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Synthesis, structural characterization and reactivity of the amino borane 1-(NPh_2)-2-[$B(C_6F_5)_2$]C_6H_4

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Dedicated to Prof. M. Frederick Hawthorne on the occasion of his 75th birthday

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Abstract

The bright red title compound **1** was synthesized from (2-lithiophenyl)diphenylamine and bis(pentafluorophenyl)boron chloride. Its reactions with small acids like H_2O and HCl proceeded easily giving zwitterionic compounds. For **1** and its water adduct **2** the crystal structures were determined, the latter featuring an ammonium borate structure containing a short intramolecular hydrogen bond bridge. Treatment of **1** with Jutzi's acid, $[H(OEt_2)_2][B(C_6F_5)_4]$, did not result in protonation of the nitrogen, but reaction of **1** with LiH in the presence of 12-crown-4, led to the isolation of the aminoborate [1-(Ph_2N)-2-{$B(H)(C_6F_5)_2$}C_6H_4][Li(12-crown-4)] (**3**). Borohydride **3** reacted with Jutzi's acid to regenerate **1** and liberate hydrogen.

Keywords: Boron; Lewis acid; Lewis base; X-ray diffraction; Hydrogen bonding

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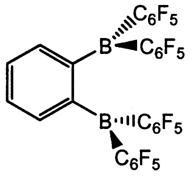
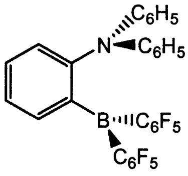
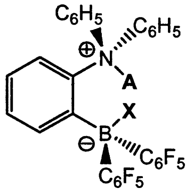
1. Introduction

Tris(pentafluorophenyl)borane is an efficient catalyst for a variety of organic reactions and co-catalyst/activator for olefin polymerization using d^0 transition metal catalysts [1–3], due to its strong Lewis acid character and stability. These applications have stimulated research towards the development of other perfluoroaryl substituted boranes. Among these, the *ortho*-phenylene bridged diboranes 1,2-$[B(C_6F_5)_2]_2C_6X_4$ (X = H, F) are particularly interesting since the proximity of the two boron centers allows for potential cooperation, such as chelation of small Lewis bases [4,5]. These diboranes inspired us to attempt the synthesis of a Lewis amphoteric *ortho*-phenylene bridged aminoborane, 1-(NPh_2)-2-[$B(C_6F_5)_2$]C_6H_4 (**1**).





1



This molecule is likely to react with $A^{\delta+}-X^{\delta-}$ compounds containing polarized bonds forming stable zwitterionic ammonium borates. For $A^+ = H^+$ and $X^- = H^-$, the zwitterion becomes a molecular dihydrogen storage device, able to release H_2 upon heating or during a chemical reaction, regenerating **1**. Certain resemblance with this hydride-proton containing molecule have systems containing a transition metal hydride in close proximity to an ammonium ion, which display dihydrogen bonding and have been studied in this respect [6]. The aminoborane **1** has also the potential to act as a "trap" for reactive molecules or fragments through the synergetic effects of the neighboring electron donor and electron acceptor sites. Similar "in series coordination" has been observed before, without the additional stabilization conferred by the chelate effect [7].

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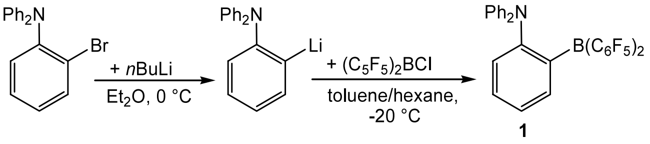
Although numerous amino boranes are known, most of these are either coordinatively saturated through intramolecular, dative boron–nitrogen bond formation, or have the amino and borane moieties well separated through a rigid carbon skeleton (i.e. *para*-phenylene). A variety of analogs of **1** with alkyl and aryl substituted nitrogen have recently been reported and studied with respect to their good fluorescence properties [8]. All these derivatives carry bulky, mesityl and duryl substituents on boron and are less suitable for coordination studies because of their reduced Lewis acidity and high steric encumbrance. The adducts of 2-$(Me_2NCH_2)C_6H_4(BMe_2)$ with MeLi have been synthesized and extensively studied by NMR [9], without preparation of the free ligand which is likely to spontaneously undergo ring closure upon B–N bond formation.

