2 was filtered and the solvent was removed by vacuum evaporation leaving a yellowish liquid. Distillation afforded **6** as a colorless liquid. Yield: 1.42 g (62%); bp: 74–76°C/40 mbar.

Raman (200 mW): ν = 3098 (4), 3075 (3), 2923 (2), 1622 (10), 1456 (4), 1273 (3), 1213 (7), 1153 (4), 1066 (5), 735 (3), 599 (4), 525 (2), 407 (3), 353 (1), 327 (4), 242 (5), 205 (4), 97 (6) cm^{-1}. IR: ν = 3100 vw, 3058 vw, 2971 w, 1662 w, 1622 vs, 1582 m, 1562 s, 1457 vs, 1380 s, 1272 m, 1231 vs, 1213 s, 1172 m, 1153 m, 1113 w, 1051 w, 993 s, 965 m, 922 s, 902 s, 871 m, 832 m, 811 m, 790 s, 755 w, 732 m, 719 m, 638 w cm^{-1}. ^{1}H NMR (C_6D_6): δ = 6.64 (m, 1H, 4-H), 6.31 (m, 2H, 3-H). ^{13}C NMR (C_6D_6): δ = 164.5 (dd, C-2, $^1J_{CF}$ = 255.6 Hz, $^3J_{CF}$ = 9.2 Hz), 135.3 (t, C-4, $^3J_{CF}$ = 11.3 Hz), 111.1 (dm, C-3, $^2J_{CF}$ = 21.8 Hz). ^{11}B NMR (C_6D_6): δ = 54.0 (s). ^{19}F NMR (C_6D_6): δ = −98.7 (m). Anal. Calcd. for $C_6H_3BCl_2F_2$ (194.80): C, 37.0; H, 1.6. Found: C, 35.8; H, 2.2.

$C_6FH_4BCl_2$ (**7**): Compound **7** was prepared from 1.76 g (5.2 mmol) **2** and 13 ml BCl_3 (1.0 M in hexane, 13.0 mmol) following the method described for **6**. Distillation afforded **7** as a colorless liquid. Yield: 1.17 g (64%); bp: 61–65°C/24 mbar.

Raman (150 mW): ν = 3071 (4), 1609 (10), 1573 (3), 1479 (3), 1301 (3), 1219 (5), 1158 (3), 1133 (2), 1103 (3), 1080 (2), 1041 (6), 962 (2), 893 (2), 805 (3), 626 (3), 542 (3), 517 (3), 481 (3), 400 (3), 366 (6), 315 (4), 278 (4), 230 (5), 184 (4), 122 (5) cm^{-1}. IR: ν = 3081 w, 3033 w, 2966 w, 1609 vs, 1568 m, 1479 vs, 1443 vs, 1379 s, 1300 m, 1277 m, 1264 m, 1214 s, 1194 m, 1156 m, 1125 m, 1105 m, 1019 m, 955 m, 922 s, 904 s, 833 m, 804 m, 761 s, 732 m, 678 m, 645 m cm^{-1}. ^{1}H NMR (C_6D_6): δ = 7.66 (m, 1H), 6.94 (m, 1H), 6.38 (m, 2H). ^{13}C NMR (C_6D_6): δ = 167.8 (d, C-2, $^1J_{CF}$ = 260.6 Hz), 138.9 (d, C-6, $^3J_{CF}$ = 3.5 Hz), 137.4 (d, C-4, $^3J_{CF}$ = 10.0 Hz), 123.9 (d, C-5, $^4J_{CF}$ = 3.5 Hz), 120 (br, C-1), 116.3 (d, C-3, $^2J_{CF}$ = 24.2 Hz). ^{11}B NMR (C_6D_6): δ = 53.0 (s). ^{19}F NMR (C_6D_6): δ = −97.9 (m). Anal. Calcd. for $C_6H_4BCl_2F$ (176.81): C, 40.8; H, 2.3. Found: C, 41.7; H, 2.9.

