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Oligomeric pentafluorophenylboron azides

Wolfgang Fraenk, Thomas M. Klapötke,* Burkhard Krumm, Heinrich Nöth, Max Suter and Marcus Warchhold

Department of Chemistry, Ludwig-Maximilians University of Munich, Butenandtstr. 5-13 (D), D-81377 Munich, Germany. Fax: (+49) 89-2180-7492; E-mail: tmk@cup.uni-muenchen.de

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The dichloroborane $C_6F_5BCl_2$ reacted with two equivalents trimethylsilyl azide to form $C_6F_5B(N_3)_2$ which trimerizes in the solid state to give $[C_6F_5B(N_3)_2]_3$ **1**, the first example of an azido substituted *N,N′,N″*-tris(diazo)triazatriboratacyclohexane. Its monomer was trapped by pyridine yielding $C_6F_5B(N_3)_2{\cdot}py$ **2**. This is in contrast to $(BF_2N_3)_3$ **3** which is trimeric in solution and in the solid state, as shown by ^{11}B NMR spectroscopy.

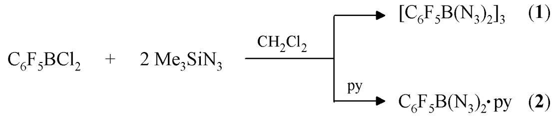
Introduction

The chemistry of boron azides commenced in 1954 with the synthesis of boron triazide and lithium tetraazidoborate.[1] Over the next decades mainly Paetzold and co-workers extensively studied their chemistry.[2a–d,3] The preparation and thermally promoted decomposition of boron azides leads, depending on the nature of the substituents, to iminoboranes, diazadiboretidines or borazines.[2c,3] Cryoscopic mass determination as well as X-ray diffraction studies on boron azides showed that these species are monomeric except for the trimeric boron dihalide azides $(BX_2N_3)_3$ (X = F, Cl or Br).[2c,4a–d]

Recently we reported on the irreversible dimerization of bis(pentafluorophenyl)boron azide, which was first indicated in 1983, being the first example of a *N,N′*-diazodiazadiboratacyclobutane.[5,6] In this report we present results of further exploration of this chemistry, the reversible trimerization of the new pentafluorophenylboron diazide $[C_6F_5B(N_3)_2]_3$ **1**, the first example of an azido *N,N′,N″*-tris(diazo)triazatriboratacyclohexane, and trapping of its monomer by pyridine yielding the adduct $C_6F_5B(N_3)_2{\cdot}py$ **2**. Here, the unique case of structural characterization of both monomeric and trimeric $C_6F_5B(N_3)_2$ is accomplished. Furthermore, not reported NMR data of the known $(BF_2N_3)_3$ **3** are given. The influence of electron-withdrawing substituents on the electron deficient boron atom and the difference between halogeno and multiply substituted pentafluorophenyl boron azides is discussed.

Results and discussion

Pentafluorophenylboron dichloride[7] was treated with two equivalents trimethylsilyl azide in a dichloromethane solution (eqn. 1). The diazide **1** was obtained as a colorless, highly



$$C_6F_5BCl_2 + 2\,Me_3SiN_3 \xrightarrow{CH_2Cl_2} [C_6F_5B(N_3)_2]_3\ (\mathbf{1}); \quad \xrightarrow{py} C_6F_5B(N_3)_2{\cdot}py\ (\mathbf{2})$$

moisture sensitive, explosive solid with a melting point of 36–39 °C. It is soluble in benzene and dichloromethane but insoluble in hexane and decomposes in chloroform. The ^{11}B NMR spectrum shows a resonance at δ 34.6, which is in the region for three-coordinated boron[8] and is in contrast to the resonance of δ 0.5 observed for trimeric $(BF_2N_3)_3$ **3**. In the ^{14}N NMR spectrum of **1** three resonances for the two azide groups (see Table 1) and in the ^{19}F NMR spectrum three resonances for the fluorine atoms of the pentafluorophenyl groups are found. These findings suggest the formation of monomeric $C_6F_5B(N_3)_2$ but differ from the solid state of **1**, shown by IR, Raman and X-ray diffraction, proving solid **1** as a trimeric boron diazide (Fig. 1). (Note: a low-temperature NMR spectrum is not possible due to the low solubility of trimeric **1**.)