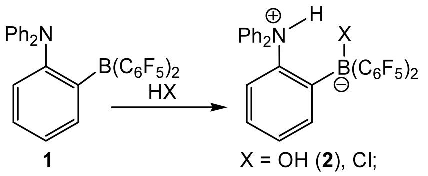
2. Results and discussion

2-Bromophenyl-diphenylamine [10] was prepared through Ullmann condensation from diphenylamine and 2-bromoiodobenzene, in analogy to a reported procedure [11]. It was then easily lithiated with *n*-BuLi and the lithiated derivative reacted smoothly with $(C_6F_5)_2BCl$ at −20 °C forming **1** in good yield (Eq. (1)). The product was isolated upon recrystallization from hexane in the form of bright red crystals. Its ^1H-, ^{19}F- and ^{11}B-NMR spectra do not display any unexpected features.



(1)

The aminoborane **1** is soluble without decomposition in aprotic organic solvents, forming intensely red solutions ($\lambda_{max} = 517.3$ nm in CH_2Cl_2), and is resistant towards oxidation by air. Although the boron–carbon bond is not readily attacked by water, the aminoborane is extremely sensitive to moisture. Reaction with traces of water yields fast and quantitatively the colorless, zwitterionic ammonium borate **2** (Eq. (2)). The reaction was obvious in the ^{19}F-NMR spectrum, where a characteristic shift to higher field ($\Delta\delta = 11.3$ ppm) of the signal corresponding to the *para*-fluorine from the borane **1** to the borate **2** is observed. In the ^{11}B-NMR spectrum, the very broad signal around 59 ppm due to the tricoordinate borane is replaced by a much sharper signal at −2 ppm, characteristic of a tetracoordinate borate. No signals for either the ammonium or the hydroxyl proton could be observed in the NMR at room temperature.



(2)

1 reacts with HCl in the same way it reacts with water, producing the ammonium borate 2-$Ph_2N(H)C_6H_4B(Cl)(C_6F_5)_2$ which displays very similar features to **2** in the NMR spectra.

The crystal structures of [1] and [2] were determined by X-ray crystallography. Selected bond lenghts and angles are given in Table 1. Both molecules are monomeric in solid state. In the aminoborane **1**, boron and nitrogen have predictably planar environments, with the sum of the bond angles being 359.8(2)° around the former and 358.2(2)° around the latter. Steric hindrance prevents, however, the planar arrangement of the boron, nitrogen and phenylene planes required for optimal electron delocalization over the entire framework. The reference phenylene plane makes an angle of 32.5(2)° with the boron plane and 38.3(2)° with the nitrogen plane. While the C(18)–N(1) bond is situated in the reference plane, forming with it an angle of only 1.8(1)°, the deviation of the boron atom out of this plane is significant, with the C(13)–B(1) bond at an angle of 7.1(1)° with respect to the same plane. As expected, there is no evidence for any tendency towards the closure of a very strained four membered CNBC ring. In fact, the angles at C(13) and C(18) imply that the repulsive steric forces prevail. The conformation of the phenyl rings at both boron and nitrogen displays the usual propeller-like arrangement.

While the C–N bonds are virtually equal, the B(1)–C(13) bond is slightly but meaningfully shorter than the other two B–C bonds, indicating the contribution of the resonance structure to the overall structure of **1**. The

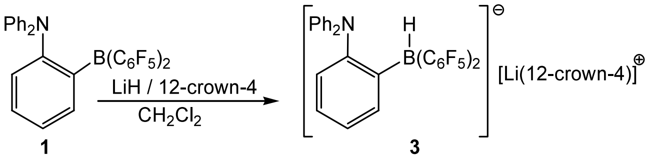
Table 1
Bond lengths (pm) and angles (°) for compounds **1** and **2** in the crystal

