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^1H and ^{19}F NMR Investigation of the Reaction of $B(C_6F_5)_3$ with Water in Toluene Solution

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Titrations of $B(C_6F_5)_3$ (**1**) with water, in toluene-d_8 solution, monitored by ^{19}F and ^1H NMR at 196 K, showed first the formation of the adduct $[(C_6F_5)_3B(OH_2)]$ (**2**) and then its stepwise transformation into the two aqua species $[(C_6F_5)_3B(OH_2)]\cdot H_2O$ (**3**) and $[(C_6F_5)_3B(OH_2)]\cdot 2H_2O$ (**4**) containing, respectively, one or two water molecules hydrogen-bonded to the protons of the B-bound water molecule. The NMR data show that in each titration step only two species were present in significant concentration: **1** and **2** up to 1 equiv, **2** and **3** between 1 and 2 equiv, **3** and **4** between 2 and 3 equiv. Above 3 equiv the solutions rapidly attained saturation and phase separation occurred (although there was evidence of interaction of **4** with more water molecules). Titrations at room temperature indicated an analogous stepwise course. Variable-temperature experiments demonstrated water exchange between the different aqua species and between the different water sites in the adducts **3** and **4** ("internal" or B-bound and "external" or H-bound). The rate of these processes increased with the amount of water bonded to $B(C_6F_5)_3$. The exchange of B-bound water among the different $B(C_6F_5)_3$ molecules (resulting in the **1** ⇔ **2** interconversion) caused the averaging of the ^{19}F resonances of **1** and **2**, above 273 K. Band shape analysis in the temperature range 235−312 K provided the kinetic constants, whose dependence on the concentration revealed a dissociative mechanism ($\Delta H^\ddagger$ 67(2) kJ mol^{-1}, $\Delta S^\ddagger$ 58(7) J mol^{-1} K^{-1}). For the adduct $[(C_6F_5)_3B(OH_2)]\cdot H_2O$ (**3**), four different dynamic processes have been recognized: (i) the exchange of H-bound water among different $[(C_6F_5)_3B(OH_2)]$ adducts (the **2** ⇔ **3** exchange) or (ii) among different $[(C_6F_5)_3B(OH_2)].H_2O$ adducts (the **3** ⇔ **4** exchange), (iii) the exchange between H-bound and B-bound water, (iv) the hopping of H-bound water between the two protons of B-bound water. This process was so fast that an averaged signal for the protons of internal water was observed even at 187 K. The rate of the process (i) increased with the concentration of **2**, so that separate ^{19}F and ^1H signals for **2** and **3** were observed only in very dilute solutions at the lowest temperatures. Linear plots of the kinetic constants (estimated from ^1H NMR spectra in the near fast exchange region, temperature range 188−214 K) vs the concentration of **2** allowed the estimation of the constant for the dissociative pathway (4 orders of magnitude faster than for the exchange of B-bound water) and for the bimolecular pathway [$\Delta H^\ddagger$ 30(2) kJ mol^{-1}, $\Delta S^\ddagger$ 3(10) J mol^{-1} K^{-1}]. Process (ii) was too fast on the NMR time scale to allow any kinetic investigation. Process (iii) caused the parallel broadening of both the ^1H signals of **3** at $T > 225$ K, with a rate quite close to that of the dissociative exchange of water among different $B(C_6F_5)_3$ molecules. The activation parameters ($\Delta H^\ddagger$ 55(2) kJ mol^{-1}, $\Delta S^\ddagger$ 7(3) J mol^{-1} K^{-1}, temperature range 233−273 K) allowed no discrimination between the exchange of an entire water molecule and the mere exchange of protons. Even small amounts of **4** accelerated process (iii), due to the occurrence of two much faster processes: the **3** ⇔ **4** exchange and the exchange between the protons of internal and external water in **4**. The study of any kind of water mobility concerning the trihydrate **4** was prevented by the occurrence of proton exchange processes (so fast as to broaden the signals of internal and external water even at 188 K), possibly favored by the acidic dissociation of the protons of the B-bonded water molecule of **4**.

Introduction

Tris(pentafluorophenyl)borane is currently extensively used as a strong Lewis acid,[1−6] particularly to promote the formation of highly active cationic catalysts for olefin polymerization.[7−15] Its use requires minimizing the amount of water present in the reaction media, due to the occurrence of equilibrium 1. Moreover, water coordinated to the strong Lewis acid $B(C_6F_5)_3$ becomes a strong Brønsted acid,[16,17] able to protonate

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[1] For a general review on properties and uses of $B(C_6F_5)_3$ see: Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345−354.

[2] A few adducts with donor molecules were already reported by the authors of its original synthesis: (a) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245−250. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1966**, *5*, 218−225.

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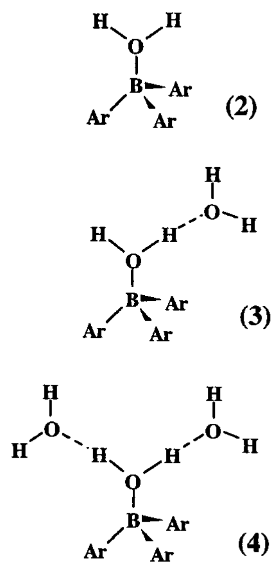
alkyl groups bound to metal centers.

$$B(C_6F_5)_3 + H_2O \Leftrightarrow [(C_6F_5)_3B(OH_2)] \qquad (1)$$

Due to the marked industrial interest in metallocene catalysts, the studies aimed at clarifying the interaction of $B(C_6F_5)_3$ with water are of both theoretical and practical significance. In fact, several works[3f,18−20] addressed this theme in some detail and reported the isolation and characterization of two different adducts of $B(C_6F_5)_3$ with water. One of them, namely, $[(C_6F_5)_3B(OH_2)]$ (**2**),[21] contains 1 equiv of water bonded to $B(C_6F_5)_3$, as confirmed by an X-ray structural investigation.[20] Others reported the preparation[22] and structural characterization[19] of a different species, containing 3 equiv of water, namely, $[(C_6F_5)_3B(OH_2)]\cdot 2H_2O$ (**4** in Chart 1). One water molecule is bonded directly to the boron atom, while the other two are bonded through hydrogen bonds to the hydrogen atoms of the coordinated water molecule. ^{17}O NMR evidence indicates that this structure is maintained also in solution, because at 273 K two separate water resonances were observed, in 1:2 ratio.[18b] Rapid exchange of boron-bound water with free water molecules was detected by variable-temperature multinuclear NMR studies, but no data were given.[19]

Chart 1



Instead a very recent paper[23] provided, from dynamic ^{19}F NMR spectroscopy, kinetic data on the exchange of water between two different $B(C_6F_5)_3$ molecules, in toluene solution. It also reported evidence of the formation, in the presence of excess water in acetonitrile solution, of a different adduct containing only 1 equiv of H-bonded water, namely, $[(C_6F_5)_3B(OH_2)]\cdot H_2O$ (**3** in Chart 1). Equilibrium deprotonation studies with a nitrogen base and ab initio calculations on the strength of the involved hydrogen bonds allowed the estimatation of the pK_a value for **3** as 8.4 in acetonitrile, indicating that this Brønsted acid must be regarded as a strong acid, comparable to HCl in acetonitrile.

We report here ^1H and ^{19}F variable-temperature NMR studies that give evidence of the stepwise formation, in

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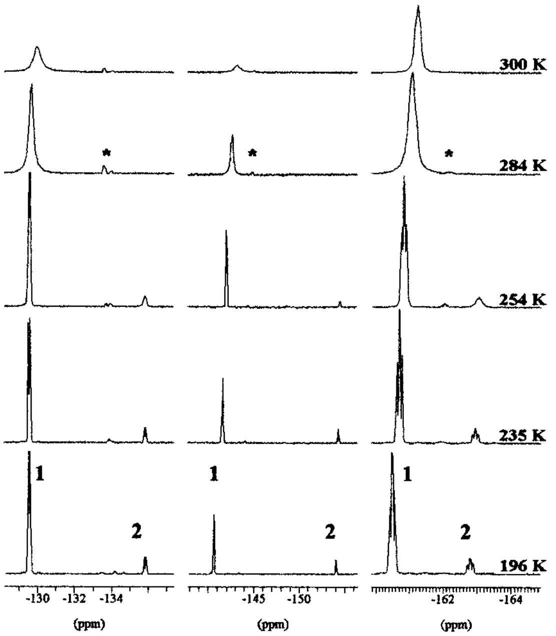

Figure 1. Variable-temperature ^{19}F NMR spectra of a sample of $B(C_6F_5)_3$ (**1**) containing ca. 10% of $[(C_6F_5)_3B(OH_2)]$ (**2**). The three regions (with different abscissas scales) refer to the *ortho*, *para*, and *meta* fluorine atoms, respectively. The three signals with the highest intensity are attributable to **1**, while the set of three minor resonances, shifted upfield, is due to adduct **2**. The asterisks mark some impurities.

toluene solution, of all three adducts of $B(C_6F_5)_3$ with water (**2**−**4**). The NMR data for each of them have been obtained, and the occurrence of several different exchange processes (between the different adducts as well as between the different water molecules inside the adducts) has been evidenced.