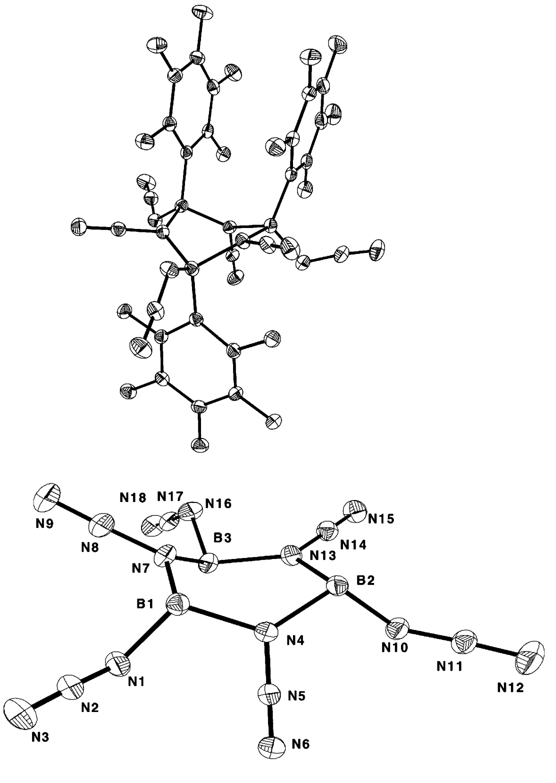


Fig. 1 Top: Molecular structure of **1** with thermal ellipsoids drawn at the 25% probability level. Bottom: View of the $B(N_3)_2$ units, showing the B_3N_3 heterocycle of **1** with thermal ellipsoids drawn at the 25% probability level. Selected bond lengths (Å) and angles (°): B(1)–N(1) 1.501(3), N(1)–N(2) 1.229(3), N(2)–N(3) 1.129(2), B(1)–N(4) 1.602(3), B(1)–N(7) 1.602(3), N(4)–N(5) 1.271(2), N(5)–N(6) 1.108(2), C(1)–B(1) 1.619(3), N(1)–N(2)–N(3) 174.6(2), N(4)–N(5)–N(6) 178.8(2), B(1)–N(1)–N(2) 121.4(2), B(1)–N(4)–N(5) 115.8(2), N(7)–B(1)–N(4) 98.5(2), B(1)–N(4)–B(2) 125.8(2).

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Table 1 Selected spectroscopic data of oligomeric boron azides[a]

Compound	$\delta\,^{11}B$	$\delta\,^{14}N$ (N_β,N_γ,N_α)	$\tilde{\nu}_{asym}(N_3)$/cm^{-1} IR/Raman	mp/°C	Ref.
$(BF_2N_3)_3$	0.5	−154, −175, −300	2208, 2154/2236	50	9, This work
$(BCl_2N_3)_3$	n.r.	n. r.	2219, 2210/2219, 2210	67	10
$(BBr_2N_3)_3$	n.r.	n. r.	2215, 2200/2215, 2200	94.5	10
Me_2BN_3[b]	62/4.9	n. r.	2128	54[c]	2(*b*), 2(*c*)
$[(C_6F_5)_2BN_3]_2$[d]	43.9	−144, −160, −322	2202/2209	76–80 (decomp)	6
$[C_6F_5B(N_3)_2]_3$[d]	34.6	−149, −168, −277	2200, 2180, 2142/2206, 2169, 2135	36–39	This work

[a] An oligomeric structure is also predicted for solid $B(N_3)_3$.[1,2*b*] [b] Shows a temperature dependent oligomerization.[2*c*] [c] 720 Torr (bp). [d] In solution monomer.

