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Hydrogen Bonding and Lewis Acid–Base Interactions in the System Bis(pentafluorophenyl)borinic Acid/Methanol

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Methanol does not significantly affect the position and the rate of the equilibrium between the monomeric ($\mathbf{1_m}$) and cyclic trimeric ($\mathbf{1_t}$) forms of bis(pentafluorophenyl)borinic acid, Ar_2BOH (**1**, Ar = C_6F_5), in CD_2Cl_2 solution. This contrasts with what was previously observed in the presence of thf and is mainly due to the stabilization of the $\mathbf{1_m}$·MeOH covalent adduct through the formation of the hydrogen-bonded dimer $[Ar_2B(OH)(MeOH)]_2$ (**7**), characterized in solution and by single-crystal X-ray analysis. This dimer can be viewed as the intermediate in the conversion of **1** into its methyl ester **6** by fast proton transfer along the hydrogen bond, which transforms the $\mathbf{1_m}$·MeOH adduct into the **6**·H_2O adduct. Extrusion of H_2O by water scavengers drives the equilibrium toward ester **6**. X-ray analysis showed that, at variance with **1**, ester **6** in the solid state is a monomer. Hindered rotation [$\Delta H^\# = 38(1)\ \mathrm{kJ\,mol^{-1}}$, $\Delta S^\# = -35(6)\ \mathrm{J\,mol^{-1}}$] around the B–OMe bond, due to O-to-B π-donation, has been observed. This π-donation lowers the Lewis acidity of **6**, as shown by the thermal instability of its adducts with MeOH and thf. Water addition to **6** affords the dimeric adduct **7**, in fast equilibrium with both $\mathbf{1_m}$ and **6**, even at 183 K, as revealed by 2D EXSY analysis. Borinic acid itself can act as a water scavenger at low temperature, so that **6** is formed also in the early stages of the titration of **1** with MeOH. The other main initial product was the adduct $[Ar_2B(OH)]_3$·MeOH (**3**) containing a MeOH molecule bound within an octaatomic –B–O(H)–B–O(Me)–H···O(H)–B–O(H)– ring. Fast proton transfer along the strong hydrogen bond was revealed by 2D EXSY analysis. At variance with thf, the adduct containing MeOH exocyclically hydrogen-bonded to $\mathbf{1_t}$ could be obtained in high concentration at 183 K only when due allowance for the kinetic requirements of the slow trimerization equilibrium was made.

Introduction

The high current interest in the uses of Lewis acids in organic synthesis and in catalysis[1] has stimulated a great number of studies on the reactivity of fluoroarylboranes.[2] Much of the work focused on tris(pentafluorophenyl)borane,[3] but related molecules have also been extensively investigated. Among these, bis(pentafluorophenyl)borinic acid $(C_6F_5)_2BOH$ (**1**, hereafter borinic acid)[4,5] has been the object of a number of fundamental and applicative studies,[6–11] because of its peculiar reactivity.

We have previously shown[8] that **1** is a cyclic trimer ($\mathbf{1_t}$, Scheme 1) in the solid state,[12] whilst in solution, complete (toluene)[8] or partial (dichloromethane)[9] dissociation to the $(C_6F_5)_2BOH$ monomer $\mathbf{1_m}$ (hereafter Ar_2BOH, Ar = C_6F_5) occurs, according to equilibrium (1).

$$cyclo\text{-}(Ar_2BOH)_3 \rightleftarrows 3\ Ar_2BOH \qquad (1)$$

The structure of the trimer is unprecedented in boron chemistry, since, unlike the well known *cyclo*-$(RBO)_3$ boroxines, it only contains tetracoordinate boron atoms. Such a structure rather resembles that of group 14 organometallic oxides, *cyclo*-$(R_2EO)_3$ (E = Si, Ge, or Sn), formed by the condensation of the corresponding $R_2E(OH)_2$ precursors. In this case, however, $\mathbf{1_t}$ arises by self-association, driven by the Lewis acidity of boron and the basicity of oxygen, without any elimination reaction.

The novelty of this structure prompted us to investigate in more detail the oligomerization reaction (in dichloromethane solution) and the effects of the presence of molecules that are able to promote intermolecular associations by Lewis acid–base or hydrogen-bonding interactions.

It was found that Lewis bases, such as water[9] or tetrahydrofuran (thf),[11] stabilize the trimeric form (whose concentration is usually very low), by formation of the hydrogen-bonded adducts **2** shown in Scheme 1 (where the labels

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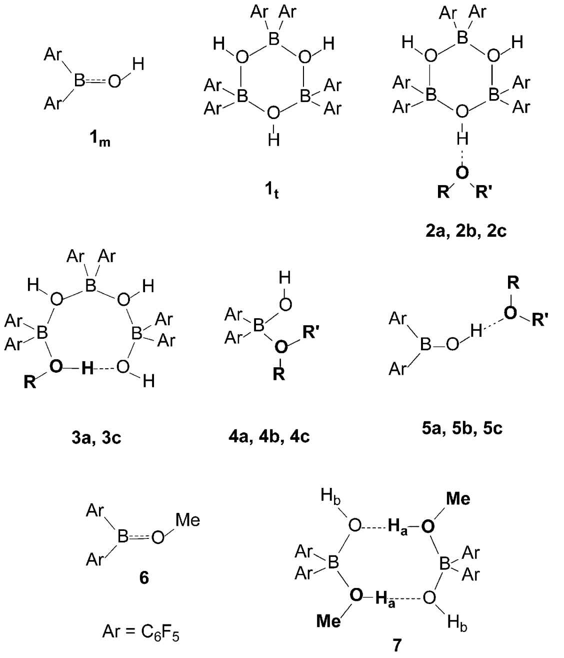
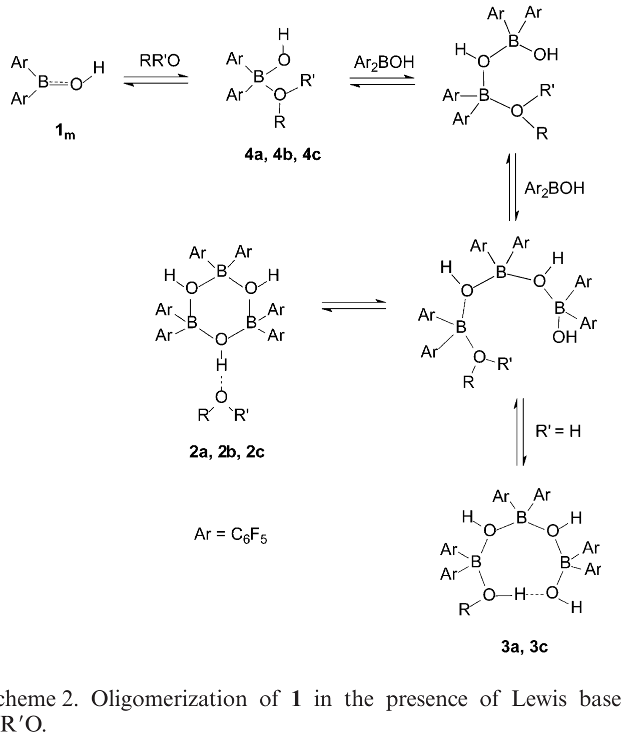