[$(C_6F_2H_3)_2BN_3]_2$ (**8**): 0.10 ml Me_3SiN_3 (0.8 mmol) were added to a solution of 0.17 g (0.62 mmol) **3** in 10 ml CH_2Cl_2 at −78°C. After additional stirring for 3 h at ambient temperature the solvent and all volatile components were removed by vacuum evaporation leaving a colorless solid. Recrystallization from CH_2Cl_2 afforded **8** as colorless crystalline solid. Yield: 0.14 g (81%); mp: 104–107°C (decomp.).

Raman (150 mW): ν = 3091 (5), 3071 (5), 2207 (6, $\nu_{asym}N_3$), 1619 (9), 1458 (2), 1353 (2), 1250 (8), 1151 (6), 1062 (7), 747 (6), 729 (3), 712 (3), 597 (2), 563 (6), 548 (3), 533 (3), 517 (3), 450 (5), 376 (4), 341 (6), 281 (4), 255 (8), 244 (6), 182 (3), 160 (4), 135 (7), 93 (10) cm^{-1}. IR (Nujol): ν = 3100 vw, 3085 vw, 2202 s (ν_{asym}-N_3), 1620 s, 1584 m, 1558 m, 1446 vs, 1286 s, 1247 s, 1229 s, 1146 m, 985 s, 897 m, 788 m, 731 m, 697 m, 634 m, 549 m, 509 m, 379 m, 366 m cm^{-1}. ^{1}H NMR (C_6D_6): δ = 7.45 (m, 1H, 4-H), 6.93 (m, 2H, 3-H). ^{13}C NMR (C_6D_6): δ = 165.6 (dd, C-2, $^1J_{CF}$ = 249.8 Hz, $^3J_{CF}$ = 12.3 Hz), 134.8 (t, C-4, $^3J_{CF}$ = 11.2 Hz), 111.7 (dm, C-3, $^2J_{CF}$ = 25.7 Hz). ^{11}B NMR (C_6D_6): δ = 44.5 (s). ^{19}F NMR (C_6D_6): δ = −103.9 (m). ^{14}N NMR (C_6D_6; $\Delta\nu_{1/2}$): δ = −147 (30 Hz, N_β), −212 (40 Hz, N_γ), −317 (300 Hz, N_α). Anal. Calcd. for $C_{24}H_{12}B_2F_8N_6$ (558.00): C, 51.7; H, 2.3; N, 15.1. Found: C, 51.1; H, 2.7; N, 13.8.

$(C_6FH_4)_2BN_3$ (**9**): Compound **9** was prepared from 0.25 g (1.06 mmol) **4** and 0.14 ml Me_3SiN_3 (1.1 mmol) in 10 ml CH_2Cl_2. After additional stirring for 3 h at ambient temperate the solvent and all volatile components were removed by vacuum evaporation leaving a colorless liquid. The crude product was condensed in a cooled vessel giving **9** as a colorless liquid. Yield: 0.20 g (77%); bp: ∼90°C/10^{-3} mbar.

Raman (200 mW): ν = 3214 (1), 3064 (7), 2140 (2, $\nu_{asym}N_3$), 1610 (10), 1481 (1), 1330 (2), 1216 (2), 1155 (3), 1034 (6), 821 (2), 767 (2), 543 (3), 403 (3), 332 (3), 284