Table 2 Selected bond lengths [Å] and angles [°] of oligomeric boron azides (average values)

Compound	B–N	N_α–N_β	N_β–N_γ	N–N–N	B–N–N	Ref.
$(BCl_2N_3)_3$	1.58	1.25	1.09	178	116	10
$[(C_6F_5)_2BN_3]_2$	1.60	1.24	1.11	178	130	6
$[C_6F_5B(N_3)_2]_3$[a]	1.50	1.23	1.13	175	121	This work
	1.60	1.27	1.11	179	116	

[a] Top column: terminal azide groups. Bottom column: bridging azide groups.

The triazatriborata heterocycle shows a slightly twisted boat conformation (Fig. 1) comparable with that found for $(BCl_2N_3)_3$.[4*d*] The X-ray study nicely displays the difference between bridging and terminal azide groups. The B–N_{ring} distances of 1.60 Å (Table 2) are longer than the B–N distances of 1.50 Å found for the covalently bound azide groups, which correspond to typical B–N single bonds. A difference is also observed for the N–N–N angles of the azide groups and the N_β–N_γ distances. The bridging azide groups are close to linearity (N–N–N 178–179°), the other azide groups are slightly bent with an N–N–N angle of 175° which is in accord with the structures of other boron azides previously determined.[4] The N_β–N_γ distance of 1.11 Å (N≡N 1.098 Å) found for the bridging azide groups is shorter than for the corresponding distance found for the terminal azide groups N_β–N_γ 1.13 Å. The vibrational spectra also reveal the presence of two different azide species. The Raman spectrum of solid **1** shows three absorptions in the region of the antisymmetric stretching vibration of the azide group ($\nu_{asym}N_3$) at 2206, 2169 and 2135 cm^{-1}. The absorption shifted to a higher wavenumber at 2206 cm^{-1} corresponds to the bridging azide groups ($\nu_{asym}N_3$: $(BF_2N_3)_3$ 2236,[9] $[(C_6F_5)_2BN_3]_2$ 2209 cm^{-1}[6]), the other to terminal azide groups. In the IR spectrum $\nu_{asym}N_3$ vibrations were found at 2200, 2180 and 2142 cm^{-1}. The low melting point of **1**, which suggests the dissociation of the trimer, encouraged us to observe **1** in the liquid phase at 40 °C by Raman spectroscopy (Fig. 2). The characteristic absorption for $\nu_{asym}N_3$ at 2206 cm^{-1} for the bridging azide groups disappears and the $\nu_{asym}N_3$ bands were now found at 2170 and 2156 cm^{-1} which confirms the dissociation of **1** into monomeric $C_6F_5B(N_3)_2$. Bis(pentafluorophenyl)boron azide decomposes at its melting point and therefore monomeric $(C_6F_5)_2BN_3$ can only be detected in solution. Characteristic data of oligomeric boron azides, that are known to our knowledge, are listed in Tables 1 and 2.

The reaction of $C_6F_5BCl_2$ with trimethylsilyl azide in the presence of pyridine yielded a stable adduct $C_6F_5B(N_3)_2{\cdot}py$ **2**, a non-explosive solid being soluble in toluene, dichloromethane and chloroform but insoluble in hexane. The crystal structure of **2** (Fig. 3) revealed the monomeric nature of pentafluorophenylboron diazide–pyridine. The B–N_α distance of 1.54 Å is comparable with the corresponding distance found for **1**, the B–N_{py} distance of 1.61 Å is similar to the B–N_{ring} distance in **1**. The N_α–N_β (1.21 Å) and the N_β–N_γ (1.14 Å) bond distances are between a N–N double (1.24 Å) and a N–N triple bond (1.098 Å). The Raman and the IR spectrum show both the characteristic $\nu_{asym}N_3$ vibrations at 2146 and 2130 cm^{-1} (IR $\nu_{asym}N_3$: $C_6H_5B(N_3)_2{\cdot}py$ 2120/2090 cm^{-1}[12*d*]). The ^{11}B NMR resonance is found at δ 1.4, a region typical for four-coordinated boron; the ^{14}N NMR spectrum shows four resonances for the azide and the pyridine nitrogen atoms.