Scheme 1. Monomeric and trimeric borinic acid and their adducts with RR′O bases (**a**: RR′O = H_2O, **b**: RR′O = thf, **c**: RR′O = MeOH).

a, **b**, and **c** refer to the adducts with water, thf, and MeOH, respectively). Moreover, the bases accelerate the attainment of the equilibrium (which is otherwise very slow, even at room temperature), by forming the intermediate adducts **4** (Scheme 1), in which the increased (with respect to $\mathbf{1_m}$) nucleophilicity of the BOH oxygen atom favors the oligomerization path depicted in Scheme 2.



Scheme 2. Oligomerization of **1** in the presence of Lewis bases RR′O.

Several differences between H_2O and thf have been observed in relation to their interaction with $\mathbf{1_m}$ and the nature of the adducts present in solution at different temperatures. In this work we have investigated the behavior of borinic acid **1** in the presence of a Lewis base with properties intermediate between water and thf, namely methanol (MeOH).[13,14] From the point of view of the hydrogen-bonding interactions, MeOH, as water, can act both as hydrogen-bond acceptor and donor. In both cases, its effectiveness is expected to be comparable to that of water.[15–17] This dual nature might result in a rich reactivity. Moreover, with methanol, the occurrence of an esterification equilibrium can be anticipated [equation (2)], and this might further complicate the scenario or even become the dominant feature.

$$Ar_2BOH + MeOH \rightleftarrows Ar_2BOMe + H_2O \qquad (2)$$

Results and Discussion

The reactivity of **1** with MeOH has been investigated mainly by titrations at high (283 K) and low (183 K) temperature, monitored by ^{1}H, ^{19}F, and ^{11}B NMR spectroscopy (the latter at 283 K only).[18]

These titrations clearly showed that the base MeOH is much less effective than thf in stabilizing the trimeric cyclic structure of $\mathbf{1_t}$. Actually, at 283 K the relative amount of the trimeric species remained very low in the early titration steps, and $\mathbf{1_t}$ disappeared completely after the addition of 1 equiv. of MeOH (Figure 1). Even at 183 K, the adduct

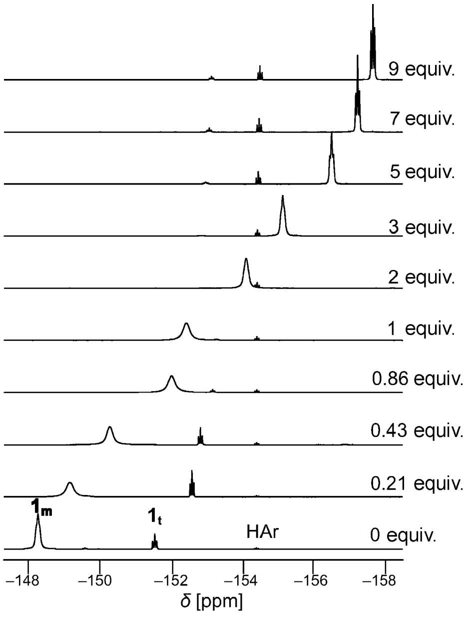


Figure 1. *para* region of the ^{19}F NMR spectra of **1** treated with increasing amounts of MeOH (the number of equivalents added is shown for each spectrum) in CD_2Cl_2 at 283 K. At this temperature, $\mathbf{1_m}$ and $\mathbf{1_t}$ are in fast exchange with their respective adducts with methanol, so that mol-fraction-weighted average resonances are observed. The formation of pentafluorobenzene (labeled as HAr) indicates some progressive decomposition.

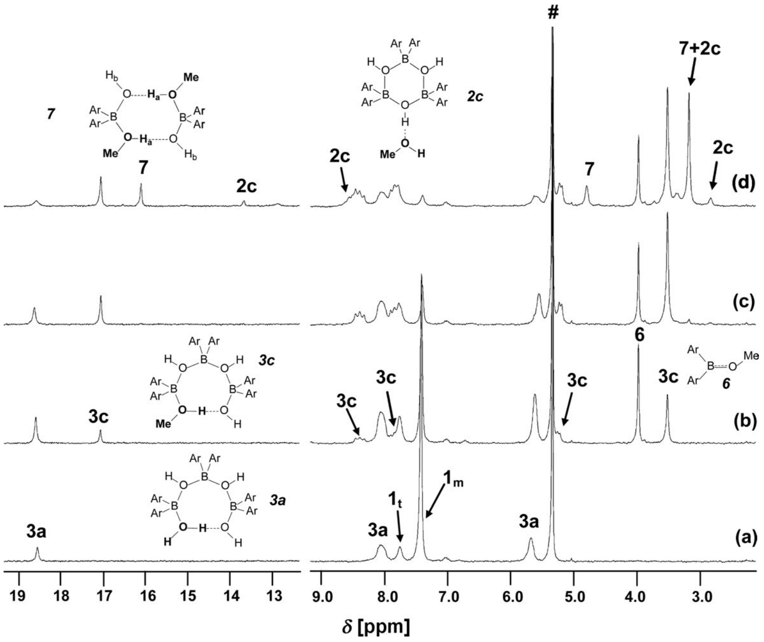


Figure 2. ^1H NMR spectra at 183 K of **1** in CD_2Cl_2 (#) in the presence of different amounts of methanol: (a) 0 equiv., (b) 0.1 equiv., (c) 0.2 equiv., (d) 0.3 equiv.