(3), 240 (3), 198 (4), 185 (6), 139 (6), 114 (8) cm^{-1}. IR: ν = 3076 m, 3060 m, 3025 w, 2165 vs/2135 vs ($\nu_{asym}N_3$), 1609 vs, 1568 vs, 1479 vs, 1443 vs, 1336 vs, 1300 vs, 1266 vs, 1208 vs, 1181 m, 1153 s, 1138 m, 1092 s, 1003 m, 958 s, 913 s, 905 s, 847 s, 822 s, 796 s, 759 vs, 712 m, 693 m, 636 m, 611 m, 589 w, 523 m cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ = 7.35 (m, 1H), 7.00 (m, 1H), 6.78 (m, 2H). ^{13}C NMR (C$_6$D$_6$): δ = 167.8 (d, C-2, $^1J_{CF}$ = 250.1 Hz), 136.3 (d, C-6, $^3J_{CF}$ = 5.7 Hz), 134.3 (d, C-4, $^3J_{CF}$ = 9.2 Hz), 124.2 (d, C-5, $^4J_{CF}$ = 3.1 Hz), 115.8 (d, C-3, $^2J_{CF}$ = 23.8 Hz). ^{11}B NMR (C$_6$D$_6$): δ = 47.5 (s). ^{19}F NMR (C$_6$D$_6$): δ = −103.1 (m). ^{14}N NMR (C$_6$D$_6$; $\Delta\nu_{1/2}$): δ = −144 (120 Hz, N$_\beta$), −167 (300 Hz, N$_\gamma$), −282 (900 Hz, N$_\alpha$). Anal. Calcd. for C$_{12}$H$_8$BF$_2$N$_3$ (243.02): C, 59.3; H, 3.3; N, 17.3. Found: C, 60.1; H, 3.9; N, 16.3.

[(CF$_3$)$_3$C$_6$H$_2$]$_2$BN$_3$ (**10**): Into a solution of 1.22 g (2.0 mmol) **5** in 10 ml hexane, 1.3 ml Me$_3$SiN$_3$ (10.0 mmol) were added at 25°C. After the solution was stirred for 14 days at ambient temperature, all volatile materials were removed by vacuum evaporation leaving **10** as a colorless solid which was analyzed without further purification. Yield: 1.17 g (95%); mp: 59–62°C.

Raman (200 mW): ν = 3110 (4), 3079 (3), 2149 (2, $\nu_{asym}N_3$), 1633 (9), 1458 (2), 1386 (3), 1382 (2), 1217 (1), 1190 (3), 1161 (3), 1145 (2), 1097 (2), 1083 (3), 741 (10), 500 (2), 306 (4), 261 (7), 204 (5), 196 (5), 152 (9), 106 (5) cm^{-1}. IR: ν = 3108 vw, 3055 vw, 2143 s ($\nu_{asym}N_3$), 1633 w, 1579 w, 1464 vw, 1367 s, 1322 m, 1288 vs, 1279 vs, 1197 vs, 1150 m, 1128 vs, 1032 (s), 918 s, 884 m, 862 m, 840 m, 801 m, 774 vw, 737 vw, 706 m, 686 s, 673 m, 666 w, 641 m, 605 vw, 480 vw cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ = 7.85 (s). ^{13}C NMR (C$_6$D$_6$): δ = 137.9 (q, C-4, $^2J_{CF}$ = 33.6 Hz), 134.9 (q, C-2, $^2J_{CF}$ = 34.4 Hz), 127.9 (s, C-3), 124.3 (q, *o*-CF$_3$, $^1J_{CF}$ = 273.8 Hz), 123.5 (q, *p*-CF$_3$, $^1J_{CF}$ = 271.9 Hz). ^{11}B NMR (C$_6$D$_6$): δ = 49.3 (s). ^{19}F NMR (C$_6$D$_6$): δ = −56.9 (s, *o*-CF$_3$), −64.7 (s, *p*-CF$_3$). ^{14}N NMR (C$_6$D$_6$; $\Delta\nu_{1/2}$]: δ = −149 (220 Hz, N$_\beta$), −153 (310 Hz, N$_\gamma$), N$_\alpha$ not detected. Anal. Calcd. for C$_{18}$H$_4$BF$_{18}$N$_3$ (615.03): C, 35.2; H, 0.7; N, 6.8. Found: C, 34.9; H, 1.0; N, 6.0. Single crystals of **10a** were obtained by recrystallization of **10** from a cooled hexane solution.