Results and Discussion

The ^1H NMR spectra of samples of $B(C_6F_5)_3$ at room temperature usually show a signal (δ 4.75 ppm in toluene-d_8, 4.70 in benzene-d_6, 6.75 in CD_2Cl_2, see also literature data in Table S1) attributable to the protons of water in the adduct $[(C_6F_5)_3B(OH_2)]$ (**2**). The formation of the adduct implies the presence of adventitious water, arising mainly from the solvent, and confirms that $B(C_6F_5)_3$ acts as a powerful water scavenger, due to its strong Lewis acidity. The room-temperature ^{19}F NMR spectra of the same samples usually exhibit three broad resonances, ratio 2:1:2 (Figure 1, top trace), due to the *ortho*, *para*, and *meta* fluorine atoms in the three equivalent aromatic rings of $B(C_6F_5)_3$. The large bandwidth, as well as some variability in the chemical shift of different samples, indicates that these resonances are dynamically averaged signals arising from the presence of varying amounts of water molecules, in fast exchange among the different molecules of $B(C_6F_5)_3$ (**1**).

Indeed on lowering the temperature, in CD_2Cl_2 or toluene-d_8, each ^{19}F signal collapsed and then gave two separate resonances, exhibiting the expected fine structure arising from the ^{19}F−^{19}F couplings (Figure 1). The set of signals shifted upfield is due to adduct **2**. The shift undergone by the resonance of the *para* fluorine atom is particularly large[24] and is diagnostic of the passing from a tri- to a tetracoordinated boron.[2b]

The fine structures of the resonances of adduct **2** differ significantly from that of $B(C_6F_5)_3$, reflecting a change in the coupling constants on passing from an unsaturated sp^2 boron, stabilized by a certain degree of $B{=}C$ interaction,[2b] to a saturated sp^3 center (see Figure S1 and Experimental Section for the numerical values of the coupling constants).[25]

To investigate the formation, in toluene solution, of $[(C_6F_5)_3B(OH_2)]\cdot nH_2O$ adducts containing hydrogen-bonded water molecules, we performed several titrations of $B(C_6F_5)_3$ with water directly in the NMR tube, at room temperature and at 196 K. The titrations were monitored through ^1H and ^{19}F NMR. It must be pointed out that such titrations imply the addition of water amounts as low as tenths of microliters, due to the limited solubility of $B(C_6F_5)_3$ in toluene (particularly at low temperatures); therefore the measured amounts of added water are affected by some unavoidable uncertainty. However, the experimental accuracy was sufficiently high to provide information on the nature of the different adducts formed in the course of the titration.

Titrations Monitored through ^{19}F NMR. During the addition of the first equivalent of water at 196 K we observed, as expected, a progressive increase in the intensities of the signals of the hydrate **2** at the expense of **1**, with no significant variation in the δ values of either **1** or **2** (Figure 2). On the contrary, at room temperature, the stepwise addition of up to 1 equiv of water caused a linear variation of the chemical shifts of all the ^{19}F resonances (Figure S2), because at room temperature, as already stated, the **1** $\Leftrightarrow$ **2** exchange is in the "near fast exchange region",[26] and therefore the observed δ values vary according to the variation in the relative populations of **1** and **2** in the course of the titration.

When the overall amount of water exceeded 1 equiv, free $B(C_6F_5)_3$ was no longer detected at 196 K. However, on increasing the amount of water, the resonances of the *meta* and *para* fluorines of the aqua species showed a significant progressive shift upfield (the signal of the *ortho* fluorines remained almost constant, showing a much smaller shift in the opposite direction, Figure 2). A closer analysis of the data clearly reveals that the variation in chemical shift was essentially linear within each titration step (1−2, 2−3 equiv), with a sharp decrease of the slopes at 2 equiv, as shown in Figure 2 (and in Table S2).

Above 1 equiv of water the shape of the titration curves determined at room temperature was quite close to that obtained at 196 K (see Figure S2 and Table S2), though the change in slope at each titration step was less clearly recognizable. Moreover, the variation in chemical shift of the resonances did not stop at ca. 3 equiv, as observed at 196 K, but continued (even if very slowly) until phase separation occurred, as evidenced by the appearance of small droplets of water in the tube. Literature data[27] indicate that at 300 K the solubility of water in toluene is ca. 0.05% w/w, corresponding to less than 0.2 equiv in the conditions of the experiment. The uptake of more than 3 equiv of water (even at 196 K, where water solubility is extremely low) indicates that $B(C_6F_5)_3$ is able to bind up to three water molecules strongly enough to overcome the water−toluene repul-

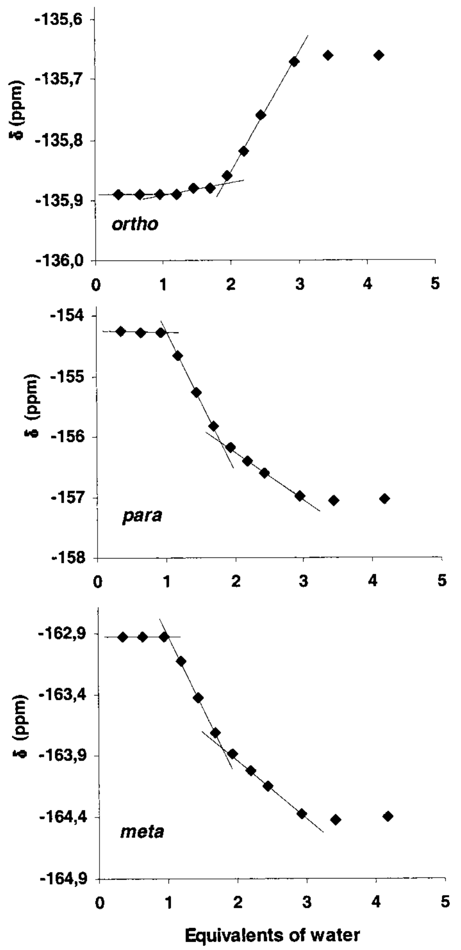

Figure 2. Variations of the chemical shifts of the ^{19}F NMR resonances of the aqua species during the titration at 196 K in toluene-d_8. The three plots have different vertical scales.

sion. The binding of other water molecules is weaker, so that the solutions rapidly attain saturation and phase separation occurs. This point will be discussed further in the light of data provided by the ^{1}H NMR monitoring at 196 K.

The shape of the titration curves of Figure 2 indicates that $B(C_6F_5)_3$ binds the three water molecules in a stepwise manner: at first only adduct **2** is formed; then the incoming water molecules interact with **2** (equilibrium 2), strongly enough to give the adduct $[(C_6F_5)_3B(OH_2)]\cdot H_2O$ (**3**). This species is still able to bind a third equivalent of water (equilibrium 3), allowing the formation of $[(C_6F_5)_3B(OH_2)]\cdot 2H_2O$ (**4**).

$$[(C_6F_5)_3B(OH_2)] + H_2O \Leftrightarrow [(C_6F_5)_3B(OH_2)]\cdot H_2O \quad (2)$$

$$[(C_6F_5)_3B(OH_2)]\cdot H_2O + H_2O \Leftrightarrow [(C_6F_5)_3B(OH_2)]\cdot 2H_2O \quad (3)$$

All the aqua species exchange H-bonded water molecules rapidly, so that dynamically averaged signals are observed even at 196 K. The change in the relative populations during the titration causes the observed shift of the signals. The fair linearity of the plots within each titration step indicates that such averaged δ values are determined mainly by the exchange of two species. This means that within each titration step only two species are present in solution in significant concentration: **2** and **3** between 1 and 2 equiv, **3** and **4** between 2 and 3 equiv (and **1** and **2** over the range 0−1 equiv, as shown by the constancy of the δ values of **2** in this step). The progressively smaller slopes reflect the expected progressively smaller differences of the ^{19}F chemical shift between the various adducts on increasing the overall number of water molecules.

Interestingly, in the titration conditions, at 196 K, the exchange between **2** and **3** was not in the "fast exchange region", since the averaged resonances for the *para* and *meta* atoms observed in the step between 1 and 2 equiv of water were structureless and broad (Figure S3a). On the contrary, the signals observed in the successive step were very sharp (Figure S3b), indicating that even at this temperature the **3** ⇔ **4** exchange was so fast that the averaged signals could show their fine structure.[28]

The titrations monitored by ^{1}H NMR support these results and provide further information.

