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^{19}F NMR Spectroscopic Investigation of the Reaction of Bis(pentafluorophenyl)borinic Acid with a "Proton Sponge": Deprotonation, Trimerization and Stepwise Dearylation

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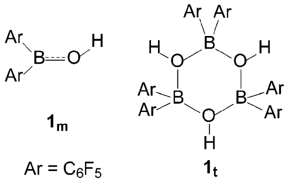
The reaction of Ar_2BOH (**1**, Ar = C_6F_5) with the proton sponge bis(dimethylamino)naphthalene (DMAN) in CD_2Cl_2 solution caused a series of strictly interlaced processes that have been investigated by variable-temperature ^1H and ^{19}F NMR spectroscopy. The very slow equilibrium between the monomeric and cyclic trimeric forms of Ar_2BOH was strongly accelerated by the presence of a catalytic amount of DMAN. Upon addition of stoichiometric DMAN (0.33 equiv.), all Ar_2BOH was converted into a mixture of two boroxinate anions, namely $[Ar_6B_3O_3H_2]^-$ (**2**) and $[Ar_5B_3O_3H]^-$ (**3**), in which the ratio of the two anions varied according to the reaction conditions. The formation of the dearylated anion **3** (accompanied by equimolar pentafluorobenzene) has been attributed to a reaction process parallel to that leading to the hexaaryl anion **2**, involving base-catalyzed hydrolysis of monomeric perfluoroborinic acid to its boronic analogue, followed by aggregation and condensation. Water plays a catalytic role in this process. In the presence of a small excess of DMAN, complete and instantaneous dearylation of **2** to **3** was observed. At temperatures lower than 233 K, the pentaaryl anion **3** was in equilibrium with its conjugate base. Slow further dearylation occurred at temperatures higher than 263 K, cleanly affording the tetraaryl anion $[Ar_4B_3O_3]^-$ (**5**). Anions **3** and **5** have also been obtained in high yields from the condensation reaction between Ar_2BOH and $ArB(OH)_2$ (in the ratio 2:1 and 1:2, respectively), in the presence of stoichiometric DMAN. Mechanisms responsible for the stepwise dearylation from **2** to **3** and then from **3** to **5** have been discussed.

Introduction

Boron–oxygen or boron–nitrogen heterocycles containing tricoordinate boron atoms are well known, and typical examples are boroxins $[RBO]_3$ and borazines $[RB(NR')]_3$, isoelectronic with benzene (30 valence electrons, v.e.s).[1] It has been recently found that bis(pentafluorophenyl)borinic acid $(C_6F_5)_2BOH$ (**1**, hereafter simply borinic acid)[2] in the solid state has the unprecedented trimeric $[(C_6F_5)_2BOH]_3$ structure,[3,4] in which each boron atom attains tetracoordination through oxygen-to-boron donor–acceptor bonds (Scheme 1).

The resulting cyclohexane-like (36 v.e.s) structure bears resemblance to that of cyclo-$(R_2EO)_3$ siloxanes or stannoxanes, but the oxygen–boron donor–acceptor interactions in **1** can easily dissociate in solution.[3] In particular, in dichloromethane a very slow equilibrium was found between the monomeric $\mathbf{1_m}$ and the trimeric $\mathbf{1_t}$ forms of $(C_6F_5)_2BOH$, which at room temperature strongly favours the monomeric species [Equation (1); Ar = C_6F_5].[5]



Scheme 1. The monomeric and trimeric forms of bis(pentafluorophenyl)borinic acid.

$$3\,Ar_2BOH \rightleftarrows [Ar_2BOH]_3 \qquad (1)$$

The position and the rate of the equilibrium are affected by the presence of Lewis bases such as water,[5] tetrahydrofuran (thf)[6] or methanol,[7] as a result of the series of reactions depicted in Scheme 2, which open alternative pathways for the monomer–trimer interconversion and stabilize the trimeric form.

The kinetic effect is particularly impressive: the equilibration, which in strictly anhydrous conditions requires hours at room temperature,[5] becomes extremely fast in the presence of Lewis bases even at very low temperatures. For instance, it was found that the addition of stoichiometric

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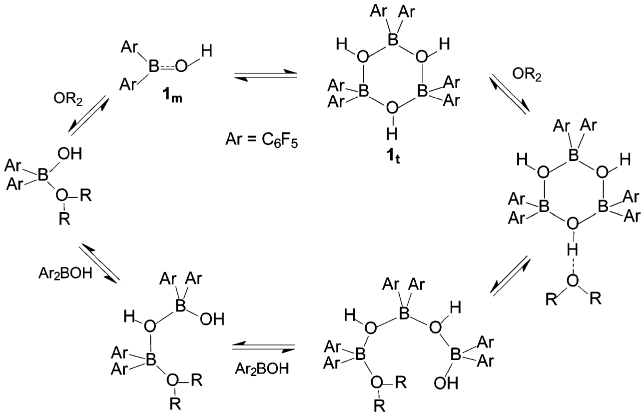
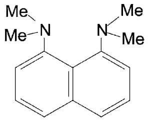


Scheme 2. The fast cyclotrimerization pathway operative in the presence of OR_2 Lewis bases such as thf.

(0.33 equiv.) thf at 193 K immediately and quantitatively converted compound **1** into its trimeric form, which was stabilized by hydrogen bonding to a thf molecule.[6] However, even in the presence of thf (or of other hydrogen-bond acceptors), the cyclic structure remained labile, and, on increasing the temperature, extensive dissociation to the monomeric form occurred.