C$_6$F$_2$H$_3$B(N$_3$)$_2$ (**11**): Compound **11** was prepared from 0.28 g (1.4 mmol) **6** and 0.4 ml Me$_3$SiN$_3$ (3.0 mmol) following the method described for **9**. Yield: 0.22 g (73%); mp: 0–2°C; bp: ∼85°C/10^{-3} mbar.

Raman (150 mW; 25°C): ν = 3098 (4), 3073 (4), 3062 (5), 2168/2157/2145 (3–5, $\nu_{asym}N_3$), 1623 (8), 1459 (2), 1347 (1), 1262 (4), 1216 (8), 1152 (3), 1065 (7), 763 (1), 697 (1), 643 (3), 599 (2), 559 (6), 512 (1), 462 (2), 446 (1), 377 (4), 350 (1), 247 (6), 216 (2), 147 (9) 116 (10) cm^{-1}. Raman (150 mW; 0°C): ν = 3095 (3), 3073 (3), 2979 (1), 2208 (3, $\nu_{asym}N_3$ bridge), 2166/2146 (1, $\nu_{asym}N_3$ terminal), 1678 (2), 1623 (7), 1457 (3), 1331 (4), 1258 (5), 1220 (4), 1152 (4), 1067 (5), 1016 (3), 955 (2), 810 (3), 747 (3), 708 (3), 657 (3), 645 (3), 601 (3), 539 (5), 510 (4), 378 (6), 341 (6), 247 (9), 140 (10), 116 (9) cm^{-1}. IR (25°C): ν = 3095 vw, 2146 vs

($\nu_{asym}N_3$), 2065 w, 1623 s, 1583 m, 1566 m, 1456 vs, 1334 sh, 1262 m, 1226 m, 1167 m, 1151 m, 1075 m, 987 s, 875 m, 833 m, 809 m, 789 s, 721 m, 692 m, 671 m, 643 m, 610 m cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ = 6.61 (m, 1H, 4-H), 6.37 (m, 2H, 3-H). ^{13}C NMR (C$_6$D$_6$): δ = 165.0 (dd, C-2, $^1J_{CF}$ = 249.4 Hz, $^3J_{CF}$ = 12.3 Hz), 134.5 (t, C-4, $^3J_{CF}$ = 10.8 Hz), 111.6 (dm, C-3, $^2J_{CF}$ = 22.0 Hz). ^{11}B NMR (C$_6$D$_6$): δ = 36.5 (s). ^{19}F NMR (C$_6$D$_6$): δ = −102.2 (m). ^{14}N NMR (C$_6$D$_6$; $\Delta\nu_{1/2}$) δ = −148 (60 Hz, N$_\beta$), −170 (80 Hz, N$_\gamma$), −281 (600 Hz, N$_\alpha$).

C$_6$FH$_4$B(N$_3$)$_2$ (**12**): Compound **12** was prepared from 0.25 g (1.4 mmol) **7** and 0.4 ml Me$_3$SiN$_3$ (3.0 mmol) following the method described for **9**. Yield: 0.20 g (75%); bp: ∼84°C/10^{-3} mbar.