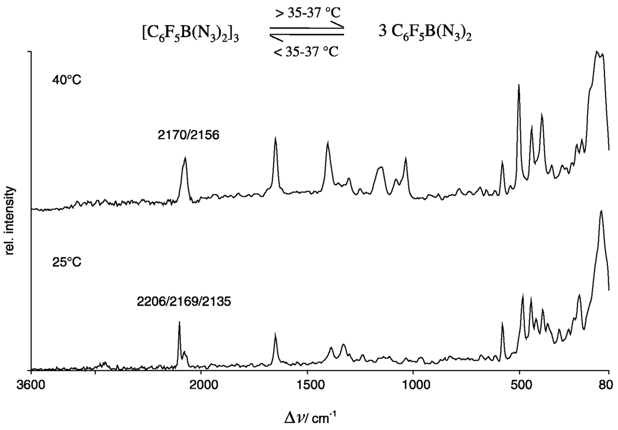

Fig. 2 Raman spectra of solid **1** (bottom), liquid **1** (top).

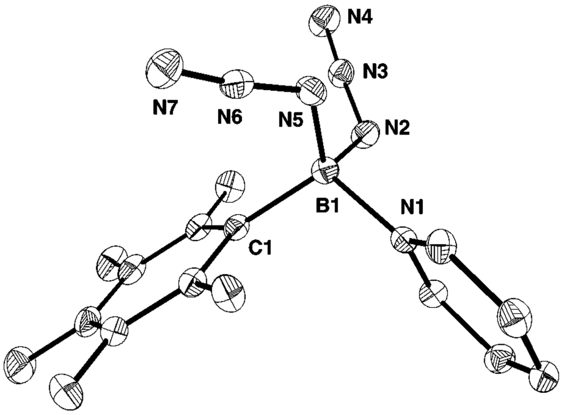

Fig. 3 Molecular structure of **2** with thermal ellipsoids drawn at the 25% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): B(1)–N(2) 1.537(3), N(2)–N(3) 1.211(3), N(3)–N(4) 1.130(3), B(1)–N(1) 1.612(3), B(1)–C(1) 1.633(3), N(2)–N(3)–N(4) 174.3(2), B(1)–N(2)–N(3) 121.0(2), N(1)–B(1)–N(2) 101.6(2), N(2)–B(1)–N(5) 109.5(2).

Table 3 Crystal data and structural refinements for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{18}B_3F_{15}N_{18}$	$C_{11}H_5BF_5N_7$
Formula weight	785.79	341.03
T/K	193	193
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$P2_12_12_1$
a/Å	14.918(2)	7.5637(6)
b/Å	13.042(1)	13.040(1)
c/Å	28.840(2)	13.4308(9)
β/°	97.463(1)	
V/Å^3	555.2(8)	1324.7(2)
Z	8	4
μ/mm^{-1}	0.195	0.160
Reflections collected	15689	7697
Independent reflections	5471 (R_{int} = 0.026)	2687 (R_{int} = 0.020)
Observed reflections	4072	2131
$R1$, $wR2$	0.0395, 0.0957 [$I > 4\sigma(I)$]	0.0380, 0.0885 [$I > 4\sigma(I)$]
(all data)	0.0596, 0.1051	0.0546, 0.0945
Flack parameter		0.1(7)

Conclusion

The behaviour of pentafluorophenylboron dichloride towards azide was investigated and found to be contrary to that of boron trihalides. The boron halides BX_3 (X = F, Cl or Br) react with only *one* equivalent of Me_3SiN_3 to give BX_2N_3 which immediately stabilize by irreversible formation of trimers. However, $C_6F_5BCl_2$ reacts with *two* equivalents of Me_3SiN_3 to form the diazide **1**. The electron-withdrawing effect of the pentafluorophenyl group is, compared to the halogen atoms, obviously weaker and therefore interactions between the $C_6F_5B(N_3)_2$ molecules are only observed in the solid state. The non-fluorinated analogue, $C_6H_5B(N_3)_2$, has been reported and characterized by NMR data and mass spectrum,[2a] but no information regarding its structure was given. The relatively low melting point of **1** indicates a low dissociation energy of this trimeric boron azide. As an adduct with pyridine, monomeric $C_6F_5B(N_3)_2$ can be stabilized.