The unexpected detection of a small amount of deprotonated $\mathbf{1_t}$ in the mixtures arising from the treatment of **1** with excess thf[6] prompted us to investigate the reactivity of **1** with the Brønsted base bis(dimethylamino)naphthalene (DMAN, Scheme 3).



DMAN

Scheme 3. Bis(dimethylamino)naphthalene.

The reaction afforded mixtures of hexa-, penta- and tetraarylboroxinates, in different ratios according to the reaction conditions, as will be presented in the following section. The processes responsible for these competitive/consecutive reactions will then be discussed.

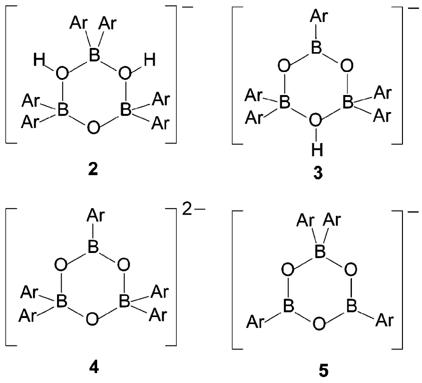
Results

Bis(dimethylamino)naphthalene (DMAN) was chosen as base, because it has good Brønsted basicity (pK_a = 12.1)[8] and negligible Lewis basicity: this allows deprotonation of borinic acid without formation of Lewis acid–base adducts with the boron atom, which might perturb the monomer–trimer equilibrium. Moreover, on using DMAN, the position of the acid–base equilibrium can be easily monitored by ^{1}H NMR spectroscopy, through the diagnostic signal of protonated DMAN (HDMAN$^+$), which lies at very low field (δ = 20.1 ppm at 173 K), because of the strong intramolecular N···H···N$^+$ hydrogen bond typical of "proton sponges".[9] The reactions have been performed directly in NMR tubes, in CD_2Cl_2 solutions.

Reactions of $(C_6F_5)_2BOH$ with 0.33 equiv. DMAN

The ^{1}H NMR spectra showed that, regardless of the reaction temperature, DMAN was quantitatively protonated by borinic acid up to 0.33 equiv. base. Above this amount, added DMAN remained unreacted,[10] indicating that all borinic acid had already been transformed into the anionic trimeric species. This was confirmed by the high conductivity value measured at room temperature upon addition of 0.33 equiv. DMAN,[11] which did not increase upon further DMAN addition.

^{19}F NMR spectra revealed the formation of two species. The first one was the anion $[Ar_6B_3O_3H_2]^-$, i.e. deprotonated $\mathbf{1_t}$ (labelled as **2** in Scheme 4). At 173 K, it exhibits two rather broad ^{19}F resonances (in a 1:2 ratio, Table 1) both in the *para* and in the *meta* regions, while in the *ortho* region at this temperature one relatively sharp and two very broad signals are observed, as shown in Figure 1.



Scheme 4. The four boroxinate anions generated by the reaction of **1** with DMAN (Ar = C_6F_5).

Table 1. ^{19}F NMR chemical shifts of anions **2**–**5** and of pentafluorobenzene HAr (at 173 K, in CD_2Cl_2). The relative intensities are given in parentheses.

	δ (^{19}F) [ppm] (relative intensity) *ortho*	*para*	*meta*	$\Delta\delta_{m,p}$[a] [ppm]
2	–135.81 (2)	–156.04 (1)	–163.35 (2)	7.3
	–138.35 (2)	–158.98 (2)	–164.76 (4)	5.8
	–139.14 (2)			
3	–132.88 (2)	–154.09 (1)	–162.97 (2)	8.9
	–137.85 (8)	–158.05 (4)	–164.31 (8)	6.3
4	–133.10 (2)	–157.90 (1)	–163.67 (2)	5.8
	–135.06 (8)	–164.14 (4)	–166.86 (8)	2.7
5	–132.56 (2)	–152.72 (1)	–162.70 (2)	10.0
	–136.80 (2)	–160.20 (1)	–165.05 (2)	4.9
HAr	–138.72 (2)	–153.87 (1)	–161.96 (2)	

[a] Chemical shift differences between the *para* and *meta* resonances on the same line. The values for $\mathbf{1_m}$ and $\mathbf{1_t}$ are 13.7 and 9.7, respectively (see ref.[15]), while that for $(C_6F_5)B(OH)_2$ is 12.0.

The second product was identified as the pentaaryl derivative $[Ar_5B_3O_3H]^-$ (**3** in Scheme 4), which shows two ^{19}F resonances in the ratio 1:4, in each of the *ortho*, *para* and *meta* regions (Table 1, Figure 1). Its formation implies elimination of one pentafluorobenzene molecule (denoted by HAr in all schemes and figures), and actually the ^{1}H and

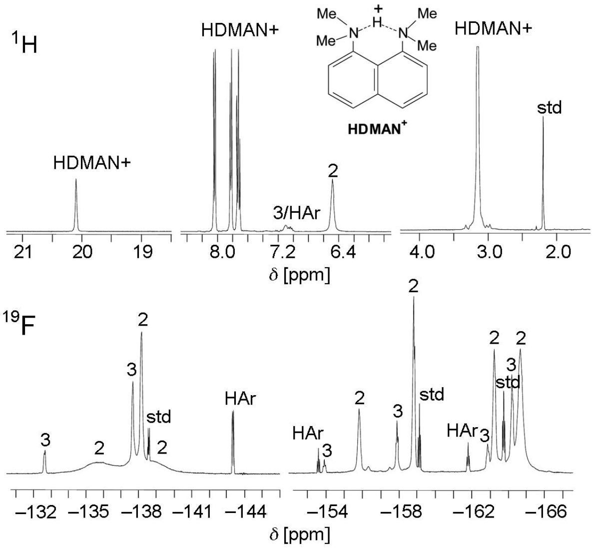


Figure 1. ^1H and ^{19}F NMR spectra (CD_2Cl_2, 173 K) of a reaction mixture arising from the treatment of **1** with 0.33 equiv. DMAN. HAr is pentafluorobenzene and the label "std" indicates the resonances of pentafluorotoluene, used as internal standard.