Raman (150 mW): ν = 3073 (6), 2165, 2147, 2138 (1–3, $\nu_{asym}N_3$), 1613 (10), 1483 (1), 1379 (1), 1222 (6), 1159 (2), 1070 (1), 1032 (4), 816 (1), 716 (1), 615 (1), 543 (2), 495 (1), 355 (4), 268 (3), 241 (3), 193 (6), 184 (6), 149 (6), 130 (10) cm^{-1}. IR: ν = 3081 w, 2141 ($\nu_{asym}N_3$) vs, 1612 m, 1570 m, 1482 m, 1444 s, 1370 m, 1319 sh, 1265 m, 1219 m, 1155 m, 1067 m, 1034 m, 975 m, 819 m, 761 m, 683 w, 659 m, 603 m, 578 w, 542 w, 517 w cm^{-1}. ^{1}H NMR (C$_6$D$_6$): δ = 7.32 (m, 1H), 6.90 (m, 1H), 6.69 (m, 2H). ^{13}C NMR (C$_6$D$_6$): δ = 166.2 (d, C-2, $^1J_{CF}$ = 249.1 Hz), 135.6 (d, C-6, $^3J_{CF}$ = 6.7 Hz), 134.5 (d, C-4, $^3J_{CF}$ = 8.8 Hz), 124.0 (d, C-5, $^4J_{CF}$ = 3.1 Hz), 115.4 (d, C-3, $^2J_{CF}$ = 24.4 Hz). ^{11}B NMR (C$_6$D$_6$): δ = 36.0 (s). ^{19}F NMR (C$_6$D$_6$): δ = −102.2 (m). ^{14}N NMR (C$_6$D$_6$; $\Delta\nu_{1/2}$): δ = −148 (60 Hz, N$_\beta$), −173 (120 Hz, N$_\gamma$), −287 (600 Hz, N$_\alpha$).

4.2. General procedure for the preparation of (R$_F$)$_2$BN$_3$·py (**13** and **14**) and R$_F$B(N$_3$)$_2$·py (**15** and **16**)

Into solutions of (R$_F$)$_2$BCl/R$_F$BCl$_2$ in CH$_2$Cl$_2$, stoichiometric amounts of Me$_3$SiN$_3$ (1:1, 1:2) and pyridine (1:1) were added at −78°C. After additional stirring for 3 h at ambient temperature, all volatile materials were removed in vacuo and the crude products were recrystallized from cooled CH$_2$Cl$_2$ solutions. The adducts were obtained as colorless solids in 80–90% yield.

(C$_6$F$_2$H$_3$)$_2$BN$_3$·py (**13**): Yield 80%; mp: 100–105°C (decomp.).

Raman (200 mW) ν = 3094 (10), 3044 (3), 2123 (1, $\nu_{asym}N_3$), 1627 (3), 1615 (6), 1575 (2), 1343 (2), 1254 (3), 1211 (2), 1149 (3), 1060 (3), 1028 (10), 755 (2), 640 (3), 557 (3), 402 (4), 251 (5), 215 (4), 98 (8) cm^{-1}. IR (Nujol, selected absorptions): ν = 3084 m, 2127 vs ($\nu_{asym}N_3$), 1626 s, 1562 vs, 1491 vs, 1438 vs, 1342 vs, 1282 vs, 1161 s, 1098 vs, 973 vs, 820 vs, 791 vs, 773 vs, 717 s, 690 vs, 658 s, 536 vs, 370 vs cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 8.77 (m, 2H, py), 8.06 (m, 1H, py), 7.61 (m, 2H, py), 7.18 (m, 2H), 6.74 (m, 4H). ^{13}C NMR (CDCl$_3$): δ = 156.2 (dd, C-2, $^1J_{CF}$ = 243.7 Hz, $^3J_{CF}$ = 13.5 Hz), 144.7 (s, C$_{py}$), 142.3 (s, C$_{py}$), 131.0 (t, C-4, $^3J_{CF}$ = 11.3 Hz), 125.7 (s, C$_{py}$), 111.4 (dm, C-3, $^2J_{CF}$ = 22.4 Hz). ^{11}B NMR (CDCl$_3$): δ = −2.5 (s). ^{19}F NMR (CDCl$_3$): δ = −103.7 (m). ^{14}N

NMR (CDCl$_3$; $\Delta\nu_{1/2}$): $\delta = -140$ (1200 Hz, N$_{py}$), -141 (90 Hz, N$_\beta$), -208 (180 Hz, N$_\gamma$), -313 (780 Hz, N$_\alpha$). Anal. Calcd. for C$_{17}$H$_{11}$BF$_4$N$_4$ (358.10): C, 57.1; H, 3.1; N, 15.7. Found: C, 57.8; H, 3.6; N, 14.4.