between $\mathbf{1_t}$ and MeOH (**2c** in Scheme 1) was a minor species (Figure 2), while in the presence of stoichiometric thf (0.33 equiv.) quantitative conversion to the trimeric adduct **2b** occurs.[11] Interestingly, **2c** became the main species in solution when a sample of **1**, treated with 0.33 equiv. of MeOH at room temperature, was very slowly cooled down to 183 K. This indicates that kinetic factors, concerning the slow monomer–trimer equilibrium, affect product distribution. In contrast, with thf the trimerization to adduct **2b** was instantaneous even at 183 K.

The very low concentration of **2c** likely explains the absence of any significant ionization up to 10 equiv. of MeOH, as demonstrated by a conductimetric titration at 273 K. By contrast, under the same conditions, ionization equilibria involving deprotonation of **2b**,[11] were observed as soon as more than 0.33 equiv. of thf were added.

Low-temperature NMR spectroscopic titrations revealed that under these conditions the interaction of borinic acid with MeOH led to the formation of three main products. The major species formed at the very beginning of the titration (Figure 2b) was identified as methyl borinate (**6** in Scheme 1, spectroscopic data in Table 1).[19]

The other main initial product detected in the low-temperature titrations (Figure 2) was **3c** (Scheme 1), in which a

Table 1. ^1H and ^{19}F chemical shifts (183 K, CD_2Cl_2) of the species described in this work.

Compound	^1H [ppm]	^{19}F [ppm][a]		
		ortho	*para*	*meta*
2c	13.59 (s, OH)	–132.33 (A2), –142.01 (A6)	–151.79 (A4)	–160.74 (A3), –160.56 (A5)
	8.53 (t, 2OH)	–135.81 (B2), –141.79 (B6)	–152.01 (B4)	–160.68 (B3), –161.92 (B5)
	3.21 (s, CH_3)	–140.53 (C2), –132.75 (C6)	–152.98 (C4)	–161.05 (C3), –163.55 (C5)
	2.86 (s, OH)			
3c[b]	17.03 (s, OH_a)	–129.79 (A6), –130.29 (A2)	–151.37 (A4)	–159.71 (A3), –160.12 (D3)
	8.41 (t, OH_c)	–130.70 (C6), –134.36 (D2)	–151.39 (B4)	–160.41 (B3), –160.65 (C3)
	7.87 (t, OH_d)	–134.70 (F2), –137.72 (B6)	–151.49 (C4)	–160.84 (B5), –161.50 (F3)
	5.24 (d, OH_b)	–137.94 (E2), –139.92 (C2)	–151.91 (D4)	–161.47 (E3), –162.17 (C5)
	3.54 (s, CH_3)	–140.29 (E6), –140.72 (B2)	–153.44 (F4)	–162.40 (E5), –162.43 (F5)
		–141.49 (F6), –143.84 (D6)	–154.23 (E4)	–162.67 (D5), –162.84 (A5)
6	4.00 (s, CH_3)	–131.11	–148.05	–161.49
		–131.90	–149.70	–160.44
7	16.06 (s, OH)	–137.05	–154.94	–162.35
	4.81 (s, OH)			
	3.21 (s, CH_3)			
8[c]	3.80 (s, CH_3+$2CH_2^{\alpha}$)	–132.20	–150.57	–161.61
	1.88 (s, $2CH_2^{\beta}$)			
9	16.61 (s, OH)	–136.34	–155.40	–162.90
	3.45 (s, $2CH_3$)			

[a] See the Experimental Section for the labeling of the ^{19}F resonances. [b] The ^1H and ^{19}F resonances are labeled according to Scheme 5. [c] Data at 203 K.

MeOH molecule is simultaneously B-bonded and H-bonded within an octanuclear ring. This species is analogous to the species **3a**, containing a water molecule instead of MeOH, which spontaneously forms [together with the anhydride Ar_2BOBAr_2,[5,20] equation (3a)] whenever dichloromethane solutions of **1** are cooled to temperatures low enough to make the very unfavorable entropy term in equilibrium 3b (see Figure 2a) less important.

$$2\ Ar_2BOH \rightleftarrows Ar_2BOBAr_2 + H_2O \qquad (3a)$$

$$3\ Ar_2BOH + H_2O \rightleftarrows [Ar_2BOH]_3{\cdot}H_2O\ (\text{isomer } \mathbf{3a}) \qquad (3b)$$

The spectroscopic data of **3c** (Table 1) are consistent with a structure of C_1 symmetry. It is worth mentioning that the five high-field *ortho* ^{19}F signals correspond to the fluorine atoms coupled with the OH protons in a scalar fashion. The same occurs for the three high-field *ortho* signals for **2c** and **2b**[11] and is in line with what was previously observed in similar systems for fluorine atoms involved in intramolecular X–H···F–C hydrogen bonding.[21]

^1H and ^{19}F EXSY experiments [Figure 3 and Figure S3 (Supporting Information), respectively] showed exchange cross-peaks between **3c** and $\mathbf{1_m}$, a behavior similar to that previously observed for **3a**.[9]

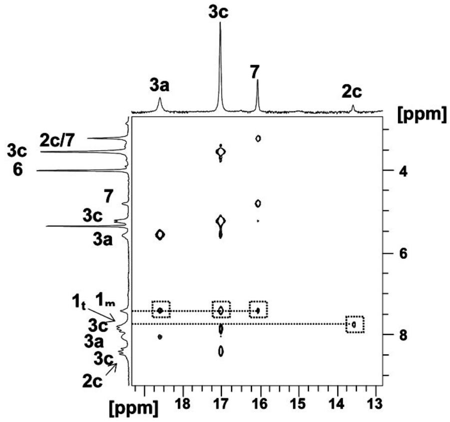


Figure 3. Section of a ^1H EXSY/NOESY experiment performed with a solution of **1** treated with 0.23 equiv. of MeOH (CD_2Cl_2, 183 K), showing the intramolecular (NOE) and intermolecular (exchanges shown by dotted squares and straight lines) correlations of the hydrogen-bonded OH protons. The methyl region of the same spectrum shows the exchange between the methoxy group of **6** and the methyl groups of adducts **7** and **3c**.