^{19}F NMR spectra always showed the signals of HAr, equimolar with respect to **3**. The presence in **3** of one trigonal boron atom was confirmed by the separation between the *para* and *meta* resonances of its singular aryl ring (Table 1), which increased with respect to **2**, as a result of the deshielding of the *para* resonance.[12–16]

The location of the OH proton on the oxygen atom bridging the two Ar_2B vertices (see Scheme 4) is confirmed by the fine structure exhibited by the proton resonance (nine lines, arising from the coupling with the eight fluorine atoms in the *ortho* position on the four aryl rings, with averaged J_{HF} = 3.3 Hz, Figure S1 in Supporting Information). Further support was provided by a [^{19}F-^1H] HOESY experiment that showed the correlation between the OH resonance and the more intense *ortho* fluorine signal.

The formulation of **3** was definitely proved by performing its synthesis through the reaction of 2 mol perfluoroborinic acid with 1 mol perfluoroboronic acid and 1 mol DMAN (in the presence of molecular sieves). ^{19}F NMR spectroscopy showed that at room temperature reaction (2) is almost quantitative and instantaneous.

$$ArB(OH)_2 + 2\,Ar_2BOH + DMAN \rightarrow [Ar_5B_3O_3H]^- + HDMAN^+ + H_2O \qquad (2)$$

The ratio of anions **2** and **3**, formed in the reaction of **1** with 0.33 equiv. DMAN, varied significantly on varying the reaction conditions. At room temperature, **3** was slightly more abundant than **2** (**3**/**2** ratio ≈ 1.3), whilst at 193 K this ratio reversed (**3**/**2** ratio ≈ 0.7). The amount of **3** further decreased when DMAN was added stepwise, in titrations performed either at room temperature or at 193 K: in these cases, when 0.33 equiv. were attained, the **3**/**2** ratio was ca. 0.5 at 298 K and 0.25 at 193 K (Figure S2).

Moreover, from these experiments, clear evidence for the catalytic role of DMAN in the equilibrium between $\mathbf{1_m}$ and $\mathbf{1_t}$ was obtained. Indeed, the titration at 193 K showed that, upon addition of less than 0.1 equiv. DMAN, the main neutral species in solution became $\mathbf{1_t}$, (Figure S2, trace b), in agreement with the idea that at very low temperature equilibrium (1) is almost completely shifted towards the trimeric form[5] (and that the dominance of $\mathbf{1_m}$ usually observed in the low-temperature spectra, as shown in trace a of Figure S2, is due to kinetic and not thermodynamic reasons). In these conditions, it became possible for the first time to observe in a wide temperature range the progressive (and reversible) shift of equilibrium (1) toward the monomeric form on increasing the temperature (Figure S3).

Transformation of the Hexaaryl Anion 2 into the Pentaaryl Species

The ratio of the anions **2** and **3** generated in the low-temperature titrations remained notably constant up to 298 K, demonstrating that **2** does not spontaneously eliminate HAr, even at high temperature. However, the complete transformation of **2** into **3**, given in reaction (3), immediately occurred upon addition at room temperature of a small excess of DMAN, above 0.33 equiv. (see Figure 2).

$$[Ar_6B_3O_3H_2]^- \rightarrow [Ar_5B_3O_3H]^- + HAr \qquad (3)$$

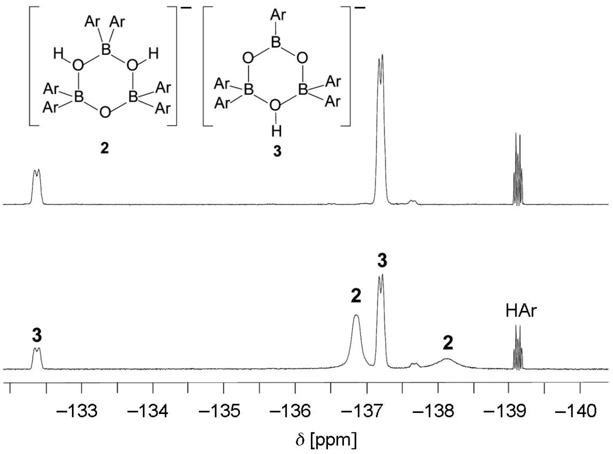


Figure 2. The *ortho* region of the ^{19}F NMR spectrum of a sample of **1** in CD_2Cl_2, treated with 0.33 (bottom) and 0.40 (top) equiv. DMAN, at 298 K.

The disappearance of **2** was complete also when the same excess of DMAN was added at very low temperature, but in that case, in addition to **3**, another trinuclear anion **4** formed, which showed in the ^{19}F NMR spectrum the same 1:4 pattern as **3** (Figure 3).