(C$_6$FH$_4$)$_2$BN$_3$·py (**14**): Yield (90%); mp: 98–102°C (decomp.).

Raman (200 mW): $\nu = 3097$ (3), 3069 (6), 2128 (1, ν_{asym}N$_3$), 1621 (3), 1604 (4), 1573 (1), 1438 (1), 1338 (1), 1289 (1), 1266 (1), 1208 (3), 1199 (3), 1155 (1), 1138 (2), 1099 (2), 1036 (5), 1026 (10), 804 (2), 791 (2), 769 (1), 726 (1), 678 (1), 647 (1), 615 (1), 538 (2), 498 (1), 483 (1), 383 (2), 298 (2), 268 (2), 228 (3), 207 (4), 189 (3), 172 (5), 118 (6) cm^{-1}. IR (Nujol, selected absorptions): $\nu = 3065$ vs, 2125 vs (ν_{asym}N$_3$), 1621 s, 1603 s, 1564 s, 1472 s, 1455 s, 1435 vs, 1360 vs, 1338 vs, 1289 s, 1241 vs, 1198 vs, 1094 s, 1025 s, 984 vs, 821 s, 792 s, 762 vs, 692 vs, 645 s, 614 s, 578 m, 532 s cm^{-1}. ^{1}H NMR (CDCl$_3$): $\delta = 8.83$ (m, 2H, py), 8.70 (m, 1H, py), 8.01 (m, 2H, py) 7.55 (m, 2H), 7.28 (m, 2H), 7.19 (m, 2H), 6.92 (m, 2H). ^{13}C NMR (CDCl$_3$): $\delta = 165.5$ (d, C-2, $^1J_{CF} = 241.6$ Hz), 145.5 (s, C$_{py}$), 141.5 (s, C$_{py}$), 135.5 (d, C-6, $^3J_{CF} = 10.7$ Hz), 129.5 (d, C-4, $^3J_{CF} = 9.2$ Hz), 125.3 (s, C$_{py}$), 123.8 (d, C-5, $^4J_{CF} = 3.1$ Hz), 114.7 (d, C-3, $^2J_{CF} = 24.6$ Hz). ^{11}B NMR (CDCl$_3$): $\delta = 2.0$ (s). ^{19}F

NMR (CDCl$_3$): $\delta = -104.7$ (m). ^{14}N NMR (CDCl$_3$; $\Delta\nu_{1/2}$): $\delta = -140$ (1500 Hz, N$_{py}$) -142 (150 Hz, N$_\beta$), -212 (300 Hz, N$_\gamma$), -308 (900 Hz, N$_\alpha$). Anal. Calcd. for C$_{17}$H$_{13}$BF$_2$N$_4$ (322.12): C, 63.4; H, 4.1; N, 17.4. Found: C, 62.5; H, 4.0; N, 15.9.

C$_6$F$_2$H$_3$B(N$_3$)$_2$·py (**15**): Yield 84%; mp: 67–70°C.