At subsequent stages of the titrations at 183 K, a third product appeared in progressively increasing concentration. Its formulation as a dimer of adduct **4c** (**7** in Scheme 1) comes from the following evidence: The spectroscopic data point to an adduct between monomeric borinic acid and MeOH, because they show a 1:1 ratio between Ar_2BOH and MeOH. The OH resonance at δ = 16.06 ppm indicates the presence of a strong hydrogen bond. The observation that only this low-field proton has a COSY correlation with the methyl group (Figure 4) rules out the hydrogen-bonded adduct **5c** in Scheme 1. The ^{11}B NMR spectroscopic data also support the formation of a covalent adduct between $\mathbf{1_m}$ and MeOH: Figure 5 shows that, on increasing the amount of MeOH, the (averaged) ^{11}B resonance progressively shifts from a position typical of tricoordination (δ = 40 ppm) toward one typical of tetracoordination (δ = 7 ppm).[3a,22] This behavior is analogous to that observed with water, although a much larger amount of MeOH (9 equiv., vs. 2.5 equiv. of H_2O) was necessary to shift the equilibrium to the right completely.

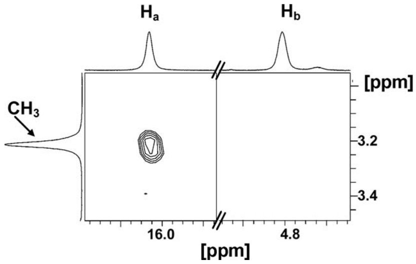


Figure 4. Selected regions of the spectrum of a ^1H COSY analysis of a CD_2Cl_2 solution of **7** (183 K), showing that the Me group has a scalar cross-peak with H_a only and not with H_b (Scheme 1). The same experiment does not show a correlation between H_a and H_b.

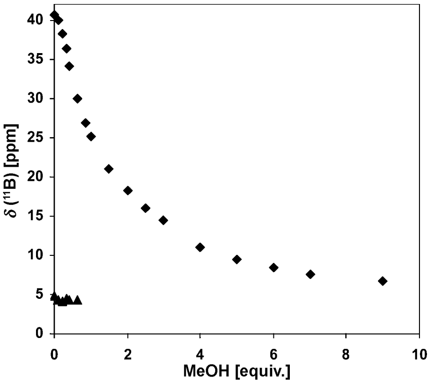


Figure 5. Variation of the chemical shifts of the (averaged) ^{11}B NMR resonances of the monomeric (♦) and trimeric (▲) species, during a titration of **1** with methanol, at 283 K.

The hydrogen-bonded dimeric structure **7** in Scheme 1 (which bears some resemblance to the dimeric form of carboxylic acids) has been supported by a solid-state single-crystal X-ray analysis (Figure 6).

Each of the boron atoms in the dimeric species **7** is bound to a hydroxido ligand, a methanol molecule, and two pentafluorophenyl groups, arranged in a tetrahedral coordination geometry. The formulation of **7** as a hydroxido/methanol species (instead of an aqua/methoxido tautomer) is based on the direct observation of the oxygen-bound hydrogen atoms and on the value of the boron–oxygen bond lengths (which are much shorter for the negatively charged hydroxido ligand relative to the neutral methanol ligand). The position of the proton could not be easily anticipated on the basis of the relative acidity of water with respect to methanol, which has been shown to be strongly dependent on the environment.[23,24]

Two [$Ar_2B(OH)(MeOH)$] moieties are tied together by two strong O–H···O asymmetrical hydrogen bonds, leading

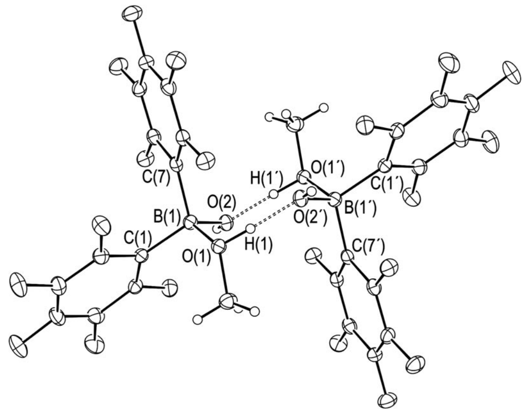


Figure 6. ORTEP drawing of the solid-state structure of the dimeric adduct $[Ar_2B(OH)(MeOH)]_2$ (**7**) with a partial labeling scheme. Selected bond lengths [pm] and angles [°]: B(1)–O(1) 154.1(2), B(1)–O(2) 147.2(2), B(1)–C(1) 162.8(3), B(1)–C(7) 163.2(3), O(1)–H(1) 96(3), H(1)···O(2′) 153(3), O(1)···O(2′) 248.18(18); O(1)–B(1)–O(2) 104.54(14), O(1)–B(1)–C(1) 107.11(13), O(1)–B(1)–C(7) 108.57(14), O(2)–B(1)–C(1) 114.69(15), O(2)–B(1)–C(7) 109.64(14), C(1)–B(1)–C(7) 111.84(14), O(1)–H(1)···O(2′) 175(3). Primes address symmetry-equivalent atoms (1 – *x*, –*y*, 1 – *z*).

to a $B_2H_2O_4$ eight-membered ring with a chair conformation. A similar dimeric structure was previously found for a related derivative, namely $[(1,5\text{-cyclooctanediyl})B(OMe)(MeOH)]_2$,[25] in which more symmetrical hydrogen-bond patterns and boron–oxygen distances are observed, as a result of the identical acidity of the two ligands sharing the proton (methoxido and methanol).