NMR spectroscopic data indicated that **4** was the conjugate base of **3** (Scheme 4), formed according to equilibrium (4). On adding DMAN the amount of **4** increased at the expense of **3**, while the addition of an acid such as CF_3SO_3H restored **3** (as shown in Figure S4). Moreover,

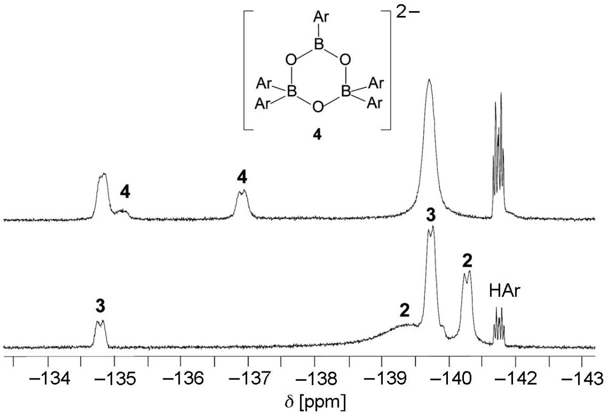


Figure 3. The *ortho* region of the ^{19}F NMR spectrum of a sample of **1** in CD_2Cl_2, treated with 0.33 (bottom) and 0.40 (top) equiv. DMAN, at 173 K.

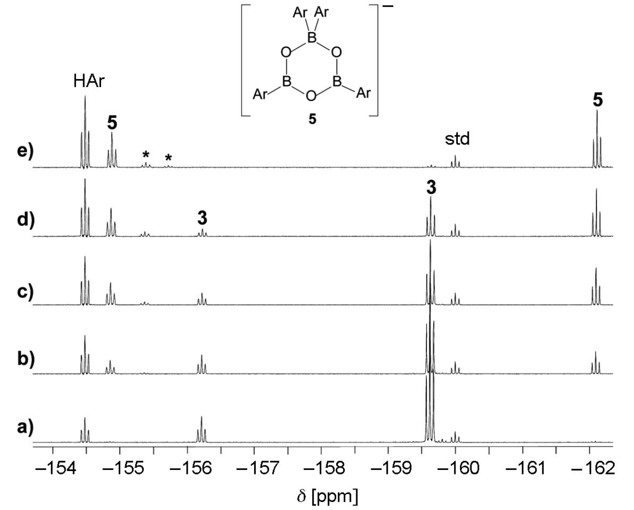


Figure 4. Time evolution of the ^{19}F NMR spectra (*para* region) of a solution of **1** in CD_2Cl_2, treated with 0.4 equiv. DMAN at 298 K immediately after DMAN addition (a), after 16 min (b), 37 min (c), 1 h (d), 4 h (e). The asterisks mark unknown byproducts. Please note the strong upfield shift of both of the resonances of **5** with respect to the low-temperature data of Table 1.

the relative amount of **4**, estimated from the ^{19}F NMR spectra, accounted for double the amount of $HDMAN^+$ in the ^{1}H NMR spectrum.

$$(HDMAN^+)[Ar_5B_3O_3H]^- + DMAN \rightleftarrows (HDMAN^+)_2[Ar_5B_3O_3]^{2-} \quad (4)$$

The dianion **4** had been previously serendipitously obtained as the counterion of a triple-decker sandwich compound of Ni^{II}, in the reaction of nickelocene with $(C_6F_5)_3B(OH_2)$.[17] In that case, the anion was identified by X-ray single crystal analysis, and no further information on this species was reported.

Proton exchange between **3** and **4** (either direct or mediated by DMAN) is relatively slow, so that the acid and its conjugate base give separated NMR resonances. The same occurs for the $\mathbf{1_t}$/**2** pair. This is attributable to the high steric crowding around the protons, which are also involved in hydrogen-bond interactions. However, proton exchange does exist, as indicated by the cross peaks between each signal of **4** and the corresponding resonance of **3** observed in a [^{19}F-^{19}F] EXSY at low temperature (Figure S5 in Supporting Information, which also shows the analogous exchange between $\mathbf{1_t}$ and **2**).

The position of equilibrium (4) shifted toward the left on increasing the temperature: **4** almost completely disappeared at 233 K, but formed again on lowering back the temperature (Figure S6 in Supporting Information). This behaviour agrees both with the expected negative entropy of the deprotonation reaction (4) (due to ion-pair formation) and with the increase of the dielectric constant of CD_2Cl_2 at low temperature.[18]

Formation of Tetraaryl Anion 5

In samples containing a slight excess of DMAN, further slower dearylation occurred, at temperatures higher than 263 K, causing the transformation of the pentaaryl anion **3** into the novel tetraaryl anion $[Ar_4B_3O_3]^-$ (**5** in Scheme 4, Figure 4).

The rate of reaction (5) increased with the amount of free DMAN, and at 298 K $t_{1/2}$ ranged from ca. 30 min in samples of **1** treated with 0.4 equiv. DMAN to 4 min in samples to which 0.8 equiv. base was added.

$$[Ar_5B_3O_3H]^- \rightarrow [Ar_4B_3O_3]^- + HAr \quad (5)$$

Anion **5** is characterized by two ^{19}F signals of equal intensity in each of the *ortho*, *para* and *meta* regions (Figure S7), attributable to the two $ArBO_2$ units and to the single Ar_2BO_2 vertex, respectively. The separations between the *para* and *meta* resonances (Table 1) are very different for the trigonal and tetrahedral boron units, which allows their distinction.[12]

This anion is novel, but its nonfluorinated analogue $[(C_6H_5)_4B_3O_3]^-$ had been previously synthesized[19,20] and structurally characterized. In the solid-state structure, deviations from planarity of the boroxin ring and the considerable π character of the bonds between the trivalent boron atoms and the neighbouring oxygen atoms were observed. Similar features should be expected for **5** too.