	1	**2**
Bond lengths		
N(1)–C	142.0(3)–142.8(3)	148.7(2)–150.2(2)
B(1)–C(1,7)	157.8(4), 159.0(4)	164.6(2), 165.7(1)
B(1)–C(13)	153.7(4)	163.4(2)
B(1)–O(1)		152.1(2)
O(1)···N(1)		253.3(2)
Bond angles		
N(1)–C(18)–C(13)	120.9(2)	117.3(2)
B(1)–C(13)–C(18)	126.2(2)	121.5(2)
O(1)–B(1)–C(13)		102.3(1)
O(1)–B(1)–C(1,7)		107.3(1), 110.7(1)
C–N(1)–C	118.6(2)–120.7(2)	112.4(1)–115.6(1)
C–B(1)–C	115.0(2)–124.0(2)	110.5(1)–113.4(1)
N(1)–H(N)···O(1)		152

C(13)–C(18) bond is with 141.6(3) pm somewhat longer than the average of the other C–C bonds in the ring (138.8(4) pm), in agreement with a resonance structure containing double bonded boron and nitrogen, although such a small difference could also be a steric effect.

The most obvious difference between **1** and **2** is the pyramidalization of boron and nitrogen in the later, with the sum of the C–N–C angles being 341.8(1)° and of the C–B–C angles 336.1(1)° (328.5° in a perfect tetrahedron). This process is accompanied by an elongation of the N–C and B–C bonds with an average of 7 and 8 pm, respectively, with respect to **1**. The water molecule is split with an O···H distance of 167 pm (O···N 253.3(2) pm), smaller than the hydrogen bond distances in solid water (1.76 pm [12]). In order to facilitate the formation of the hydrogen bond, the O–B–C(13) angle is more acute (102.32(13)°) than the other two O–B–C angles (average: 109.0(1)°) Table 1.

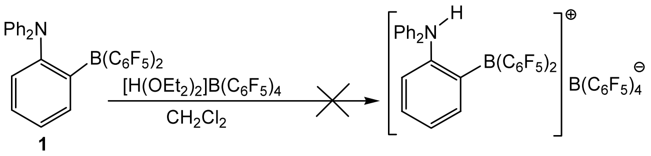
The slow reaction of **1** with lithium hydride in presence of a crown ether leads to the colorless borate **3**, which crystallizes out of a benzene solution (Eq. (3)).



(3)

The solubility of **3** in hydrocarbons is limited, but it dissolves well in polar solvents like dichloromethane. Although no signal corresponding to the boron hydride could be observed in the NMR even at −60 °C, the peaks at −2.4 ppm in the ^{11}B-NMR spectrum and at −165.5 ppm corresponding to the *para*-fluorine in the ^{19}F-NMR spectrum are characteristic for a borate ion.

Reaction of **3** with Jutzi's acid, $[H(OEt_2)_2][B(C_6F_5)_4]$ [13] failed to give a zwitterion of type **2** but instead regenerated **1** with liberation of hydrogen and most likely $[Li(12\text{-crown-}4)][B(C_6F_5)_4]$. The reaction took only a few minutes to complete at −30 °C. In fact, an ammonium cation could not be produced even by direct combination of **1** with $[H(OEt_2)_2][B(C_6F_5)_4]$ (Eq. (4)). No reaction was observed refluxing the reaction mixture in dichloromethane for 2 days, while reflux in toluene produced tris(pentafluorophenyl)borane as the only identifiable product.



(4)

The aminoborane **1** proves to be able to act as a Lewis acid/Lewis base trap, reacting with small acids like H_2O and HCl to form zwitterionic products containing an intramolecular hydrogen bond bridge. However, it fails to yield a "dihydrogen adduct" of type **2**, as well as a cationic ammonium ion. The latter finding confirms that the basicity of the amino group is significantly reduced by extended electron delocalization involving the aromatic rings and the borane moiety. The basicity of the nitrogen center in an aminoborane of type **1** would have to be significantly higher in order to thermodynamically favor the formation of a dihydrogen adduct over the elimination of hydrogen in the reaction of **3** with $[H(OEt_2)_2][B(C_6F_5)_4]$.