Upon increasing the amount of MeOH at low temperature, the relative amount of **7** progressively increased, but simultaneously a gelatinous white precipitate began to form: the higher the concentration of **1**, the lower the amount of MeOH needed to induce the precipitation. Likely, this precipitate, which reversibly dissolves on increasing the temperature, is constituted by hydrogen-bonded oligomers, made from $\mathbf{1_m}$ and its adduct with MeOH, in different relative amounts according to the composition of the solutions.

Synthesis and Characterization of Methyl Borinate 6

The methyl ester of bis(pentafluorophenyl)borinic acid, ester **6**, can be easily and quantitatively obtained by treating **1** with one equivalent of MeOH in the presence of effective water scavengers, such as activated 3-Å molecular sieves, which are necessary to drive equilibrium (2) to the right. Ester **6** has been previously obtained by reaction of MeOH with Ar_2BH or Ar_2BCl, or by decomposition of an unusual ion pair, featuring an OMe group bridging the two boron centers of the diborane $1,2\text{-}C_6F_4(Ar_2B)_2$.[19] In addition, the other previously known alkyl or aryl Ar_2BOR esters had been obtained by routes different from the simple reaction of **1** with alcohols or phenols.[7h,26–29]

As mentioned above, methyl borinate is formed even in the absence of an external water scavenger, upon treatment of borinic acid with small amounts of MeOH, at 183 K. Indeed, after addition of 0.1 equiv. of MeOH, almost 60% of the alcohol was converted into the borinate, as shown in Figure 2b.

This surprising finding can be explained by the "dehydrating capability" exhibited at low temperature by the solutions of **1** itself, due to the stabilization of the released water molecule within the hydrogen-bonded ring of adduct **3a** (equilibrium 3b). In agreement with this, the formation of the borinate ester under the latter conditions was accompanied by an increase in the concentration of the water-containing adduct **3a** (see Figure 2b). When the amount of free **1** decreased, this reaction (which "consumes" 4 mol of **1** per mol of **6** formed) stopped, and no further increase in the amount of **6** was observed in the subsequent titration stages.[30]

At low temperature, the two aryl rings became nonequivalent, so two ^{19}F signals are observed in each of the *ortho*, *para*, and *meta* regions (see Figures S1–S4 in Supporting Information).[19] This behavior, analogous to that previously observed for $\mathbf{1_m}$[8] and other esters of diarylborinic acids,[28,31] arises from the hindered rotation around the B–O bond, as further confirmed by the scalar and dipolar couplings observed, at 183 K, between the hydrogen atoms of the methoxy group and the *ortho* fluorine atoms of only one perfluorinated ring. Band-shape analysis of the *para* ^{19}F signals in the temperature range 197–281 K provided the kinetic parameters for the rotation of the OMe group around the Ar_2B–O bond. The kinetic constants turned out to be about one order of magnitude smaller than those previously measured for the rotation of the OH group around the corresponding Ar_2B–O bond in $\mathbf{1_m}$ (Figure 7). The analysis of the activation parameters indicates that this is attributable to the entropy term, rather than to a stronger oxygen-to-boron π donation in **6**: $\Delta H^{\#} = 38(1)\ \text{kJ mol}^{-1}$, $\Delta S^{\#} = -35(6)\ \text{J mol}^{-1}\text{K}^{-1}$ for **6** vs. $\Delta H^{\#} = 42(1)\ \text{kJ mol}^{-1}$, $\Delta S^{\#} = 14(3)\ \text{J mol}^{-1}\text{K}^{-1}$ for $\mathbf{1_m}$. The unfavorable activation entropy for **6** is possibly due to the higher steric requirements of the methyl group with respect to a proton, which reduces the conformational freedom in the transition state.

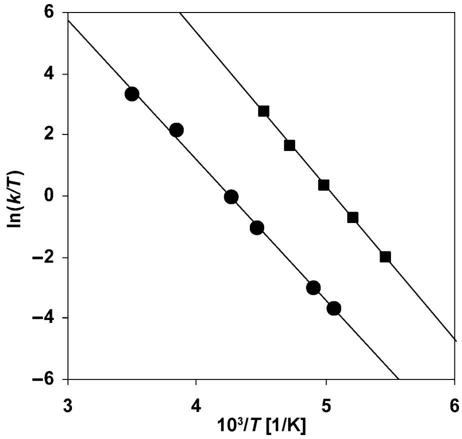


Figure 7. Eyring plot of the kinetic constants for the hindered rotation around the B–OR bond in **1** (R = H, ■) and **6** (R = Me, ●).

The NMR spectroscopic data did not show for **6** any evidence of a trimeric form analogous to $\mathbf{1_t}$. Actually, a methyl group is too bulky to be hosted in the small pockets between adjacent pentafluorophenyl rings. Steric hindrance is the key factor determining the extent of dimerization also in the case of the related Ar_2BNR_2 derivatives, which may give rise to monomer–dimer equilibria.[32] X-ray analysis confirmed that **6** has a monomeric structure also in the solid state.

The boron atom in ester **6** is bound to a methoxido ligand and two pentafluorophenyl groups, arranged in a trigonal planar coordination geometry (see Figure 8). The short boron–oxygen distance found in **6** is in agreement with the partial double-bond character of this interaction and is the shortest so far observed within esters of a borinic acid.[28,33] In addition, an optimal π overlap between the p orbitals of boron and oxygen is granted by the coplanar arrangement of the substituents at the two centers, the OMe group lying on the $(C_{ipso})_2BO$ plane.