When the mixture was kept (many hours or days) at room temperature, the resonances of the tetraaryl derivative **5** progressively decreased in intensity, while the signals of HAr increased, together with several unassigned resonances.

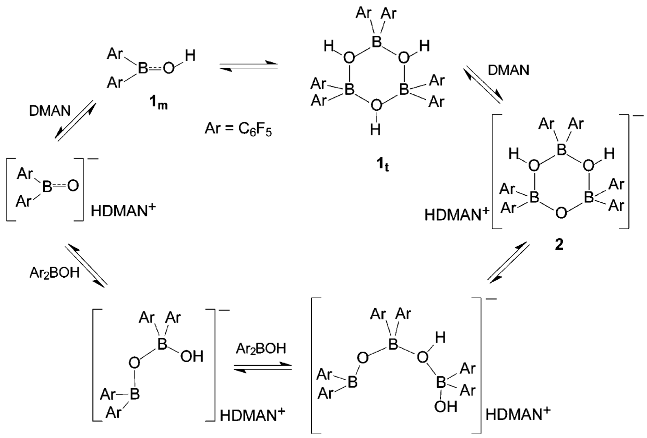
We have obtained anion **5** in high yields also by treating a 1:2 mixture of perfluoroborinic and perfluoroboronic acids with 1 equiv. DMAN (with respect to borinic acid), in the presence of molecular sieves, as shown in reaction (6), which is analogous to reaction (2) above. The related nonfluorinated analogue had been prepared in a similar way, by condensation of 1 mol borinic anhydride with 4 mol boronic acid in the presence of a strong base.[20]

$$Ar_2BOH + 2\ ArB(OH)_2 + DMAN \rightarrow [Ar_4B_3O_3]^- + HDMAN^+ + 2\ H_2O \quad (6)$$

Discussion

The Trimerization Process

The accelerating effect of DMAN on equilibrium (1) between $\mathbf{1_m}$ and $\mathbf{1_t}$ can be explained by the series of reactions shown in Scheme 5, closely resembling those in Scheme 2.[21] In the presence of a Lewis base, the key factor was the increased nucleophilicity of the oxygen atom in the $Ar_2B(OH)(OR_2)$ Lewis acid–base adduct, which allowed intermolecular attack on the boron atom of another monomeric unit.[5,6] Here, deprotonation of $\mathbf{1_m}$ generates the $[Ar_2BO]^-$ anion, which is obviously a much more effective nucleophile than $Ar_2B(OH)(OR_2)$.



Scheme 5. The cyclotrimerization path promoted by DMAN.

Notably, in the presence of DMAN, equilibrium (1) became so fast that cross-peaks could be observed between the ^{19}F signals of $\mathbf{1_m}$ and $\mathbf{1_t}$, in 2D EXSY maps at 253 K (Figure S8 in Supporting Information). As a result of the fast equilibrium between neutral monomeric and trimeric species, anion **2** is the final product of deprotonation, whatever the site of deprotonation ($\mathbf{1_m}$ or $\mathbf{1_t}$) may be. Actually, the $[Ar_2BO]^-$ anion is a too strong Lewis base to exist free in the presence of unreacted $\mathbf{1_m}$ (a Lewis acid). This accounts for the stability of anion **2** at room temperature, where the neutral $\mathbf{1_t}$·thf adduct would extensively dissociate to yield the monomeric species.[6]

Although thermodynamically favoured, the trimeric cyclic structure of **2** remains labile and subject to fast reversible fragmentation at room temperature. A 2D EXSY experiment showed exchange between **2** and $\mathbf{1_m}$ (Figure 5), confirming that the aggregation equilibria of Scheme 5 are very fast in both directions. In any case, after addition of 0.33 equiv. DMAN, no detectable monomeric species remained in solution.

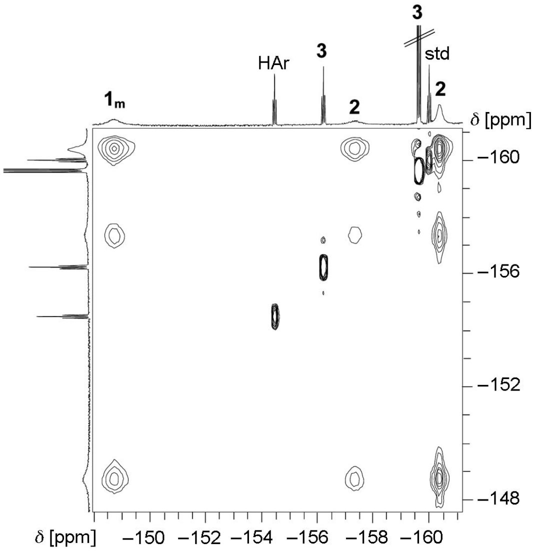


Figure 5. The *para* region of a ^{19}F EXSY experiment of a solution of **1** treated with 0.29 equiv. DMAN, showing the exchange between **2** and $\mathbf{1_m}$ (CD_2Cl_2, 298 K).