Titrations Monitored through ^{1}H NMR. The experiment at 196 K was performed twice and the satisfactory reproducibility of the results is shown in Figure 3. The addition of the first equivalent of water caused the increase in intensity of the signal of water directly bound to $B(C_6F_5)_3$, with no significant variation in its chemical shift (δ 4.65) and bandwidth, as the **1** ⇔ **2** exchange does not affect this signal.

As soon as the amount of added water exceeded 1 equiv, a sharp signal appeared at a chemical shift (δ 0.46 ppm) close to that of free water in toluene (δ 0.28 ppm[29] at this temperature), attributable to the protons of a water molecule hydrogen-bonded through its oxygen atom, as in adduct **3**. During the addition of the second equivalent of water the intensity of this signal increased proportionally to the amount of added water, while its chemical shift and bandwidth remained constant (Figures 3c and 3d). This is a very diagnostic point: it is reasonable to assume that free water, if present (no signal was observed at δ 0.28 ppm), would be in fast exchange with the "external" (H-bonded) water molecule of **3**, and therefore the observed chemical shift would vary in the course of the titration, following the variation of the ratio between free and H-bonded water (proportional to $[\mathbf{2}]^{-1}$ according to equilibrium 2). Therefore the constancy of the observed δ (a maximum change of 0.02 ppm, and downfield, was measured over the titration range from 1 to 2 equiv) indicates that at this temperature the concentration of truly free water was negligible. In other words, water uptake by adduct **2** at 196 K must be considered to be substantially quantitative, in agreement with what was shown by the ^{19}F titration at this temperature.

As to the signal of "internal" (i.e., B-bonded) water, the shift toward higher frequencies and the broadening observed above 1 equiv of water (Figures 3a and 3b) are attributable to the fast exchange of H-bonded water molecules between the different molecules of $[(C_6F_5)_3B(OH_2)]$, so that the B-bonded water molecules exchange their environment between **2** and **3** (before 2 equiv) or **3** and **4** (above 2 equiv).[30]

The sharpening of the signal of internal water as the amount of added water approached 2 equiv (Figure 3a) reflects the disappearance of the first exchange partner of **3** (i.e., the monoadduct **2**), while the successive

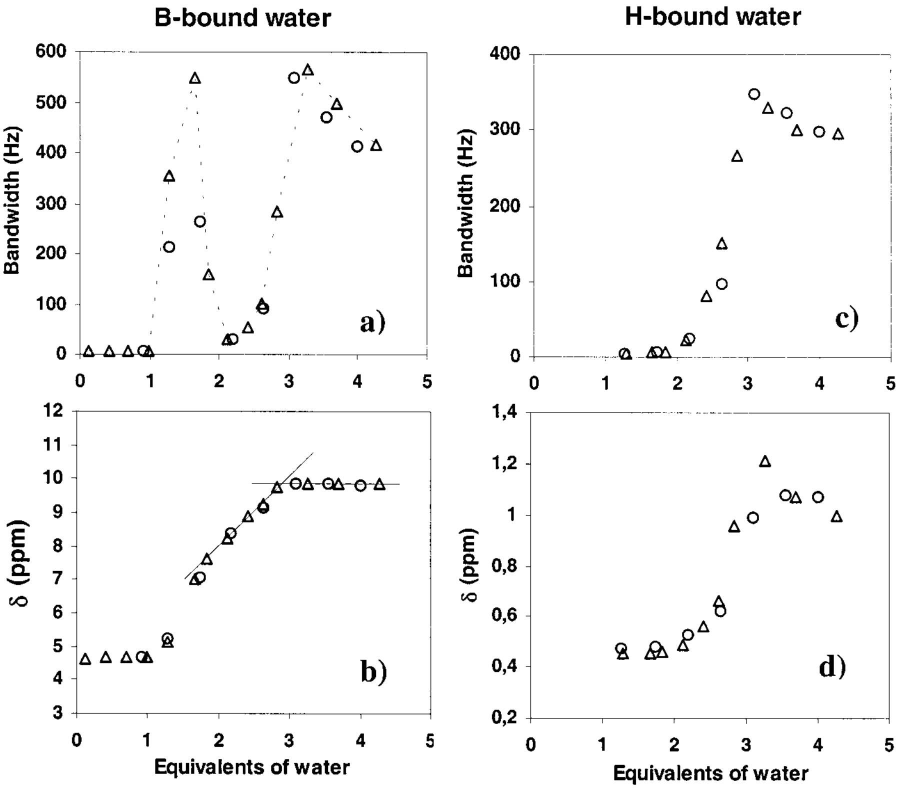

Figure 3. Bandwidth (a, c) and chemical shift (b, d) variations of the ^{1}H resonances of the B-bound (a, b) and H-bound (c, d) water molecules, during the titration at 196 K in toluene-d_8.

broadening (that involves also the signals of external water, Figure 3c) reveals the appearance in solution of a novel exchange partner (i.e., **4**). Both these findings provide further strong evidence that the water uptake occurs in a stepwise manner, leading to the transformation of most of **2** into **3** before a significant amount of **4** is formed.[31]

Above 3 equiv, the δ value for B-bonded water remained noticeably constant (Figure 3b), as above-reported for the ^{19}F resonances (Figure 2), indicating the completion of the transformation of **3** into **4**. Contrary to the previous titration step this completion did not imply the sharpening of the resonances of internal and external water, which remained very broad (Figures 3a and 3c). This is attributable to the fast exchange of protons between the two types of water molecules in **4**, which at higher temperatures averages the two signals of **4**.

There is evidence that at 196 K even the external water molecules of **4** are able to establish H-bonding interactions with other water molecules. In fact, if B(C$_6$F$_5$)$_3$ was able to interact with only three water molecules, phase separation and freezing should have occurred as soon as the amount of water had gone beyond 3 equiv, due to the extremely low solubility of water in toluene at 196 K.[32] On the contrary, we observed the formation of ice on the walls of the NMR tube only when more than 3.5 equiv of water had been added. Moreover, the bandwidth of the signal of external water was larger than expected on the base of its exchange with only the internal water molecule of **4**, suggesting the occurrence of fast exchange with other water molecules.[33] The interaction of the protons of "external" water of **4** with these novel water molecules is expected to strongly deshield the involved protons, as always occurs for H-bonding interactions. This is just what we observed when the amount of added water approached 3 equiv: indeed in both experiments at this point of the titration the chemical shift of external water underwent a sharp increase, from ca. δ 0.65 to ca. 1 ppm, as shown in Figure 3d. These "third-sphere" interactions were not strong enough to affect the δ values of the signal of B-bound water and the ^{19}F signals, which remained constant above 3 water equivalents, as previously described (Figures 3b and S2). However, they caused a slight slowing down of the exchange between internal and external water in **4**, as shown by the decrease in bandwidth of the signal of B-bonded water (and to a lesser extent of that of external water) on increasing the amount of added water.[34]

The room-temperature ^{1}H titration was less informative, as in this case there was a single signal throughout the titration. Its bandwidth increased from 1 to 2 equiv of water (Figure S4a), then progressively decreased, eventually resulting in a relatively sharp signal when 3 equiv of water was added. This behavior is consistent with a room-temperature titration course essentially analogous to that occurring at 196 K. Indeed the protonic signal is broadened (and shifted, Figure S4b)

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(21) It was isolated in high yields as a white powder by precipitation from a pentane solution of B(C$_6$F$_5$)$_3$ that had been treated with 1 equiv of water,[3f,18] or by a conproportioning reaction between 1 equiv of **3** and 2 equiv of B(C$_6$F$_5$)$_3$.[18a] Its IR spectrum in the solid state shows two sharp ν(OH) bands, indicating that **2** can be formulated as a true adduct, rather than as an ionic H[HOB(C$_6$F$_5$)$_3$] species.[3f]

(22) It was obtained by exposure of solid B(C$_6$F$_5$)$_3$ to water vapor[18a] or by slow evaporation of a CDCl$_3$ solution of B(C$_6$F$_5$)$_3$ containing several equivalents of water,[19] or else by precipitation from an Isopar E/cyclohexane mixture treated with 3 equiv of water.[16]

Table 1. ^{19}F and ^{1}H NMR Chemical Shifts (δ, toluene-d_8) for $B(C_6F_5)_3$ and Its Three Adducts with Water, As Determined in the Titrations at 196 K of Solutions ca. 0.1 M, Where Dynamically Averaged Signals for 2 and 3 Were Observed (values in italics have been measured at 190 K in much more diluted solutions (ca. 0.005 M), where the signals for 2 and 3 were well separated)

	^{19}F			^{1}H	
compound	*ortho*	*para*	*meta*	B-bound	H-bound
$B(C_6F_5)_3$ (**1**)	−129.56	−140.77	−160.51		
	−129.51	*−140.28*	*−160.36*		
$[(C_6F_5)_3B(OH_2)]$ (**2**)	−135.89	−154.25	−162.93	4.65	
	−135.77	*−153.83*	*−162.64*	*4.65*	
$[(C_6F_5)_3B(OH_2)]\cdot H_2O$ (**3**)	−135.85[a]	−156.2[a]	−163.9[a]	8.0[a]	0.46
	−135.77	*−155.83*	*−163.63*	*7.89*	*0.38*
$[(C_6F_5)_3B(OH_2)]\cdot 2H_2O$ (**4**)	−135.66	−157.0	−164.4	9.9	0.7[b]
	−135.52	*−156.71*	*−164.16*	*10.0*	*n.d.*[c]

[a] Values extrapolated from the titration curves at 2 equiv of water, **3** being in fast exchange with **2** or **4** in these conditions. [b] Value extrapolated from the initial slope of the titration curve of Figure 3d, between 2 and 3 equiv of water. [c] The position of the observed broad signal (ca. 1.0 ppm) was affected by the presence of "free" water, as discussed in the text.