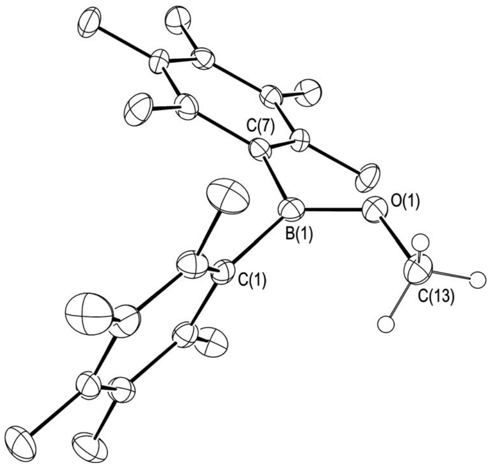
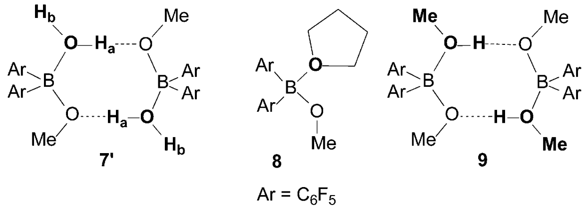


Figure 8. ORTEP drawing of the solid-state structure of the ester [Ar_2BOMe] (**6**) with a partial labeling scheme. Selected bond lengths [pm] and angles [°]: B(1)–O(1) 132.4(3), B(1)–C(1) 158.6(4), B(1)–C(7) 157.4(4), O(1)–C(13) 144.8(3); O(1)–B(1)–C(1) 123.5(2), O(1)–B(1)–C(7) 118.0(2), C(1)–B(1)–C(7) 118.5(2), B(1)–O(1)–C(13) 123.3(2); C(1)–B(1)–O(1)–C(13) 0.8(4), C(1)–B(1)–O(1)–C(13) –177.8(2).

The behavior of methyl ester **6** in the presence of oxygen bases is expected to be much simpler than that of the corresponding acid, **1**, because **6** cannot act as a hydrogen-bond donor and is not involved in a monomer–trimer equilibrium, as opposed to **1**. In agreement with this expectation, the reaction of **6** with 1 equiv. of thf at 203 K cleanly produced the Lewis acid–base adduct $Ar_2B(OMe)(thf)$ (**8** in Scheme 3, NMR spectroscopic data in Table 1). The adduct was stable only at very low temperature: indeed, already at 233 K the chemical shifts of the ^1H and ^{19}F resonances (averaged by fast exchange between free **6** and its adduct **8**) indicated almost complete dissociation of **8**. This proves the very poor Lewis acidity of boron in methyl borinate.



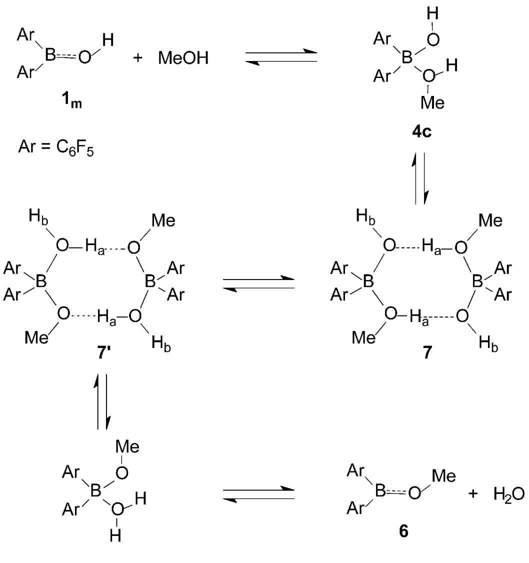
Scheme 3. Adducts of methyl borinate with Lewis bases.

The addition of one equivalent of MeOH afforded rapidly and selectively a covalent adduct, $Ar_2B(OMe)(MeOH)$ (**9**, NMR spectroscopic data in Table 1). The dimeric structure depicted in Scheme 3, analogous to that of **7**, is suggested by the presence of a strong hydrogen bond, revealed by the proton resonance at $\delta = 16.6$ ppm. The observation of a unique methyl resonance is consistent with a fast (even at 183 K) proton transfer between the OMe moieties.[34] Also in this case, reversible dissociation of the adduct occurred at temperatures higher than 233 K (equilibrium 4), where the observed ^1H, ^{19}F, and ^{11}B signals were averaged by fast exchange between **9**, methyl borinate, and free MeOH.

$$Ar_2BOMe + MeOH \rightleftarrows Ar_2B(OMe)(MeOH) \tag{4}$$

The reaction of methyl borinate **6** with water, monitored at 183 K, afforded a species exhibiting ^1H and ^{19}F signals identical to those of the above-discussed dimeric adduct **7** (Scheme 1). Actually, a simple proton oscillation along the O–H···O interaction would transform the dimeric form of the adduct between methyl borinate and H_2O (**7′** in Scheme 3) into tautomer **7** and vice versa. The ^1H COSY spectrum (Figure 4) suggests that the main species in solution is really **7**, because the hydrogen-bonded proton H_a has a scalar correlation with the methyl group and not with the other OH proton, H_b.

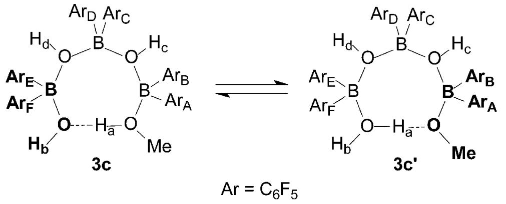
Moreover, crystals grown from a solution of methyl borinate treated with water were shown by X-ray analysis to contain tautomer **7**, proving that protonation of the boron-bound methoxy group by boron-bound water does occur.



Scheme 4. The esterification–hydrolysis equilibrium.

Nevertheless, the (transient) existence of **7′** must be assumed to account for the exchange of **7** with both $\mathbf{1_m}$ and methyl borinate **6** (Scheme 4), observed in ^{1}H and ^{19}F EXSY maps at low temperature.

An analogous proton transfer along the hydrogen bond of **3c** explains the surprising finding that **3c** exchanges not only with $\mathbf{1_m}$ but also with methyl borinate **6**. Different aryl rings are involved in the two exchange processes: a ^{19}F EXSY experiment at 183 K (Figure S3 in Supporting Information) shows cross-peaks between $\mathbf{1_m}$ and the rings of **3c** labeled as E and F in Scheme 5, whilst methyl borinate **6** has cross-peaks with rings A and B.



Scheme 5. Proton transfer in oligomer **3c** and the resulting interchange of **1** and **6** as chain terminals.