3. Experimental

3.1. General remarks

All experiments were performed under a purified argon atmosphere, with complete exclusion of air and moisture, using glovebox and Schlenk techniques. The solvents were dried and deoxygenated prior to use [14]. NMR experiments were performed on a Bruker AMX-300 instrument, using internal (C_6D_5H and $CDHCl_2$ for ^{1}H with $\delta = 7.15$ and 5.32 ppm, respectively) or external (C_6F_6 for ^{19}F, with $\delta = -163.0$ ppm and $BF_3 \cdot Et_2O$ for ^{11}B, with $\delta = 0.0$ ppm) reference. Elemental analyses were performed by the Analytical Instrumentation Centre at the University of Calgary. $(C_6F_5)_2BCl$ [15,16] and $[H(OEt_2)_2][B(C_6F_5)_4]$ [13] were synthesized according to published procedures, all other reagents are commercial products.

3.1.1. 1-Br-2(NPh$_2$)C$_6$H$_4$

To a round bottom flask containing toluene (11 ml) equipped with a Dean–Stark trap were added in the following order with efficient stirring diphenylamine (2.99 g, 17.67 mmol), 2-bromoiodobenzene (5 g, 17.67 mmol), 1,10-phenantroline (116 mg, 0.64 mmol), copper(I) iodide (122 mg, 0.64 mmol), and finely divided potassium hydroxide (7.75 g, 138 mmol). The mixture was refluxed (125 °C) over night, while the color of the solution changed from orange to brown, colorless and finally green. After cooling to room temperature, toluene (50 ml) and water (50 ml) were added, the green organic phase was separated and the solvent removed on a Rotavap, leaving behind a dark green oil. Chromatography on silica gel using hexane:ethyl acetate 99:1 gave the product as a first fraction. Solvent removal and vacuum distillation yielded the desired compound (2.15 g, 37%) with satisfactory purity. B.p. 160–180 °C per 5×10^{-3} Torr. ^{1}H-NMR (282 MHz, 27 °C, C_6D_6) δ (ppm): 6.60 (m), 6.91 (m), 6.96 (m), 7.00 (s), 7.01–7.07 (m), 7.12 (m), 7.19–7.31(m), 7.39 (m), 8.07 (m). MS (EI, 70 eV, positive): [M$^+$].

3.1.2. *1-(Ph_2N)-2-[$B(C_6F_5)_2$]C_6H_4 (**1**)*

1-Br-2(NPh_2)C_6H_4 (2.153 g, 6.64 mmol) was lithiated at 0 °C in diethyl ether (60 ml) using a 1.6 M solution of *n*-BuLi in hexane (4.15 ml, 6.65 mmol). The solution was allowed to warm up to room temperature and stirred over night, the solvent was removed in vacuo and the solid residue suspended in hexane. Filtration yielded the lithium derivative as a fine white powder. Without further purification, 1-Li-2-(NPh_2)C_6H_4 (1 g, 3.98 mmol) was suspended in 60 ml toluene and added slowly at −20 °C to a solution of $(C_6F_5)_2BCl$ (1.514 g, 3.98 mmol) in hexane (40 ml). Immediately, intense bright red coloration indicated formation of the product. The reaction mixture was stirred over night at room temperature, the solvent was removed and the residue extracted with hexane (50 ml). The hexane extract was reduced to 10 ml and cooled to −50 °C. After 2 days, the product deposited as a red crystalline solid and the supernatant was decanted off. Yield: 1.70 g, 73%. Elemental analysis for $C_{30}H_{14}BF_{10}N$: Anal. Found (Calc.): C, 61.23 (61.15); H, 2.03 (2.39); N 2.39 (2.38%); UV–Vis: CH_2Cl_2, λ_{max} (nm) (log(ε), dm^3 mol^{-1} cm^{-1}): 517.3 (3.28), 286.2 (4.12), 228.0 (4.14); ^{1}H-NMR (300 MHz, 27 °C, C_6D_6) δ (ppm): 6.69–6.81 (m, 7H), 6.87–6.92 (m, 4H), 7.00–7.08 (m, 1H), 7.13 (d, 2H); ^{19}F-NMR (282 MHz, 27 °C, C_6D_6) δ (ppm): −161.7 (4F, *m*-C_6F_5), −147.3 (2F, *p*-C_6F_5), −128.1 (4F, *o*-C_6F_5); ^{11}B-NMR (96 MHz, 27 °C, C_6D_6) δ (ppm): 58.8 (s, br) Fig. 1.