Table 2. Bandwidth (ω) of the ^{19}F Resonances of the *para* Fluorine Atoms of 1 and 2, Measured at Different Concentrations, in Toluene-d_8 at 260 K (last column shows the kinetic constants provided by the bandshape analysis of the same spectra)

[**1**] × 10^{2} (M)	[**2**] × 10^{2} (M)	[**2**]/[**1**]	ω(**1**) (Hz)	ω(**2**) (Hz)	k_{12} (s^{-1})
6.59	1.11	0.17	51[a]	85	50
5.4	2.3	0.43	62	85	90
3.35	4.35	1.3	110	88	260
2.08	5.62	2.7	196	88	560
1.51	4.09	2.7	195	87	550
1.19	3.21	2.7	196	87	550

[a] Broad multiplet due to ^{19}F−^{19}F couplings.

first by the three-site exchange among the water molecule of **2** and the two types of water present in **3** and successively by the four-site exchange involving **3** and **4**. The maximum broadening observed around 2 equiv agrees with the presence of **3** as the main species in solution (the signals of internal and external water of **3** being almost collapsed at this temperature, as described below), while the sharpening at about 3 equiv indicates the near completion of the transformation of **3** into **4**, whose water molecules give a dynamically averaged resonance at temperatures higher than 240 K. The observed δ value (ca. 3.9 ppm) is indeed quite close to the weighted average of the resonances of internal and external water in **4**, see Table 1. Addition of water above 3 equiv shifted the signal further upfield, as expected, until phase separation occurred.

Variable-temperature spectra have been acquired, in different conditions, to investigate the kinetics of the dynamic processes revealed by the titration experiments.

Kinetic Measurements Concerning Water Exchange between Different Species. The rate of the **1** ⇔ **2** exchange at different temperatures was evaluated from the ^{19}F NMR spectra, the ^{1}H NMR spectra being uninformative on this process. A preliminary experiment, performed at 260 K (see Experimental Section), showed that the lifetime of **2** was independent of the concentrations of both **1** and **2** (Table 2), while the reciprocal of the lifetime of **1** (i.e., the kinetic constant k_{12} describing the exchange from site **1** to site **2**) increased linearly with the [**2**]/[**1**] concentration ratio (Table 2, Figure 4). This indicates[26,35] that the exchange rate is determined by the dissociation of water from adduct **2**, in agreement with previous findings.[23] Band shape analysis was performed on the ^{19}F NMR spectra obtained from two samples containing different concentrations of **1** and **2** (see Experimental Section), affording activation parameters identical within experimental uncertainty [first experiment: $\Delta H^{\ddagger}$ 67(2) kJ mol^{-1}, $\Delta S^{\ddagger}$ 58(7) J mol^{-1} K^{-1}; second experiment $\Delta H^{\ddagger}$ 68(2) kJ mol^{-1}, $\Delta S^{\ddagger}$ 59(6) J mol^{-1} K^{-1}]. The value of $\Delta H^{\ddagger}$ reasonably agrees with the recently reported value [$\Delta H^{\ddagger}$ 19(1) kcal mol^{-1}],[23] while the activation entropy differs significantly [lit.[23] 24 eu], in line with the high uncertainty affecting the $\Delta S^{\ddagger}$ values obtained by extrapolation of Eyring plots to $1/T = 0$.[36]

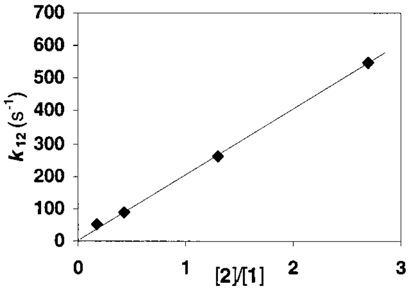

Figure 4. Kinetic constants for the exchange from $B(C_6F_5)_3$ (**1**) to $[(C_6F_5)_3B(OH_2)]$ (**2**) vs the concentrations ratio.

The rate of the **2** ⇔ **3** exchange, differently from the previous one, might in principle be evaluated from both ^{19}F and ^{1}H NMR spectra. In both cases, however, the available kinetic information consisted mainly in the

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(23) Bergquist, C.; Bridgewater, B. M.; Harlan, C. J.; Norton, J. R.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 10581−10590.

(24) In toluene (196 K): Δδ −6.3 for the *ortho*, −13.5 ppm for the *para*, and −2.4 for the *meta* atoms. In CD_2Cl_2 at 196 K we observed comparable shifts: Δδ −7.7 (*ortho*), −11.6 (*para*), −2.1 (*meta*) ppm: $B(C_6F_5)_3$ (**1**) −128.3 (*o*, 2), −144.0 (*p*, 1), −161.5 (*m*, 2); $[(C_6F_5)_3B(OH_2)]$ (**2**) −136.0 (*o*, 2), −155.6 (*p*, 1), −163.6 (*m*, 2). On increasing the temperature, in CD_2Cl_2, the signals shifted slightly upfield (<0.5 ppm up to the highest temperature where separate signals for **1** and **2** were detectable, i.e., ca. 250 K). This suggests that the previously reported[20] NMR data for **1** acquired at room temperature in CD_2Cl_2 (see Table S1) might in fact be averaged signals arising from a mixture of **1** and **2** in which **1** was largely dominant. Also the differences reported in the same paper between the ^{19}F signals of **2** and **2**-d_2 most likely arise from slightly different amounts of H_2O in the two samples. The ^{2}H δ value of −1.83 ppm, reported in that paper for **2**-d_2, was most likely due to a misprint (for the same species we have measured at 180 K a value quite close to that of the ^{1}H derivative at the same temperature, i.e., 7.0 ppm).

(25) The values of J_{FF} provided by our simulations compare well with literature data concerning substituted pentafluorobenzenes: Wray, V. *J. Chem. Soc., Perkin Trans. 2* **1978**, 855−861.

(26) Drago, R. S. *Physical Methods for Chemists*; Saunders College Publishing: Ft. Worth, 1992.

bandwidth of signals above the coalescence temperature ("near fast exchange region"), since separated ^1H or ^{19}F resonances for **2** and **3** could be observed only in a very limited range of temperatures and concentrations (the rate of the process decreases with the concentration of $[(C_6F_5)_3B(OH_2)]$, as described below). The accuracy of the kinetic analysis in these conditions depends critically upon the accuracy in the estimation of $\Delta\nu_0$,[37] i.e., the separation (in Hz) between the two sites in the absence of exchange, which is usually extrapolated at a given temperature from the relationship δ vs T observed at temperatures where the exchange does not affect chemical shift. In the present case no information was available for **3**, since the slow exchange region was attained only at the lowest temperatures and no trend could be evaluated. The data available for **2** indicate that the ^{19}F signals varied their chemical shift with temperature (and with concentration) more significantly than the ^1H resonance.[39] Therefore we performed the kinetic analysis almost exclusively on the ^1H NMR data[40] and used only a few ^{19}F experiments to check that the same kinetic constants allowed to reproduce satisfactorily both the ^{19}F and ^1H spectra (see Experimental Section). In this way we confirmed that the averaging of the ^1H and ^{19}F resonances arises from the same dynamic process (the **2** ⇔ **3** exchange).

The temperature window useful for measuring the rate of this exchange from the ^1H NMR spectra is rather narrow, as at temperatures higher than ca. 225 K a different process (the mutual exchange between the two water molecules of **3**, see below) attains a rate high enough to affect the bandwidth of the protonic resonances.[41] Despite these intrinsic experimental limits (uncertainty in $\Delta\nu°$ and narrow temperature range), the band-shape analysis of the spectra acquired in the interval 189−214 K provided some mechanistic insight.