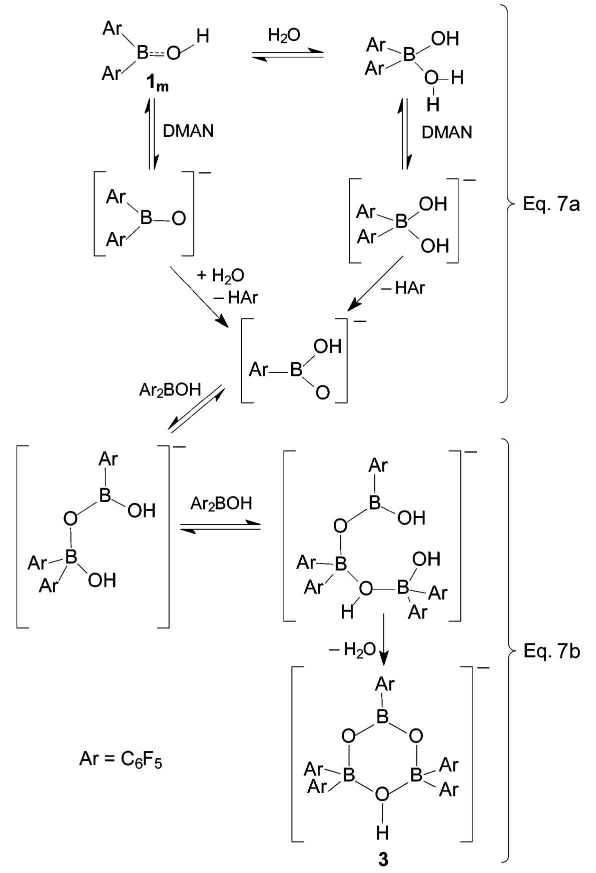
The Dearylation Process

The formation of the dearylated anion **3** is observed in two different contexts: (i) in the reactions of **1** with stoichiometric or substoichiometric DMAN ($\leq$ 0.33 equiv.), when **3** is formed simultaneously with **2**, and (ii) in the presence of excess DMAN ($>$ 0.33 equiv.), when **1** is not present anymore, and the concentration of **3** increases at the expense of **2**.

The observation that **2** is rapidly and completely transformed into **3** in the presence of free DMAN might suggest that the formation of **3** always takes place via intermediate **2**. This would imply that the dearylation of **2** occurs at a rate comparable to that of its formation from **1**. This hypothesis is not completely unreasonable, as acid-base reactions involving proton sponges are known to be slow.[8,22] However, it was rejected by the results of the stepwise titrations, since a lower amount of **3** was obtained when DMAN was added to solutions already containing **2**.

In the first context, therefore, dearylation is not consecutive, but rather parallel to the formation of **2**, and the observed (variable) ratios of anions **2** and **3** are dictated by the kinetics of the competing processes leading to **2** and **3**.

The formation of **3** likely comprises as first step the base-catalyzed hydrolysis of monomeric borinic acid $\mathbf{1_m}$ to the boronate anion [Equation (7a)], by the action of adventitious water. The boronate anion would then rapidly condense with 2 mol borinic acid [Equation (7b)], affording **3** and restoring the molecule of water consumed in the first step (as depicted in the lower part of Scheme 6). In this process, therefore, water has a catalytic role. The involvement of $\mathbf{1_m}$ in the formation of **3** is supported by the reduced yields of **3** in the stepwise titrations at low temperature, where borinic acid is mainly in its trimeric form.



Scheme 6. Mechanism accounting for the formation of the pentaaryl anion **3** by base-catalyzed hydrolysis of $\mathbf{1_m}$ followed by aggregation and condensation.

$$Ar_2BOH + H_2O + DMAN \rightarrow [ArB(OH)O]^- + HAr + HDMAN^+ \quad (7a)$$

$$[ArB(OH)O]^- + 2\,Ar_2BOH \rightarrow [Ar_5B_3O_3H]^- + H_2O \quad (7b)$$

Reaction (2), mentioned previously, proved the feasibility of the second step of this mechanism. The first step is well established in the literature. It is well known[2,23] that in the presence of water monomeric perfluorophenylboranes undergo stepwise replacement of their aryl substituents by OH groups, with production of pentafluorobenzene [Equation (8)].

$$Ar_nB(OH)_m + H_2O \rightarrow Ar_{n-1}B(OH)_{m+1} + HAr\ (n = 3\text{–}1;\ m = 0\text{–}2) \quad (8)$$

These hydrolysis reactions (hydrodeboration, from the point of view of the aryl group) have been observed also with aryl rings not containing fluorine atoms, particularly for dihydroxyboranes, and are usually performed in protic solvents under either acid or base catalysis.[24] In the upper part of Scheme 6 both of the initial steps hypothesized in the literature[24b,25] for base-catalyzed hydrodeboration, involving either direct deprotonation of $\mathbf{1_m}$ or deprotonation of its water adduct, have been reported.

Furthermore, the dearylation from **2** to **3** observed in the second context, when **1** has already been completely consumed, might occur via dearylation of $\mathbf{1_m}$. Indeed, the observed exchange between **2** and $\mathbf{1_m}$ implies that the cyclic structure of anion **2** is continuously destroyed (at least partially) and rebuilt at a very high rate. Therefore, the "transient" $\mathbf{1_m}$ molecule generated in this process could be "intercepted" by water, and, in the presence of DMAN, it could undergo fast hydrolysis [Equation (7a)] and then condensation to give dianion **4**, in equilibrium with **3**. The shift toward the left of equilibrium (4) above 233 K indicates that the role of DMAN in this process is catalytic.

A dearylation process mediated by the cleavage of the oligomeric cyclic structure might be hypothesized also for the successive slower formation of **5** from **3**.[26] In this case, however, there is no proof of fast reversible fragmentation of **3**, since no exchange between **3** and $\mathbf{1_m}$ was revealed by EXSY experiments (Figure 5). Therefore, the fragmentation of **3**, if it occurs, should be much slower than that of **2**, in agreement with the lower rate of reaction (5), relative to reaction (3).