3.1.3. *1-(Ph_2NH)-2-[$B(OH)(C_6F_5)_2$]C_6H_4 (**2**)*

A benzene solution of **1** was exposed to the air. Within a few minutes, the color of the solution faded and disappeared. Evaporation of the solvent left behind the product quantitatively, as a colorless crystalline solid. ^{1}H-NMR (300 MHz, 27 °C, C_6D_6) δ (ppm): 6.57 (dd, 1H, $^1J_{HH} = 8.0$ Hz, $^2J_{HH} = 0.6$ Hz), 6.67–6.76 (m, 10 H), 6.89 (dt, 1H, $^1J_{HH} = 7.4$ Hz, $^2J_{HH} = 1.4$ Hz), 7.03 (dt, 1H, $^1J_{HH} = 7.4$ Hz, $^2J_{HH} = 1.0$ Hz), 7.38 (d, 1H, $^1J_{HH} = 7.5$ Hz); ^{19}F-NMR (282 MHz, 27 °C, C_6D_6) δ (ppm): −164.4 (4F, *m*-C_6F_5), −158.6 (2F, *p*-C_6F_5), −133.3 (4F, *o*-C_6F_5); ^{11}B-NMR (96 MHz, 27 °C, C_6D_6) δ (ppm): −0.8 (s) Fig. 2.

3.1.4. *1-(Ph_2NH)-2-[$B(Cl)(C_6F_5)_2$]C_6H_4*

To a dichloromethane solution of **1** was added the stoichiometric amount of 1 M HCl in THF. The solution discolored immediately. Evaporation of the solvent left behind the product quantitatively, as a colorless crystalline solid. ^{1}H-NMR (300 MHz, 27 °C, CD_2Cl_2) δ (ppm): 7.05 (d, 1H, $^1J_{HH} = 8.1$ Hz), 7.19 (d, 1H, $^1J_{HH} = 7.4$ Hz), 7.29 (d, 1H, $^1J_{HH} = 6.9$ Hz), 7.33–7.37 (m, 4H), 7.45–7.47 (m, 5H); ^{19}F-NMR (282 MHz, 27 °C, CD_2Cl_2) δ (ppm): −165.6 (4F, *m*-C_6F_5), −159.2 (2F, *p*-C_6F_5), −129.5 (4F, *o*-C_6F_5); ^{11}B-NMR (96 MHz, 27 °C, CD_2Cl_2) δ (ppm): −2.2 (s).

3.1.5. *[1-(Ph_2N)-2-{$B(H)(C_6F_5)_2$}C_6H_4][Li(12-crown-4)] (**3**)*

LiH (20 mg, 2.5 mmol) was added to a solution containing **1** (150 mg, 0.25 mmol) and 12-crown-4 ether

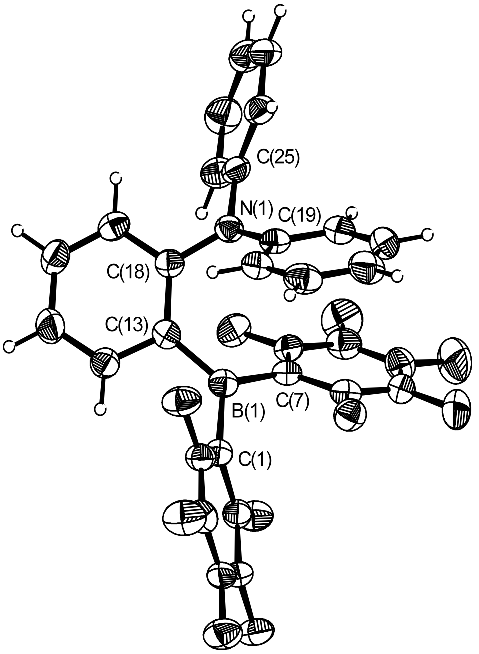


Fig. 1. Molecular structure of 1-(NPh_2)-2-[$B(C_6F_5)_2$]C_6H_4 (**1**) in the crystal.