Conclusions

This work has shed further light on the complex speciation equilibria in which bis(pentafluorophenyl)borinic acid is involved, in dichloromethane solution, in the presence of molecules that are able to act as Lewis bases and hydrogen-bond acceptors or donors.

Methanol has been found to be unable to mimic the most impressive features of the interaction of **1** with thf: neither instantaneous trimerization upon addition of stoichiometric base at low temperature, nor ionization upon addition of an excess of the reactant have been observed.

The key feature explaining this different reactivity is the hydrogen-bond-donating capability of MeOH, which allows the formation of dimeric species **7**. This stabilizes the monomeric form of **1** (competing with the extra stabilization of the trimer, provided by its hydrogen bonding with the Lewis base) and at the same time traps the covalent adduct (hampering the first steps of the oligomerization, Scheme 2). This explains why MeOH is much less effective than thf in increasing the trimerization rate.

Another significant feature emerging from our studies is the high lability of the aggregates formed in these mixtures, as shown by the exchanges, detectable even at 183 K, of dimeric species **7**, or of trimeric adduct **3c**, with both acid **1** and ester **6**. In both cases this implies proton transfer along the B–O(H)···H–O(Me)–B hydrogen bonds and fast reversible dissociation of the covalent adducts.

The results are of interest not only for a better understanding of the basic chemical properties of these fluoroarylboranes, but also from the point of view of their possible applications. Actually, most of the uses of these species are based on their Lewis acidity, and it has already been observed that the acidity of **1** is intermediate between those of $B(C_6F_5)_3$ and $(C_6F_5)B(OH)_2$.[1] The data reported here show that methyl ester **6** shares with **1** a relatively poor Lewis acidity, due to the oxygen-to-boron π donation. This may be of advantage in certain catalytic applications, where the reversibility of bond activation is crucial: for instance it has been shown that the related isopropyl ester is a very effective catalyst for the polymerization of propylene oxide, while the much stronger Lewis acid $B(C_6F_5)_3$ vigorously and irreversibly reacts with the substrate itself, hampering the progress of the polymerization.[27]

Moreover, the studies reported here have provided evidence for the importance of hydrogen-bonding interactions, either in competing with the formation of Lewis acid–base adducts or in stabilizing some of them. We therefore suggest that the catalytic role of **1** might be related not only to its Lewis acidity, but also to its hydrogen-bond-donor/acceptor capability. Actually, hydrogen bonding is emerging as an effective tool in metal-free organocatalysis,[35] particularly for carbonyl derivatives;[36] and therefore synergic Lewis acid–base and hydrogen-bonding interactions might be involved in the reactions catalyzed by **1**, which mostly concern carbonyl species.

Experimental Section

General: All manipulations were performed under nitrogen, in oven-dried Schlenk-type glassware. CD_2Cl_2 (C.I.L.) and MeOH (Fluka) were dried on activated molecular sieves. $(C_6F_5)_2BOH$ 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.[37] Pentafluorotoluene ($C_6F_5CH_3$, 1 µL) was added to each sample as internal standard for both ^{1}H and ^{19}F NMR spectra.

Interaction Between $(C_6F_5)_2BOH$ (1) and MeOH: A typical experiment was performed as follows: The appropriate amount of $(C_6F_5)_2BOH$ was weighed under nitrogen directly into the NMR tube and then dissolved in CD_2Cl_2, affording typically 0.10-M solutions. Stepwise additions of MeOH were performed by using a 10-µL microsyringe. It was checked that the results did not change upon performing the MeOH addition either at room temperature or at 183 K. After each addition, the tube was briefly shaken and rapidly inserted into the NMR probe at 183 K. The titration course (up to 1 equiv.) was monitored by ^{1}H and ^{19}F NMR spectroscopy at 183 K. 2D experiments (^{1}H COSY and NOESY, ^{19}F COSY and NOESY, [^{19}F–^{1}H] HOESY, [^{19}F–^{1}H] COSY) were performed at different titration steps. Some of these experiments are shown in Figures S1–S4 in Supporting Information. The δ values of all the observed species are reported in Table 1.

The results of a typical experiment are shown in Figure 2. In the first steps of the titration (up to ca. 0.1 equiv.) the formation of **6** and **3c** was observed. The ^{19}F spectrum of **3c** shows 30 partially overlapping signals (C_1 symmetry, Table 1, and Figure S1 in Supporting Information), while its ^{1}H spectrum exhibits one CH_3 and four OH resonances. A {^{19}F}-^{1}H spectrum (Figure S5 in Supporting Information) proved that the multiplicities of the three OH signals at δ = 8.41, 7.87, and 5.24 ppm are due to H–F through-space coupling with fluorine atoms, which were identified by a [^{19}F–^{1}H]

COSY experiment at 183 K. An AB system results from strong coupling between the two *ortho* ^{19}F signals at –139.92 ppm (C2, according to the ring labels of Scheme 5) and –140.72 ppm (B2), both coupled with H_c at δ = 8.41 ppm (t, apparent J_{HF} = 19 Hz). The same occurs for the other two ^{19}F signals at –140.29 ppm (E6) and –143.84 ppm (D6), coupled with H_d at δ = 7.87 ppm (with the same J_{HF}). The ^{1}H signal at δ = 5.24 ppm (H_b) is coupled to one fluorine atom only (–141.49 ppm, F6); J_{HF} = 12 Hz.

Upon further additions of MeOH, **2c** and **7** were formed (Figure 2, Table 1). Adduct **2c** was identified by its four ^{1}H signals (ratio 1:2:3:1) and fifteen ^{19}F resonances, in agreement with C_2 symmetry. The three couples of magnetically nonequivalent rings were arbitrarily labeled as follows: A and B were the labels for those on the hydrogen-bonded Ar_2B–O(H)–BAr_2 moiety and C for those bound to the boron atom on the symmetry axis. The two high-field *ortho* ^{19}F signals at –140.53 and –142.01 ppm, both coupled to the proton at δ = 8.53 ppm (t, apparent J_{HF} = 18 Hz), are strongly coupled, giving rise to an AB system. The resonances have been assigned by 2D experiments performed on a sample containing **2c** as the main component, obtained as follows: a CD_2Cl_2 solution of **1** (0.12 M) treated with MeOH (0.33 equiv.) was slowly cooled down to 183 K, and ^{1}H and ^{19}F NMR spectra were acquired at several intermediate temperatures.