However, it is also possible to envisage, for both reactions (3) and (5), a fully different mechanism [Equations (9a)–(9c)], leading to dearylation without opening and fragmentation of the cycle.[27] Deprotonation of the monoanions by DMAN [Equation (9a)] would give unstable dianions, from which one aryl anion could be eliminated [Equation (9b)] and then protonated by HDMAN$^+$ [Equation (9c)].

$$[Ar_nB_3O_3H_m]^- + DMAN \leftrightarrows [Ar_nB_3O_3H_{m-1}]^{2-} + HDMAN^+\ (n = 6\text{–}5;\ m = 2\text{–}1) \quad (9a)$$

$$[Ar_nB_3O_3H_{m-1}]^{2-} \rightarrow [Ar_{n-1}B_3O_3H_{m-1}]^- + Ar^- \quad (9b)$$

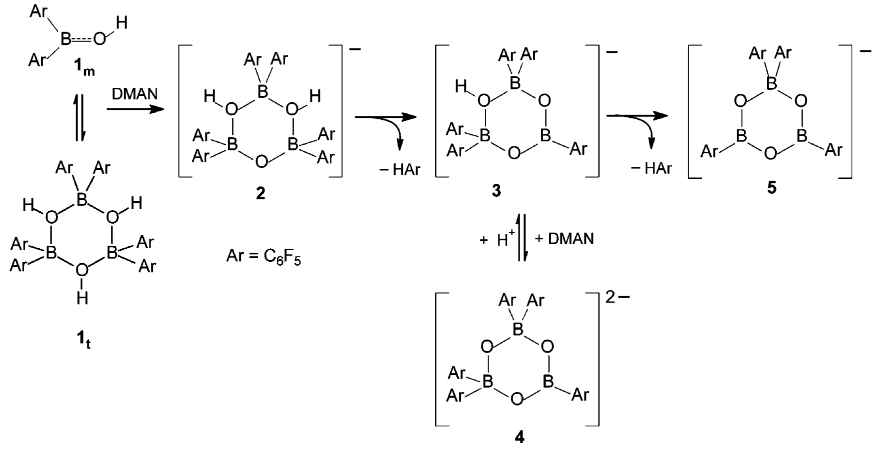
$$Ar^- + HDMAN^+ \rightarrow HAr + DMAN \quad (9c)$$

The elimination of Ar$^-$ is a crucial step of any proposed mechanism for base-catalyzed hydrodeboration of monomeric boranes.[24b,25] In our cyclic systems, Ar$^-$ lability should be enhanced by intramolecular oxygen-to-boron π-donation. Moreover, it is known that perfluorocarbanions have a better leaving ability than their hydrocarbon analogues.[25] The much higher rate of reaction (3) with respect to reaction (5) agrees with the higher lability of Ar$^-$ from a hexa- rather then from a pentaaryl dianion.

Conclusions

Most of the previous investigations on bis(pentafluorophenyl)borinic acid focussed on its Lewis acidity and showed that a seemingly innocent action such as the addition of a Lewis base to the Lewis acid **1** in fact triggered a series of complex association equilibria. This work has shown that another simple action, i.e. the addition of a Brønsted base to the Brønsted acid **1**, also has a number of unexpected effects.

First of all, the addition of DMAN has a dramatic effect on the monomer–trimer equilibrium. A "catalytic" amount of base made the equilibrium so fast that the exchange between $\mathbf{1_m}$ and $\mathbf{1_t}$ became detectable by 2D EXSY experiments. Moreover, in the presence of stoichiometric



Scheme 7. A summary of the deprotonation/cyclotrimerization/dearylation reactions promoted by DMAN.

(0.33 equiv.) DMAN, the equilibrium was completely shifted toward the cyclic oligomeric (deprotonated) form **2**, even at room temperature, where its neutral counterpart $\mathbf{1_t}$ is strongly disfavoured.

Furthermore, DMAN promotes extremely fast dearylation processes.[28,29] Boroxinates containing five or four aryl groups had been previously obtained in very few cases[17,19,20] (and sometimes serendipitously),[17,19] but this is the first time that a clean stepwise dearylation process is described, leading from a hexaaryl (36 v.e.s) to a pentaaryl (34 v.e.s) and then to a tetraaryl (32 v.e.s) B_3O_3 anionic cyclic oligomer, as summarized in Scheme 7.

From the phenomenological point of view, these dearylation processes appear new, because each step results in the conversion of one boron atom from tetra- to tricoordination, rather than in the replacement of one OH for one Ar group, as it occurs in the previously known hydrodeboration processes involving monomeric arylboranes (which are actually hydrolysis reactions).

From the point of view of the true reaction pathway, the novelty might be less striking in the hypothesis that in the initial steps pentafluorobenzene elimination occurs by base-catalyzed hydrolysis of monomeric borinic acid. Although hydrolysis reactions of monomeric perfluoroarylboranes are well established, the instantaneous formation of the cyclic dearylated anions driven by Lewis acid–base interactions followed by condensation (water elimination) remains remarkable for the combined catalytic roles of adventitious water and DMAN.