Raman (100 mW): $\nu = 3098$ (7), 2142/2118 (1, ν_{asym}N$_3$), 1628 (2), 1577 (1), 1341 (2), 1245 (1), 1210 (2), 1149 (1), 1072 (2), 1028 (10), 1005 (4), 645 (2), 548 (1), 430 (2), 395 (2), 251 (6), 231 (3), 128 (6) cm^{-1}. IR (Nujol, selected absorptions): $\nu = 3104$ w, 3068 w, 2144 s/2128 s (ν_{asym}N$_3$), 1615 s, 1488 m, 1459 vs, 1444 vs, 1379 s, 1300 s, 1248 s, 1223 vs, 1138 m, 1089 s, 985 s, 840 s, 788 s, 698 m, 610 s cm^{-1}. ^{1}H NMR (CDCl$_3$): $\delta = 8.79$ (m, 2H, py), 8.19 (m, 1H, py), 7.74 (m, 2H, py), 7.20 (m, 1H), 6.75 (m, 2H). ^{13}C NMR (CDCl$_3$): $\delta = 165.4$ (dd, C-2, $^1J_{CF} = 245.2$ Hz, $^3J_{CF} = 13.8$ Hz), 144.4 (s, C$_{py}$), 142.8 (s, C$_{py}$), 130.7 (t, C-4, $^3J_{CF} = 11.1$ Hz), 126.0 (s, C$_{py}$), 111.4 (dm, C-3, $^2J_{CF} = 22.3$ Hz). ^{11}B NMR (CDCl$_3$): $\delta = 2.0$ (s). ^{19}F NMR (CDCl$_3$): $\delta = -105.0$ (m). ^{14}N NMR (CDCl$_3$; $\Delta\nu_{1/2}$): $\delta = -142$ (90 Hz, N$_\beta$), -146 (1100 Hz, N$_{py}$), -212 (180 Hz, N$_\gamma$), -317 (600 Hz, N$_\alpha$). Anal. Calcd. for C$_{11}$H$_8$BF$_2$N$_7$ (287.04): C, 46.0; H, 2.8; N, 34.2. Found: C, 45.3; H, 2.3; N, 32.9.

Table 1
Crystal data and structure refinements

	1	3	8	10a	14
Empirical formula	C$_{14}$H$_{12}$F$_4$Sn	C$_{12}$H$_6$BClF$_4$	C$_{24}$H$_{12}$B$_2$F$_8$N$_6$	C$_{36}$H$_9$B$_2$F$_{36}$N$_3$O	C$_{17}$H$_{13}$BF$_2$N$_4$
Formula mass	374.95	272.43	558.00	1205.04	322.12
Temperature (K)	200(3)	193	200(3)	200(3)	200(2)
Crystal size (mm)	0.40 × 0.35 × 0.15	0.10 × 0.10 × 0.10	0.25 × 0.19 × 0.03	0.19 × 0.13 × 0.07	0.30 × 0.06 × 0.05
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$[a]	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	10.277(1)	12.211(1)	8.554(2)	15.1923(2)	9.7607(5)
b (Å)	11.344(1)	9.0361(8)	8.966(2)	8.3995(1)	8.9463(5)
c (Å)	11.929(1)	10.3571(9)	9.717(2)	33.6148(6)	18.1494(1)
B (°)		93.041(2)	65.08(2)[b]	101.609(1)	95.041(2)
V (Å^3)	1390.8(3)	1141.2(2)	579.6(2)	4201.8(1)	1578.7(1)
Z	4	4	1	4	4
Density (calculated) (g/cm^3)	1.791	1.586	1.599	1.905	1.355
Absorption coefficient (mm^{-1})	1.865	0.362	0.143	0.226	0.099
$F(0\,0\,0)$	728	544	280	2352	664
θ range (°)	2.78–27.97	1.67–29.37	2.46–28.05	1.24–25.00	3.09–27.48
Index range	$-13 \leq h \leq 13$	$-15 \leq h \leq 15$	$-11 \leq h \leq 11$	$-18 \leq h \leq 17$	$-12 \leq h \leq 11$
	$-14 \leq k \leq 14$	$-11 \leq k \leq 11$	$-11 \leq k \leq 11$	$-9 \leq k \leq 9$	$-11 \leq k \leq 11$
	$-15 \leq l \leq 15$	$-13 \leq l \leq 13$	$-11 \leq l \leq 12$	$-39 \leq l \leq 38$	$-22 \leq l \leq 23$
Reflections collected	10817	6525	4982	39716	12290
Independent reflections	3305 ($R_{int} = 0.0580$)	2325 ($R_{int} = 0.0285$)	2571 ($R_{int} = 0.0478$)	7375 ($R_{int} = 0.1037$)	3565 ($R_{int} = 0.0959$)
Observed reflections	2359	1695	1396	4430	1950
Maximum and minimum transmission	0.7715, 0.5470	0.9828, 0.6576	0.9814, 0.9961		
Data/restraints/parameters	3305/0/174	2325/0/187	2571/0/205	7375/0/787	3565/0/269
Goodness-of-fit, F^2	0.907	1.034	0.832	1.076	1.008
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0252, 0.0641	0.0389, 0.1017[c]	0.0400, 0.0765	0.0700, 0.1882	0.0624, 1099
$R1$, $wR2$ (all data)	0.0392, 0.0681	0.0592, 0.1128	0.0930, 0.0885	0.1295, 0.2252	0.1364, 0.1350
Largest difference peak/hole (e/Å^3)	0.256/−0.442	0.157/−0.305	0.267/−0.200	0.714/−0.392	0.208/−0.196