At each temperature, the kinetic constants describing the exchange from the bis-hydrate adduct **3** to the monohydrate adduct **2** ($k_{\mathbf{32}}$) varied linearly with the concentration of **2**, as shown in Figure 5, with intercepts quite different from zero. This suggests that in this case, at variance with the **2** ⇔ **1** exchange, two mechanistic pathways contribute to the exchange, as shown in Scheme 1. The dissociative pathway (a) would give $k_{\mathbf{32}} = k_1$ and $k_{\mathbf{23}} = k_1[\mathbf{3}]/[\mathbf{2}]$, while the bimolecular mechanism (b) would give $k_{\mathbf{32}} = k_2[\mathbf{2}]$ and $k_{\mathbf{23}} = k_2[\mathbf{3}]$.[26,35] If both the mechanisms were operative,

$$k_{\mathbf{32}} = k_1 + k_2[\mathbf{2}] \qquad (4)$$

and

$$k_{\mathbf{23}} = k_1[\mathbf{3}]/[\mathbf{2}] + k_2[\mathbf{3}] \qquad (5)$$

The experimental data agree with this. Indeed, according to eq 5, neither the plots of $k_{\mathbf{23}}$ vs [**3**] nor vs [**3**]/[**2**] were linear, as shown in Figure S5. On the contrary, the plots of $k_{\mathbf{32}}$ vs [**2**] depicted in Figure 5 were linear, as required by eq 4, and their intercepts and slopes provided the values of k_1 and k_2 reported in Table 3.

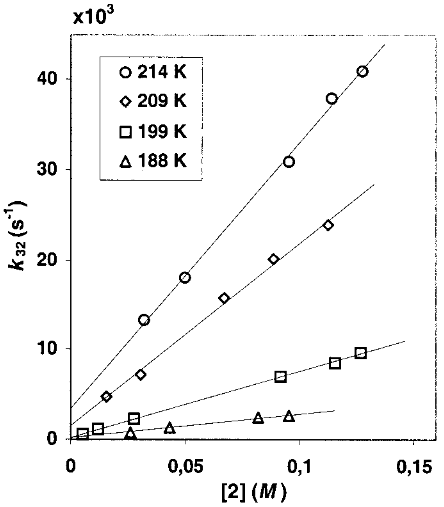

Figure 5. Kinetic constants for the exchange from $[(C_6F_5)_3B(OH_2)]\cdot H_2O$ (**3**) to $[(C_6F_5)_3B(OH_2)]$ (**2**) vs the concentration of **2**, measured at different temperatures.

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(27) H. Stephen, T. Stephen, *Solubilities of Inorganic and Organic Compounds*; Pergamon Press: London, 1963; Vol I, Part I, p 477.

(28) The hypothesis that the different behavior exhibited by mixtures of **2** and **3** with respect to mixtures of **3** and **4** was due to a smaller $\Delta\delta$ between the involved resonances rather than to a faster exchange process can be rejected, since the chemical shift difference between the *sharp* resonances of the *para* fluorines of **3** and **4** (0.8 ppm) was strictly comparable with that concerning the *broad* signals of the *meta* fluorines of **2** and **3** (ca. 1 ppm).

(29) This chemical shift is sound, even if its intensity in neat toluene-d_8 was just above the detection limit, because it lies on the straight line determined by the values measured at temperatures in the range 273−213 K.

(30) On the ^1H NMR time scale the **2** ⇔ **3** exchange is slower than in the ^{19}F scale (^1H $\Delta\nu$ ca. 1000 Hz; maximum ^{19}F $\Delta\nu$ ca. 500 Hz, for *para* atoms), and in the conditions of the titration its rate was very close to the coalescence region. Therefore the mole-fraction weighted averaging of the resonances was not realized, causing a nonlinear behavior of the averaged δ in this region (Figure 3b). The much faster **3** ⇔ **4** exchange, on the contrary, resulted in averaging of the chemical shifts according to the relative populations of the two adducts, in all the conditions examined. The linearity of δ vs the equivalents of water observed between 2 and 3 equiv arises from the following considerations: $\delta_{obs} = x_{\mathbf{3}}\delta_{\mathbf{3}} + (1 - x_{\mathbf{3}})\delta_{\mathbf{4}} = \delta_{\mathbf{4}} + (\delta_{\mathbf{3}} - \delta_{\mathbf{4}})x_{\mathbf{3}}$ (where $x_{\mathbf{3}}$ indicates the molar fraction of **3**). If adduct formation can be considered quantitative, above 2 equiv it would be $x_{\mathbf{3}} = 3 - e_W$ (where e_W indicates the equivalents of added water), and therefore $\delta_{obs} = (3\,\delta_{\mathbf{3}} - 2\delta_{\mathbf{4}}) - (\delta_{\mathbf{3}} - \delta_{\mathbf{4}})e_W$.

(31) At exactly 2 equiv of water the dominant "amphyprotic" species **3** is expected to be accompanied by small amounts of equimolar **2** and **4**. The available evidence agrees with this expectation, although it does not allow quantitative estimates. Indeed we have observed in repeated experiments that the maximum sharpening of the signal of B-bound water (ca. 20 Hz at 196 K) was attained in the presence of a small excess of water (less than 10%, as estimated from the integrated intensities of the resonances of external and internal water). This is reasonable considering that the line-width of this signal is affected more by the **2** ⇔ **3** than by the **3** ⇔ **4** exchange, due to the higher $\Delta\delta$ of the involved signals. Therefore in the presence of equal (low) amounts of **2** and **4** (i.e., at exactly 2 equiv of water) the signal is expected to be somewhat broader than at a further point of the titration, where the influence on the bandwidth of (decreasing) **2** was overcome by that of (increasing) **4**.

(32) We have verified that the addition of 0.2 μL of water (corresponding to ca. 0.2 equiv in the conditions of the experiments of Figure 3) to 0.5 mL of toluene caused clouding of the solution, at 196 K.

(33) Unfortunately, the broad signal of external water in these conditions partially overlapped the signals of the methyl of toluene and of the traces of pentane, residual from the purification of $B(C_6F_5)_3$, thus hampering the accurate estimate of the integration ratio between external and internal water.

(34) The differences, in the last stage of the titration, between the two experiments of Figure 3 are most likely related to the abovementioned unavoidable inexactness in estimating the amount of added water, particularly in those stages of the titration where the control of the effective water content from the integrated intensities is hampered by partial overlap with other signals, due to their large bandwidth. Note however the very good agreement between the two experiments as far as the final bandwidths of both the signals are concerned. The slight erraticity of the δ values of external water at the end of the titration (to be contrasted with the perfect constancy of the signal of internal water) probably reflects the higher sensitivity of external water to the solution conditions (in particular to the concentration, 0.048 (△) and 0.10 (○) M, respectively).

(35) Brown, T. L., *Acc. Chem. Res.* **1968**, *1*, 23−32.

Scheme 1

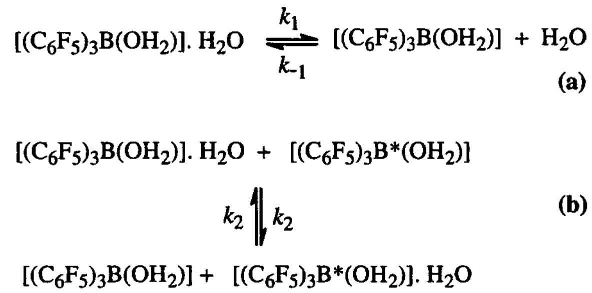


Table 3. Least-Squares Data of the Straight Lines Fitting the Plots of k_{32} vs [2] (in parentheses the uncertainties on the last digit)

temp (K)	$k_1 \times 10^{-3}$ (s^{-1})	$k_2 \times 10^{-4}$ ($M^{-1}\,s^{-1}$)
188	0.22(9)	2.6(1)
194	0.39(15)	5.5(1)
199	0.33(12)	7.3(2)
206	0.76(5)	18.1(3)
209	1.6(6)	20.3(8)
214	3.4(7)	29.6(8)

The k_1 values are much higher than those concerning the **2** ⇔ **1** exchange: extrapolation at 214 K of the kinetic constants for the **2** ⇔ **1** exchange provides a value (ca. 0.2 s^{-1}) more than 4 orders of magnitude smaller than that determined at the same temperature for the **3** ⇔ **2** exchange (ca. 3500 s^{-1}, Table 3). This indicates, not surprisingly, that the dissociation of the hydrogen-bound water molecule is much faster than the dissociation of the molecule covalently bound to the boron atom. The Arrhenius plot for k_1 was too scattered to allow any discussion (Figure 6), while the activation parameters for the bimolecular pathway were better defined: $\Delta H^{\ddagger}$ 30(2) kJ mol^{-1}, $\Delta S^{\ddagger}$ 3(10) J mol^{-1} K^{-1}. The $\Delta S^{\ddagger}$ value close to zero might be consistent with a mechanism in which external water interchanges its H-bonded [$(C_6F_5)_3B(OH_2)$] partner when **2** and **3** are inside the same solvent cage, as the result of a rapid reversible association. However, the well-known low accuracy of the values of $\Delta S^{\ddagger}$, particularly when obtained from data in a quite narrow temperature range, imposes caution in the mechanistic inference. Experiments at variable pressure, aimed at measuring $\Delta V^{\ddagger}$, might provide more sound information.