Experimental

General

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, infrared spectra on a Nicolet 520 FT-IR spectrometer as neat solids between KBr plates. The elemental analyses were performed with a C, H, N-Analysator Elementar Vario EL instrument. NMR spectra were recorded on a JEOL EX400 instrument. Chemical shifts are recorded with respect to $(CH_3)_4Si$ (^1H, ^{13}C), $BF_3{\cdot}OEt_2$ (^{11}B), CH_3NO_2 (^{14}N) and $CFCl_3$ (^{19}F). For the determination of the melting points, samples were heated in capillaries in a Büchi B540 instrument. C_6F_5H, Me_2SnCl_2, BF_3, BCl_3 (1.0 M in hexane), Me_3SiN_3, *n*-BuLi (2.5 M in hexane) and pyridine were used as received (Aldrich, Fluka, FluoroChem). $(C_6F_5)_2SnMe_2$ and $C_6F_5BCl_2$ were prepared as described.[7,11] Elemental analyses were performed for all compounds, but only useful results are reported. Mass spectra were recorded, but were not expressive regarding the structures. **CAUTION**: compounds **1** and **3** are explosive; appropriate safety precautions must be taken.

Preparations

$[C_6F_5B(N_3)_2]_3$ 1. A solution of 1 mmol (0.248 g) $C_6F_5BCl_2$ in CH_2Cl_2 (10 mL) was treated with 2 mmol trimethylsilyl azide at −78 °C. After stirring for 12 h at ambient temperature the solution was monitored by ^{19}F NMR spectroscopy showing complete conversion into monomeric compound **1**. The solution was concentrated and cooled to −25 °C. Colorless crystals formed, isolated and dried *in vacuo*. Yield 0.13 g (50%), mp 36–39 °C. IR (Nujol): 3405vw, 2200/2180/2142 (vs, $\nu_{\text{asym}}N_3$), 1650vs, 1523vs, 1487vs,1477vs, 1381s, 1299s, 1260w, 1197s, 1162s, 1146s, 1105s, 1081s, 980 (sh), 821s, 765w, 738m, 724m, 674m, 644s, 579w, 543w, 488vw and 447vw cm^{-1}. Raman (50 mW): 2206/2169/2135 (1–5, $\nu_{\text{asym}}N_3$) 1650 (3), 1391 (2), 1331 (3), 1301 (1), 1240 (2), 1143 (1), 1114 (1), 962 (1), 826 (1), 726 (1), 582 (5), 488 (8), 467 (4), 449 (5), 426 (4), 392 (4), 371 (3), 339 (3), 315 (3), 272 (3), 246 (4), 226 (5), 217 (6), 186 (5), 118 (10) and 86 (6) cm^{-1}. ^{13}C-{^{19}F} NMR (100.6 MHz, C_6D_6): δ 146.6 (*o*-C), 142.2 (*p*-C), 136.4 (*m*-C) and 103 (br, CB). ^{11}B NMR (128.3 MHz, C_6D_6): δ 34.6s. ^{14}N NMR [28.9 MHz, C_6D_6, $\Delta\nu_{1/2}$/Hz]: δ −149 (60, N_β), −168 (150, N_γ) and −277 (900, N_α). ^{19}F NMR (376.1 MHz, C_6D_6): δ −131.7 (m, *o*-F, 2F), −147.7 (m, *p*-F, 1F) and −160.6 (m, *m*-F, 2F). Calc. for $C_6BF_5N_6$: C, 27.5; N, 32.1. Found: C, 28.3; N, 30.9%.