[a] Flack parameter: −0.03(5).

[b] $\alpha = 63.16(2)$, $\gamma = 65.98(2)$.

[c] $I > 4\sigma(I)$.

$C_6FH_4B(N_3)_2 \cdot py$ (**16**): Yield 81%; mp: 65–70°C.

Raman (200 mW): $v = 3091$ (4), 3063 (4), 2139/2130/2112 (1–2, $v_{asym}N_3$), 1624 (2), 1609 (3), 1577 (2), 1480 (1), 1335 (2), 1212 (2), 1152 (1), 1095 (1), 1026 (10), 1005 (3), 805 (1), 734 (1), 648 (2), 541 (1), 495 (2), 360 (1), 300 (3), 264 (2), 236 (3), 114 (7) cm^{-1}. IR (Nujol, selected absorptions): $v = 3063$ w, 2962 m, 2127 vs ($v_{asym}N_3$), 1609 m, 1570 m, 1459 s, 1401 m, 1370 s, 1335 s, 1260 m, 1199 m, 1091 m, 903 m, 801 m, 765 m, 691 m, 607 w, 534 w cm^{-1}. ^1H NMR (CDCl$_3$): $\delta = 8.70$ (m, 2H, py), 8.16 (m, 1H, py), 7.70 (m, 2H, py), 7.61 (m, 1H), 7.22 (m, 1H), 7.10 (m, 1H), 6.82 (m, 1H). ^{13}C NMR (CDCl$_3$): $\delta = 165.0$ (d, C-2, $^1J_{CF} = 242.2$ Hz), 144.1 (s, C$_{py}$), 142.6 (s, C$_{py}$), 134.3 (d, C-6, $^3J_{CF} = 9.2$ Hz), 130.4 (d, C-4, $^3J_{CF} = 8.5$ Hz), 125.8 (s, C$_{py}$), 123.8 (d, C-5, $^4J_{CF} = 3.1$ Hz), 114.7 (d, C-3, $^2J_{CF} = 24.6$ Hz). ^{11}B NMR (CDCl$_3$): $\delta = 3.0$ (s). ^{19}F NMR (CDCl$_3$): $\delta = -108.6$ (m). ^{14}N NMR (CDCl$_3$; $\Delta v_{1/2}$): $\delta = -135$ (1400 Hz, N$_{py}$), -141 (90 Hz, N$_\beta$), -204 (150 Hz, N$_\gamma$), -316 (900 Hz, N$_\alpha$). Anal. Calcd. for C$_{11}$H$_9$BFN$_7$ (269.05): C, 49.1; H, 3.4; N, 36.4. Found: C, 48.4; H, 2.9; N, 35.1.

4.3. X-ray crystallography

Data for compounds **1** and **8** were collected on a Stoe IPDS image plate area detector, for compound **3** on a Siemens SMART CCD detector and for compounds **10a** and **14** on a KappaCCD using Mo-Kα-radiation. The structures were solved by direct methods (SHELXS '97) [32,33] and refined by means of full-matrix least squares on F^2 using SHELXL 97. Hydrogen atoms were omitted in all figures (Table 1).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 157863 (**8**), 157864 (**14**), 157865 (**10a**), 157866 (**3**) and 157867 (**1**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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