The finding that the rate of the **2** ⇔ **3** exchange can be reduced by reducing the concentration of **2** suggested the possibility of observing separated ^{1}H and ^{19}F resonances for the two aqua species by recording spectra in very dilute solutions. Figure 7 shows the spectra obtained at different stages of a "titration"[42] performed in a solution ca. 0.007 M of $B(C_6F_5)_3$ at 190 K. In these conditions the *meta* and *para* fluorine atoms of **2** and **3**, as well as the protons of B-bound water in the two adducts, give well-separated (even if broad) signals, which coalesce on increasing the temperature (Figure S6). Band shape analysis of the ^{19}F and ^{1}H NMR spectra in which **2** and **3** were simultaneously present provided kinetic constants for the **3** ⇔ **2** exchange, from which the values of k_2 and k_1 were evaluated (see Experimental Section). The k_2 value [3.3(3) × 10^4 s^{-1} M^{-1}, 190 K] was in very good agreement with the values obtained from the experiments of Table 3, while the k_1 value [83(8) s^{-1}] was significantly smaller, as shown in the Arrhenius plot of Figure 6. Despite this, we consider this value more trustable, as it was obtained in conditions much closer to infinite dilution.

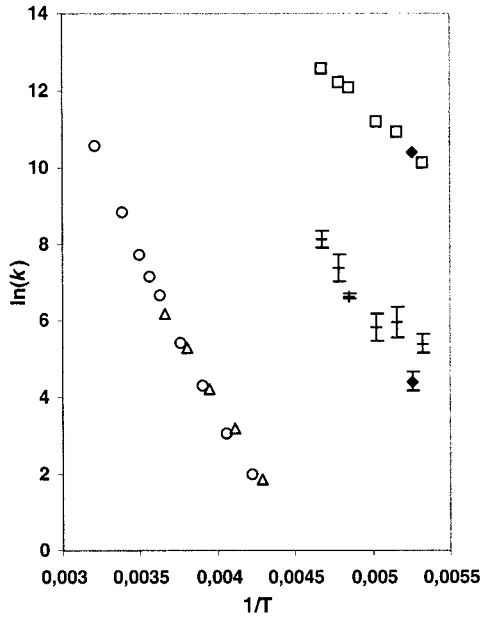


Figure 6. Arrhenius plot of the kinetic constants determined in this work: (○) **2** ⇔ **1** exchange, (□) k_2 for the **3** ⇔ **2** exchange, (+) k_1 for the **3** ⇔ **2** exchange (the vertical lines indicate the errors), (△) exchange of internal and external water in **3**. The k_1 and k_2 values for the **3** ⇔ **2** exchange obtained from the spectra recorded in very diluted solutions (experiment of Figure 7) are depicted by the symbol ◆.

The spectra of Figure 7f,g show that, even at very low concentrations, mixtures of **3** and **4** give only dynamically averaged signals. In fact, the **4** ⇔ **3** exchange could not be investigated kinetically: in the ^{19}F time scale its rate was always in the fast exchange region, while in the ^{1}H NMR spectra the signals were broadened by other exchange processes, as previously discussed.

Other Dynamic Processes within Adduct 3. Scheme 2 depicts the exchange processes in which the water molecules of **3** could be involved. The hopping of the external water molecule between the two protons of internal water is very fast even at the lowest temperatures, as shown by the unique signal exhibited by these protons. The observed chemical shift (ca. 8 ppm) should therefore be viewed as dynamically averaged between a hydrogen-bonded proton and a "free" proton of a B-bonded water molecule.[43]

To investigate the other processes of Scheme 2, we acquired variable-temperature ^{1}H NMR spectra of samples of $B(C_6F_5)_3$ treated with different amounts of water. The spectra of samples in which the adduct **3** was the dominant species (ca. 2 equiv of water) showed at temperatures above 210 K the progressive and parallel broadening of the resonances of both the water sites of **3** (Figures S7 and S8a), indicating exchange between the two sites. The kinetic constants for this process, however, had to be measured in samples treated with smaller amounts of water, to ensure that the presence of the trihydrate **4** was negligible. Indeed **4** provides an intermolecular, faster pathway for this exchange, through two processes both very fast at temperatures above 210 K: the exchange of H-bonded water between **3** and **4** and the exchange between the protons of internal and external water in **4**. For this

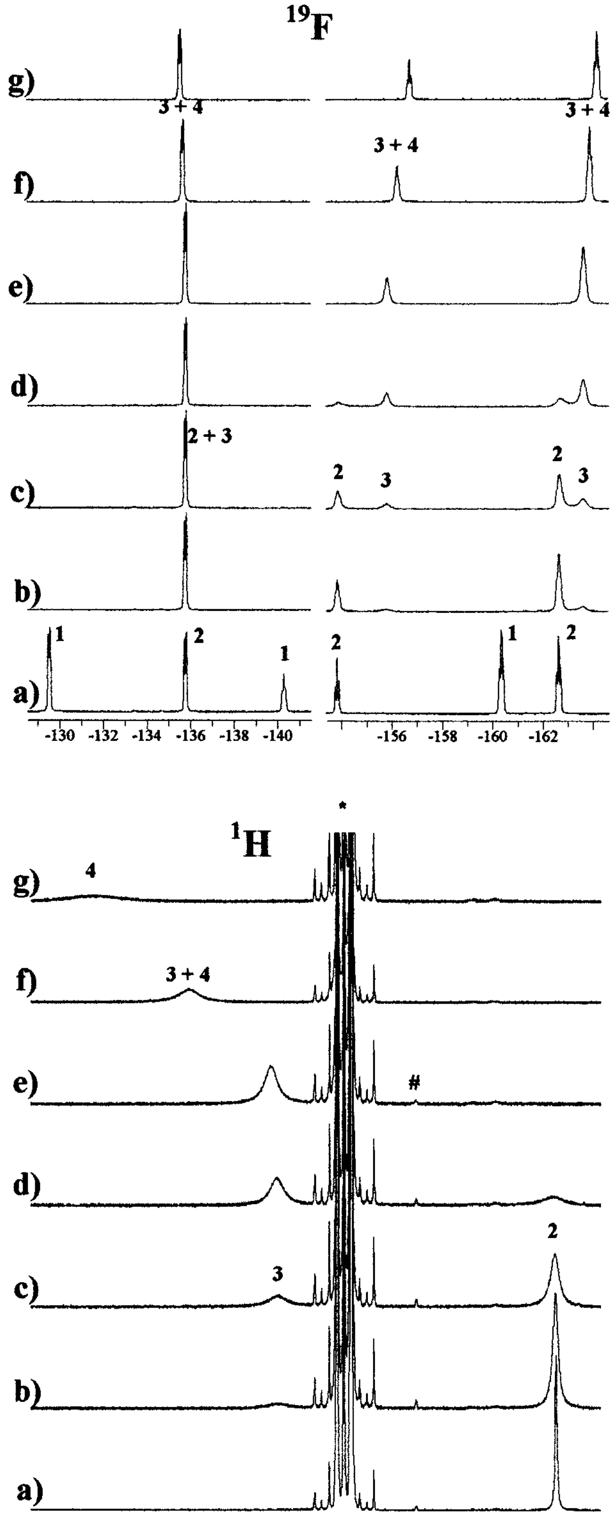
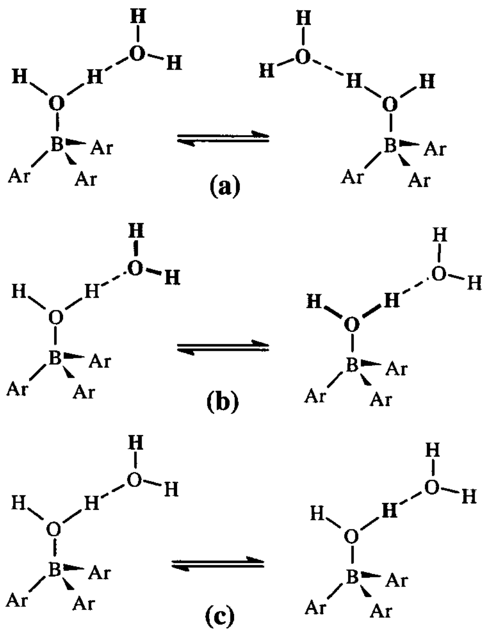


Figure 7. ^{19}F and ^1H (region of the "internal" protons) NMR spectra corresponding to the progressive addition of wet toluene-d_8 to a very diluted solution of $B(C_6F_5)_3$ (initially 0.0074 M) at 190 K. The equivalents of water[42] in the different spectra were as follows: (a) 0.5, (b) 1.1, (c) 1.3, (d) 1.7, (e) 2.0, (f) 2.5, (g) >3. The asterisk marks the aromatic protons of toluene (including the ^{13}C satellites). The symbol # indicates a small amount of $(C_6F_5)_2BOH$ present as impurity in the sample of $B(C_6F_5)_3$.

reason, small increases in the amount of water just above 2 equiv strongly broadened the resonance of H-bonded water (see Experimental Section and Figure S8b).