Species **7** has three ^{1}H resonances (ratio 1:1:3) and only one set of ^{19}F signals (Table 1). Large colorless crystals of **7** suitable for X-ray analysis were obtained at 248 K by slow diffusion of pentane in a CD_2Cl_2 solution of **6** (0.05 M) treated with water (1 equiv., 0.35 µL).

The titrations monitored at 283 K by ^{1}H, ^{19}F, and ^{11}B NMR spectroscopy were performed analogously.

Preparation of Methyl Borinate 6: MeOH (1 equiv.) was added to an NMR tube containing a solution of **1** (0.094 M) in CD_2Cl_2 (0.510 mL) in the presence of freshly activated 3-Å molecular sieves. The tube was kept at room temperature, and the progress of the reaction was followed by ^{1}H and ^{19}F NMR spectroscopy, showing the almost quantitative formation of **6** after 4 h. The NMR spectroscopic data at 183 K are reported in Table 1, while the δ values at room temperature (dynamically averaged in the case of the ^{19}F resonances) are the following: ^{1}H NMR δ = 3.94 ppm; ^{19}F NMR: δ = –132.50 (*o*), –149.73 (*p*), –161.75 (*m*) ppm.

Reaction Between Methyl Borinate and thf: A CD_2Cl_2 solution of **6** (0.16 M) was treated with thf (1 equiv.) at room temperature directly in an NMR tube. ^{1}H and ^{19}F NMR spectra at 203 K showed the quantitative formation of adduct **8**, which exhibits only one set of ^{19}F signals, while the ^{1}H NMR spectrum shows two signals at an integration ratio of 7:4, due to accidental overlap of the methyl signal and the low-field thf signals (Table 1). On increasing the temperature, progressive dissociation of adduct **8** occurred, as shown by the shift of the ^{1}H, ^{19}F, and ^{11}B signals towards the positions of **6** and free thf.

Reaction Between Methyl Borinate and MeOH: A CD_2Cl_2 solution of **6** (0.06 M) was treated with MeOH (1 equiv.) as described above. ^{1}H and ^{19}F NMR spectra at 203 K showed the quantitative formation of the dimeric adduct **9** depicted in Scheme 3 (Table 1). ^{1}H COSY and NOESY spectra recorded at 183 K showed correlation between the OH proton and the (unique) methyl resonance. At room temperature, the positions of the ^{1}H, ^{19}F, and ^{11}B resonances indicated almost complete dissociation.

Reaction Between Methyl Borinate and H_2O: A CD_2Cl_2 solution of **6** (0.05 M) was treated with H_2O (1 equiv.) as described above. ^{1}H and ^{19}F NMR spectra at 203 K (acquired immediately after the addition of water to avoid the formation of the gelatinous precipitate) showed the almost quantitative formation of the adduct **7**. On raising the temperature to 298 K, the position of the ^{1}H, ^{19}F, and ^{11}B resonances indicated that, in this diluted solution, adduct **7** was no longer present.

X-ray Diffraction Structural Analysis: Data for [Ar_2BOMe] (**6**): $C_{13}H_3BF_{10}O$, M_r = 375.96, triclinic, $P\bar{1}$ (No. 2), a = 7.339(2) Å, b = 7.455(2) Å, c = 12.291(2) Å, α = 90.99(1)°, β = 97.25(1)°, γ = 99.30(1)°, V = 657.8(3) Å^3, T = 110(2) K, Z = 2, $F(000)$ = 368, $\lambda(\text{Mo-}K_\alpha)$ = 0.71073 Å, $\mu(\text{Mo-}K_\alpha)$ = 0.214 mm^{-1}, T_{min} = 0.901, $1.7° \le \theta \le 26.0°$, 10113 measured reflections, 2566 independent reflections (R_{int} = 0.0315, R_σ = 0.0276), 1953 reflections with $I > 2\sigma(I)$, $R[F, I > 2\sigma(I)]$ = 0.0366, $wR(F^2$, all data) = 0.0834, S = 1.088, data/parameters = 2566/229, $\Delta\rho_{max,\ min}$ = +0.30, –0.28 e Å^{-3}.

Data for [$Ar_2B(OH)(MeOH)$] (½**7**): $C_{13}H_5BF_{10}O_2$, M_r = 393.98, triclinic, $P\bar{1}$ (No. 2), a = 6.014(2) Å, b = 10.101(2) Å, c = 12.425(2) Å, α = 73.02(1)°, β = 77.49(1)°, γ = 73.48(1)°, V = 684.7(3) Å^3, T = 110(2) K, Z = 2, $F(000)$ = 388, $\lambda(\text{Mo-}K_\alpha)$ = 0.71073 Å, $\mu(\text{Mo-}K_\alpha)$ = 0.216 mm^{-1}, T_{min} = 0.815, $1.7° \le \theta \le$ 26.0°, 8372 measured reflections, 2698 independent reflections (R_{int} = 0.0262, R_σ = 0.0237), 2394 reflections with $I > 2\sigma(I)$, $R[F, I > 2\sigma(I)]$ = 0.0349, $wR(F^2$, all data) = 0.0792, S = 0.997, data/parameters = 2698/246, $\Delta\rho_{max,\ min}$ = +0.37, –0.26 e Å^{-3}.

Residual factors are defined as follows: $R_{int} = \Sigma|F_o{}^2 - \langle F_o{}^2\rangle|/\Sigma F_o{}^2$, $R_\sigma = \Sigma\sigma(F_o{}^2)/\Sigma F_o{}^2$, $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, and $wR(F^2) = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^4]^{1/2}$. Goodness-of-fit is defined as $S = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_d - n_p)]^{1/2}$, in which n_d and n_p are the number of data and parameters.

CCDC-660635 and -660636 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Figures S1–S5 showing details of the NMR spectroscopic characterization.

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