Experimental Section

General: All manipulations were performed under N_2, in oven-dried Schlenk-type glassware. The CD_2Cl_2 solvent (C.I.L.) was dried on activated molecular sieves. Bis(dimethylamino)naphthalene (Aldrich) and $(C_6F_5)B(OH)_2$ (Aldrich) were used as received. $(C_6F_5)_2BOH$ was a gift from Basell Polyolefins. NMR spectra were acquired with a Bruker AVANCE DRX-300 spectrometer (equipped with a 5-mm TBI probe or with a 5-mm QNP probe), and with a Bruker AVANCE DRX-400 spectrometer (equipped with a 5-mm BBI probe). ^{19}F NMR spectra were referenced to external $CFCl_3$. The temperature was calibrated with a standard CH_3OH/CD_3OD solution.[30] Pentafluorotoluene ($C_6F_5CH_3$, 1 µL) was added to each sample, as internal standard for both ^1H and ^{19}F NMR spectra.

NMR Spectroscopic Monitoring of the Reaction between 1 and DMAN: The appropriate amount of **1** was weighed under N_2 directly into a NMR tube and then dissolved in CD_2Cl_2, affording typically 0.10-M solutions. Then DMAN was added, with a microsyringe, from a CD_2Cl_2 solution prepared immediately before the experiment (typically ca. 1 M). In the low-temperature experiments, the tube was introduced in an acetone–dry-ice bath, before DMAN addition, and precautions were taken to limit as much as possible the heating of the sample during shaking and transfer of the tube to the cool NMR probe (173 K). After each addition ^1H and ^{19}F NMR spectra were recorded, either at 173 K or at 298 K, that showed the formation of pentafluorobenzene and of the cyclic anions described in the Results section (NMR spectroscopic data at low temperature are in Table 1; significant temperature dependence of the chemical shifts has been observed for many resonances). COSY and NOESY 2D experiments were performed, when necessary, to assign the resonances. ^{19}F EXSY experiments at different temperatures allowed detection of the intermolecular exchange processes discussed in the text.

Reaction between $(C_6F_5)_2BOH$, $(C_6F_5)B(OH)_2$ and DMAN (Molar Ratio 2:1:1), in the Presence of Molecular Sieves: $(C_6F_5)_2BOH$ (15.8 mg, 0.044 mmol) and $(C_6F_5)B(OH)_2$ (4.6 mg, 0.022 mmol) were dissolved in CD_2Cl_2 (500 µL) directly in a NMR tube, in the presence of freshly activated 3-Å molecular sieves. Some undissolved $(C_6F_5)B(OH)_2$ was present. Then a CD_2Cl_2 solution of DMAN (17 µL, 0.98 M) was added at room temperature (slightly below the stoichiometric amount). Immediately, the solution became clear, and the ^{19}F NMR spectrum showed the presence of the pentaaryl anion **3** (formed quantitatively with respect to DMAN), together with unreacted $(C_6F_5)_2BOH$ (0.005 mmol) and (C_6F_5)-$B(OH)_2$ (0.010 mmol).

Reaction between $(C_6F_5)_2BOH$, $(C_6F_5)B(OH)_2$ and DMAN (Molar Ratio 1:2:1), in the Presence of Molecular Sieves: $(C_6F_5)_2BOH$ (9.6 mg, 0.026 mmol) and $(C_6F_5)B(OH)_2$ (11.2 mg, 0.053 mmol) were dissolved in CD_2Cl_2 (660 µL) directly in a NMR tube in the presence of freshly activated 3-Å molecular sieves. A white precipitate of $(C_6F_5)B(OH)_2$ was present. Then a CD_2Cl_2 solution of DMAN (22 µL, 0.98 M) was added. Immediately, all the precipitate dissolved, and the ^{19}F NMR spectrum showed the presence of anions **5** (ca. 45%) and **3** (ca. 20%), together with unreacted $(C_6F_5)B(OH)_2$. The presence of **3** is attributable to the competitive occurrence of the condensation of the boronate anion with **1**, favoured by the low solubility of $(C_6F_5)B(OH)_2$.

Supporting Information (see footnote on the first page of this article): Eight figures showing details of the NMR spectroscopic characterization.

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[10] This is strictly true at temperatures higher than 233 K. Otherwise, a slight increase of the concentration of HDMAN$^+$ was observed, which was due to the formation of dianion **4**, as described in the following discussion in the paper.

[11] The value of 509 µS cm^{-1}, measured for a 0.065 M solution of **1** in CH_2Cl_2, is very similar to that (625 µS cm^{-1}) measured for a 0.058 M solution of NBu_4PF_6 at room temperature.

[12] It has been previously shown[13–15] that in perfluoroarylboranes the separation between the *meta* and *para* ^{19}F NMR signals ($\Delta\delta_{m-p}$), which is large for neutral tricoordinate boron compounds, progressively decreases on going to neutral tetracoordinate boron centres and to anionic borates, because of the upfield shift of the *para* resonance, resulting from the shielding caused by the increased electron density on the boron atom. For an application of these considerations to borinic acid derivatives, see ref.[16]

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[26] The feasibility of the condensation of one borinic and two boronic units to give the tetraaryl anion **5** has been demonstrated [Equation (6)].

[27] Intramolecular γ-elimination, via a four-centred transition state, might also be hypothesized, but this would not agree with the need for base catalysis.

[28] As suggested by a reviewer, we checked that a weaker Brønsted base, namely 4-Me-2,6-tBu$_2$-pyridine (pK_a = 6.9)[29] is able to promote the same dearylation processes, but in this case the rate was significantly lower. Actually, in a room-temperature titration, quantitative formation of **2** was observed up to 0.33 equiv. base without any significant formation of **3**. Dearylation of **2** to **3** occurred very slowly ($t_{1/2} \approx 2.5$ h) only when the amount of base was increased to 0.5 equiv. Much slower was the dearylation of **3** to **5** ($t_{1/2} \approx 8$ h).

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