Scheme 2



The kinetic constants were computed through eq 6,[38] by the observed broadening ($\omega - \omega^\circ$) of the signal of external water (the signal of internal water in these conditions being broadened also by the **2** ⇔ **3** exchange).

$$k = \pi(\omega - \omega^\circ) \qquad (6)$$

From these constants, the following activation parameters have been estimated: $\Delta H^\ddagger$ 55(2) kJ mol^{-1}, $\Delta S^\#$ 7(3) J mol^{-1} K^{-1}. The observed proton exchange could result from both the exchange of the entire water molecules (process b of Scheme 2) or the mere exchange of some protons (process c). The values of the kinetic constants are very similar to those determined for the dissociative exchange of B-bound water among different $B(C_6F_5)_3$ molecules (the **1** ⇔ **2** exchange), as apparent in the Arrhenius plot of Figure 6. Also the activation enthalpy, smaller but not very different from that determined for the latter process (67 kJ mol^{-1}), supports the idea of a true water exchange process, in which the hydrogen-bonded water molecule assists the dissociation of the boron-bonded molecule. The value of the activation entropy, close to zero, is in line with the hypothesis of a concerted process in which no water molecule escapes the solvent cage.

On the other hand, the alternative hypothesis (exchange of protons instead of water) might find support in the recent report[23] that **3**, in acetonitrile solution, behaves as a strong acid. Such acidic dissociation would provide an easy path for proton exchange between the two water molecules (Scheme 3). The formation of a

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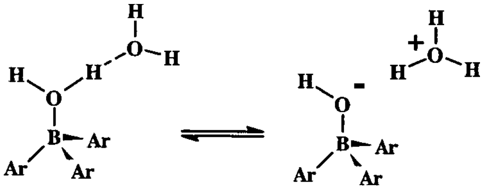
(36) Wilkins, R. G., *Kinetics and Mechanism of Reactions of Transition Metal Complexe*, II ed.; VCH: Weinheim, 1991.

(37) For an exchange between two equally populated sites (in conditions in which $\Delta\nu_0$ is much higher than the broadening of the signal) $k = \pi(\Delta\nu_0)^2/2(\omega - \omega^\circ)^{38}$ (where ω indicates the bandwidth of the resonance), from which it can easily be obtained that $\sigma(k)/k = 2\sigma(\Delta\nu_0)/\Delta\nu_0$ (assuming negligible the error in the measurement of the broadening).

(38) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

Scheme 3



zwitterionic species by proton transfer between neutral reactants is thermodynamically unfavored in a poor polar solvent such as toluene, and an unfavorable equilibrium constant makes a reaction slow.[44] The observation at low temperatures of a sharp resonance for the protons of external water agrees with this, indicating that in toluene, at least up to 220 K, no kinetically significant acidic dissociation takes place in **3**. The increase in temperature could however lead to a more favorable position for this endothermic reaction (if entropic effects could be neglected, due to the poor solvating power of toluene), and therefore the hypothesis of proton exchange cannot be ruled out. Noteworthy, our activation energy (57 kJ mol^{-1}) coincides with the minimum value estimated for the activation energy of the reaction of ionization of water, on the basis of the heat of the reverse reaction.[44] Experiments with $H_2{}^{17}O$ would be necessary to discriminate between the two processes.

Moreover, we might speculate that the additional water molecule present in the trihydrate **4** could provide some stabilization to the ionic couple formed by the acidic dissociation, most likely by solvating the cation to give the $H_5O_2^+$ species. A more favorable position of the acidic dissociation equilibrium might explain why proton exchange between internal and external water is much easier in **4** than in **3**.[45] Support for the thesis that the observed fast exchange in **4** arises from the exchange of hydrogen atoms and not of water molecules is provided by literature data[18b] that report the observation, at 273 K, of two separate ^{17}O NMR water resonances for **4** (δ 22 and 2.3 ppm, in 1:2 ratio).[46]

Conclusions

The three aqua species originating from the reaction of $B(C_6F_5)_3$ with water have been previously characterized and some information on their properties given, as reported in the Introduction. The present study, however, provides the first detailed investigation in solution of the equilibria ruling the formation and interconversion of the aqua derivatives.

The titration experiments have shown that in toluene the formation of the aqua derivatives $[(C_6F_5)_3BOH_2]$ (**2**), $[(C_6F_5)_3BOH_2]\cdot OH_2$ (**3**), and $[(C_6F_5)_3BOH_2]\cdot 2OH_2$ (**4**) occurs in a stepwise manner, on adding stoichiometric water, at 196 K and also at room temperature. Therefore the behavior in toluene contrasts with what has been reported for the donor solvent acetonitrile, where the formation of only the bis-hydrate **3** was observed,[23] in the presence of the excess of water necessary to overcome the competition of the solvent for the Lewis acid. In toluene the monohydrate **2** and the bis-hydrate **3** are intermediate species, and it is very difficult (or impossible) to obtain solutions containing one of them as the "only" aqua species. Thus solutions of $B(C_6F_5)_3$ treated with *exactly* 2 equiv of water contain not only **3** but also small amounts of equimolar **2** and **4** (the greater the difference between the constants ruling equilibria 2 and 3, the smaller these amounts).

The available data did not allow the determination of the constants of these equilibria, but some (qualitative) conclusions can be drawn. The recently reported[23] computational study of the aqua adducts of $B(C_6F_5)_3$ indicates that the strength of the H-bond in **3** is significantly higher in the gas phase than in acetonitrile (-12.9 vs -7.8 kcal mol^{-1}) for the stabilization of the reactants of reactions 2 by solvation. The same computations also indicate that the H-bond strength decreases from **3** to **4** by more than 3 kcal mol^{-1} in the gas phase,

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(39) For the ^{19}F signals of **2**, plots of δ vs temperature had a slope of ca. 8 ppb/K for the *para* and ca. 4 ppb/K for the *meta* ^{19}F signals (the *ortho* signals are kinetically useless). For the ^{1}H resonance the analogous plot had a much smaller slope (ca. 1 ppb/K). Moreover, plots of δ vs the overall concentration (**1** and **2**) for the *para* ^{19}F signal had a slope of ca. -3 ppm/M at 196 K and ca. -1 ppm/M at 300 K. For the proton the slope at 300 K was ca. $+1$ ppm/M, while at 196 K no clear effect of the concentration on the chemical shift could be recognized.

(40) Another reason for favoring ^{1}H over ^{19}F experiments lies in the smaller relative errors $\sigma(\Delta\nu_0)/\Delta\nu_0$ affecting the ^{1}H signals,[37] due to the higher $\Delta\nu_0$ for the protonic resonances (assuming that the uncertainty $\sigma(\Delta\nu_0)$ in the estimate of the chemical shift difference was the same for ^{1}H and ^{19}F signals).

(41) In the ^{19}F time scale the range of usable temperatures was not wider, because at temperatures higher than ca. 220 K, in the normal concentration range, the exchange is so fast as to be kinetically useless.

(42) In such diluted solutions the amounts of water that we had to add were too small to allow any reliable measurement (1 equiv corresponding to ca. 0.1 μL). Therefore the "titration" was performed by the addition of aliquots of wet toluene-d_8, and the equivalents of water mentioned in the caption of Figure 7 were computed from the integrated intensities or (above 2 equiv) from the position of the averaged signals.

(43) This process is most likely responsible for what was observed in the spectra for the lowest temperatures and concentrations, where the signal of B-bound water of **3** had a bandwidth somewhat larger than expected taking into account only its exchange with **2**.

(44) Moore J. W.; Pearson, R. G. *Kinetics and Mechanism*; John Wiley: New York, 1981; p 342.