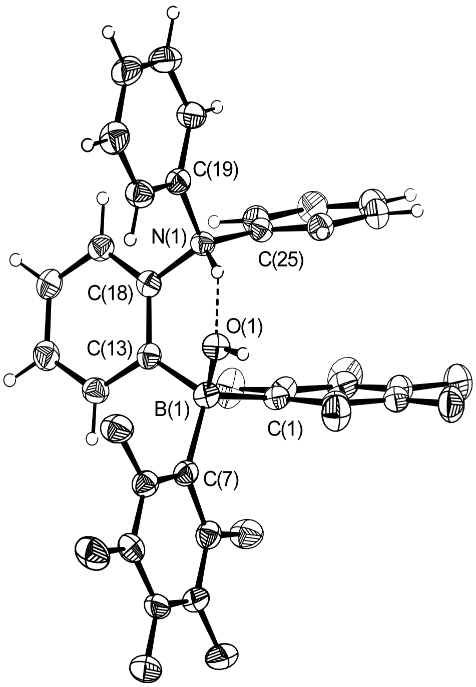


Fig. 2. Molecular structure of 1-[N(H)Ph_2]-2-[$B(OH)(C_6F_5)_2$]C_6H_4 (**2**) in the crystal.

Table 2
Crystallographic data for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{30}H_{14}BF_{10}N$	$C_{30}H_{16}BF_{10}NO$
Formula weight (g mol^{-1})	589.23	607.25
Crystal size (mm^3)	0.15 × 0.12 × 0.05	0.17 × 0.10 × 0.08
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Z	2	2
a (pm)	903.24(4)	980.78(3)
b (pm)	1079.33(4)	1086.21(4)
c (pm)	1342.55(8)	1316.97(5)
α (°)	96.761(2)	105.1706(14)
β (°)	92.183(2)	104.4606(15)
γ (°)	102.979(3)	101.0140(20)
V (nm^3)	1.26372(10)	1.26091(8)
D_{calc} (mg m^{-3})	1.549	1.599
Absorption coefficient (mm^{-1})	0.14	0.15
θ Range (°)	3.4–27.5	3.4–30.0
Reflections collected/R_{int}	10621/0.053	12526/0.030
Data/parameters	5689/379	7075/392
Goodness-of-fit on F^2	1.00	1.02
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.056$, $wR_2 = 0.120$	$R_1 = 0.052$, $wR_2 = 0.108$
R indices (all data)	$R_1 = 0.141$, $wR_2 = 0.148$	$R_1 = 0.095$, $wR_2 = 0.127$
Largest difference peak and hole (e nm^{-3})	190 and −250	250 and −260

(45 mg, 0.25 mmol) in 5 ml benzene. The flask was capped and left standing for 2 weeks, while the solution discolored and colorless crystals of product deposited on the bottom and were separated. Yield: 126 mg, 64%. ^{19}F-NMR (282 MHz, 27 °C, CD_2Cl_2) δ (ppm): −166.8 (4F, m-C_6F_5), −164.9 (2F, p-C_6F_5), −129.1 (4F, o-C_6F_5); ^{19}F-NMR (282 MHz, 27 °C, CD_2Cl_2) δ (ppm): −167.3 (4F, m-C_6F_5), −165.5 (2F, p-C_6F_5), −130.8 (4F, o-C_6F_5); ^{11}B-NMR (96 MHz, 27 °C, CD_2Cl_2) δ (ppm): −2.4 (s).

3.2. X-ray crystallographic analyses

X-ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on a Rigaku AFC6S diffractometer. Details of the crystallographic data and data analysis are given in Table 2.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 205366 and 205367 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +33-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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