$C_6F_5B(N_3)_2{\cdot}C_5H_5N$ 2. 2 mmol trimethylsilyl azide (0.230 g) was added to a solution of 1 mmol (0.248 g) $C_6F_5BCl_2$ and 1 mmol (0.080 g) pyridine in 10 mL CH_2Cl_2 at −78 °C. After stirring for 12 h at ambient temperature, the solvent was removed *in vacuo* and the remaining oil crystallized from CH_2Cl_2 giving compound **2** as colorless crystals. Yield 0.27 g (80%), mp 88–90 °C. IR (Nujol): 3110w, 3105w, 2146/2130 (vs, $\nu_{\text{asym}}N_3$) 1648s, 1628m, 1523s, 1458vs, 1383vw, 1350m, 1332s, 1320m, 1291m, 1214m, 1107vs, 1027vw, 972s, 963s, 950s, 924vs, 858w, 837s, 765vs, 727vw, 690vs, 660vw, 630vw, 610vw, 580vw and 491vw cm^{-1}. Raman (150 mW): 3159 (1), 3104 (5), 3093 (4), 2146/2130 (1, $\nu_{\text{asym}}N_3$) 1648 (1), 1629 (1), 1579 (2), 1379 (1), 1351 (2), 1332 (2), 1216 (2), 1164 (1), 1098 (1), 1028 (10), 950 (1), 651 (2), 581 (2), 492 (4), 479 (2), 447 (3), 429 (3), 395 (3), 281 (1), 260 (1), 215 (2), 178 (2) and 120 (7) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.78 (m, 2H), 8.26 (m, 1H) and 7.79 (m, 2H). ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ 147.9 (*o*-C, dm, $^1J_{CF}$ 247.9), 144.3 (*o*-C, s), 143.4 (*p*-C, s), 140.9 (*p*-C, dm, $^1J_{CF}$ 253.3), 137.3 (*m*-C, dm, $^1J_{CF}$ 249.8 Hz), 126.3 (*m*-C, s) and 112 (br, CB). ^{11}B NMR (128.3 MHz, $CDCl_3$): δ 1.4s. ^{14}N NMR [28.9 MHz, $CDCl_3$, $\Delta\nu_{1/2}$/Hz]: δ −143 (80, N_β), −145 (350, N-py), −201 (250, N_γ) and −316 (650, N_α). ^{19}F NMR (376.1 MHz, $CDCl_3$): δ −135.4 (m, *o*-F, 2F), −154.3 (m, *p*-F, 1F) and −162.3 (m, *m*-F, 2F). Calc. for $C_{11}H_5BF_5N_7$: C, 38.7; H, 1.5; N, 28.8. Found: C, 38.7; H, 1.4; N, 28.4%.

$(BF_2N_3)_3$ 3. (see also Ref. 10). BF_3 (0.068 g, 1 mmol) was condensed onto a frozen solution of trimethylsilyl azide (0.12 g, 1 mmol) in CH_2Cl_2 (10 mL) at −196 °C. The solution was allowed to warm up slowly and stirred for 6 h at room temperature. The solvent and all volatile products were removed by vacuum evaporation leaving a colorless, explosive, highly moisture sensitive solid. The solid was purified by sublimation (1013 mbar/ 45 °C). Yield 0.07 g (75%), mp 50 °C. IR (Nujol): 3410m, 3300s 2208/2154 (vs/s, $\nu_{asym}N_3$), 1340w, 1297vs, 1257s, 1149s, 1053m, 933m, 910m, 845m, 664w, 631vs and 509vw cm^{-1}. Raman (100 mW): 2236 (7, $\nu_{asym}N_3$), 1255 (2, ν_s N_3), 812 (1), 577 (3), 482 (1), 397 (3), 283 (2) and 149 (10) cm^{-1}. ^{11}B NMR (128.3 MHz, CD_2Cl_2): δ 0.5s. ^{14}N NMR [CD_2Cl_2, $\Delta\nu_{1/2}$/Hz]: δ −154 (60, N_β), −175 (110, N_γ) and −300 (600, N_α). ^{19}F NMR (376.1 MHz, CD_2Cl_2): δ −147.6 (^{11}B, q, $^1J_{BF}$ 25.8 Hz).

X-Ray crystallography

Data for compounds **1** and **2** were collected on a Siemens SMART Area detector using Mo-Kα radiation. The structures were solved by direct methods (SHELX 97)[12] and refined by means of full-matrix least squares on F^2 using SHELXL 97 (Table 3).

CCDC reference number 186/2245.

See http://www.rsc.org/suppdata/dt/b0/b007626k/ for crystallographic files in .cif format.

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