(45) Variable-temperature spectra of samples containing more than 3 equiv of water showed a unique signal for all the water protons at temperatures as low as 243 K, while for **3** coalescence was attained only at room temperature. Moreover, at 188 K, where no exchange on the NMR time scale was detectable for **3**, the two signals of **4** were very broad, as already described in the comments of the low-temperature titration.

(46) The separation between the ^{1}H signals of **4** (ca. 2700 Hz) is much higher than that between the ^{17}O resonances (ca. 1300 Hz on assuming that the literature measurements were run at the maximum field, 11.7 T; this information is not reported in the paper). The process averaging the protons of water therefore does not involve the oxygen atoms.

(47) Assuming a value of -15 eu for the entropy involved in the formation of the H-bond (see reference 23 and references therein), the $\Delta H°$ value computed for acetonitrile solution (-7.8 kcal mol^{-1}) would give values of 2.4×10^5 and 2.4×10^2 for the constants of equilibrium 2, at 196 and 300 K, respectively. Our data indicate that equilibrium 3 is ruled by constants smaller than equilibrium 2 (to account for the stepwise formation of **3** and **4**), but high enough to drive the equilibrium almost completely to the right, even at room temperature. Therefore we must assume that in toluene $\Delta H°$ for equilibrium 2 is somewhat more negative than in acetonitrile.

(48) See for instance: (a) Helm, L.; Merbach, A. E. *Coord. Chem. Rev.* **1999**, *187*, 151−181. (b) Lincoln, S. F.; Merbach, A. E. *Adv. Inorg. Chem.*, **1995**, *42*, 1−88. (c) Merbach, A. E. *Pure Appl. Chem.* **1987**, *59*, 161−172.

(49) See for instance: (a) Schah-Mohamedi, P.; Shenderovich, I. G.; Detering, C.; Limbach, H.-H.; Tolstoy, P. M., Smirnov, S. N.; Denisov, G. S.; Golubev, N. S. *J. Am. Chem. Soc.* **2000**, *122*, 12878-12879. (b) Smirnov, S. N.; Golubev, N. S.; Denisov, G. S.; Benedict, H.; Schah-Mohamedi, P.; Limbach, H.-H. *J. Am. Chem. Soc.*, **1996**, *118*, 4094−4101, and references therein.

(50) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

(51) Washburn, E. W.; Clarence, J. W.; Dorsey, E.; Bchowsky, F. R.; Kemenc, A. *International Critical Tables of Numerical Data. Physics, Chemistry and Technology*; McGraw-Hill: New York, 1933; Vol. III.

while in acetonitrile it increases by ca. 1.5 kcal mol^{-1}. Our results (the stepwise nature of the process and the formation of the trihydrate even at room temperature) imply equilibrium constants decreasing progressively from reaction 1 to reaction 3, but remaining sufficiently high for all the equilibria to strongly favor the hydrated species, even at room temperature. Therefore these data agree with previous computations if one assumes that in toluene the energies of the H-bonds are closer to those computed for the gas phase rather than to those concerning acetonitrile solutions.[47] This is quite reasonable, considering the poor solvation of water by toluene.

The titrations, as well as variable-temperature experiments for samples of $B(C_6F_5)_3$ with different amounts of added water, evidenced several types of dynamic behavior involving water molecules. A dissociative mechanism accounts for the exchange of water of the "first coordination sphere" (B-bound) among different $B(C_6F_5)_3$ molecules, which leads to the **1** ⇔ **2** interconversion. This process is much slower (about 4 orders of magnitude) than the dissociation of water of the "second coordination sphere" (H-bonded), which leads to the **2** ⇔ **3** interconversion. Interestingly, for the latter process also a bimolecular exchange pathway is available.

Any study on the mobility of the water molecules in the trihydrate **4** was prevented by the occurrence of proton exchange processes, possibly favored by the acidic dissociation of the protons of the B-bonded water molecule. Therefore the use of ^{17}O NMR will be necessary to investigate this point and also to ascertain the true nature of the process responsible for the exchange of protons of internal and external water in $[(C_6F_5)_3B(OH_2)]\cdot H_2O$ (**3**). Further mechanistic insight could be provided also by variable-pressure measurements (aimed at estimating $\Delta V^{\ddagger}$),[48] by the investigation of hydrogen/deuterium isotope effects (in order to better characterize the properties of the hydrogen bonds),[49] and by studies involving molecules with different hydrogen-bond donor–acceptor properties, such as methanol.

Finally, there is evidence (at least at 196 K) that even the H-bonded molecules of water in the trihydrate **4** are able to establish some H-bonding interactions with other, more external, water molecules. Therefore in toluene solution $B(C_6F_5)_3$ is such a strong Lewis acid that it can polarize even the "external" (H-bonded) water molecules, leading to "third-sphere" interactions sufficiently strong to partly overcome the water–toluene repulsion.

Experimental Section

All the manipulations were performed under nitrogen using oven-dried Schlenk-type glassware. Deuterated solvents (C.I.L. or Isotec Inc.) were used as received or anhydrified on activated molecular sieves (the use of more efficient anhydrification procedures was unnecessary, since our chemistry involved the addition of water). $B(C_6F_5)_3$ was purchased from Boulder Scientific and purified by continuous extractions with refluxing *n*-pentane (final water content ca. 0.15% w/w, as determined by Karl-Fisher analysis).

^1H and ^{19}F NMR spectra were acquired on a Bruker AVANCE DRX-300 spectrometer, equipped with a 5 mm BBI probe (90° pulse: ^1H 8.5 μs, ^{19}F 26 μs). ^{19}F NMR spectra were referenced to external $PhCF_3$ ($\delta = -63.72$ ppm). The temperature was calibrated with a standard CH_3OH/CD_3OD solution.[50]

The scalar coupling constants $^nJ_{F-F}$ for $B(C_6F_5)_3$ and $B(C_6F_5)_3(OH_2)$ were estimated from the simulation (Bruker WINDAISY software) of a ^{19}F NMR spectrum recorded in toluene-d_8 at a temperature (223 K) low enough that the exchange process does not affect the ^{19}F NMR band shape. **$B(C_6F_5)_3$**: −129.6 (m, *ortho*), −141.5 (tt, *para*), −160.7 (m, *meta*) ($^3J_{23} = -24.0$, $^4J_{24} = 6.6$, $^5J_{25} = 8.8$, $^4J_{26} = 1.0$, $^3J_{34} = -22.0$, $^4J_{35} = -5.0$ Hz); **$[B(C_6F_5)_3(OH_2)]$**: −135.9 (m, *ortho*), −154.3 (t, *para*), −162.9 (m, *meta*) ($^3J_{23} = -24.1$, $^4J_{24} = -2.3$, $^5J_{25} = 8.2$, $^4J_{26} = -1.0$, $^3J_{34} = -21.3$, $^4J_{35} = -2.0$ Hz). The presence of the H-bonded water molecules does not affect significantly these coupling constants, because the patterns of the resonances observed at the final stages of the titrations are identical to those of **2**.

The kinetic constants for the different exchange processes were obtained though the simulations of the ^{19}F and ^1H NMR spectra with the Bruker WIN-DYNAMICS software.

The amount of solvent in the kinetics experiments was determined by weighing; it was transformed into volume on using the values of density at the proper temperatures, calculated by the formula $d_T = d_0 + \alpha t + \beta t^2$, where t is the temperature (°C), d_0 is the density at 0 °C (0.954), and the parameters α and β had the values tabulated for C_6H_8 ($\alpha = 5.159 \times 10^{-4}$, $\beta = 3.68 \times 10^{-7}$).[51]

Titrations of $B(C_6F_5)_3$ with H_2O. A typical procedure was as follows. A sample of $B(C_6F_5)_3$ was weighted into an NMR tube, under N_2, and dissolved in toluene-d_8. A ^{19}F NMR spectrum was acquired, at 260 K, to measure the relative amounts of $B(C_6F_5)_3$ and $[(C_6F_5)_3B(OH_2)]$ in solution. Then the NMR tube was warmed to room temperature, and the proper amount of water (Milli-Q) was added under N_2, on using a 10 μL microsyringe. The tube was closed with a rubber septum, carefully shaken, and introduced into the NMR probe, previously thermostated at the temperature of the titration (196 or 300 K). After attainment of thermal equilibrium (ca. 10 min) the ^1H or ^{19}F spectrum was acquired, and the tube was again extracted from the probe and warmed to room temperature, to perform a novel water addition. The concentrations in the different experiments were in the range 0.05–0.18 M, and the amount of water added in each titration step was typically in the range 0.2–0.5 μL. When possible (titrations at 196 K monitored by ^1H NMR, above 1 equiv), the integration ratios between the signals of internal and external water were used to check the accuracy of water addition: the errors were usually found to be lower than 10%.

Solubility of Water in Toluene with and without $B(C_6F_5)_3$. A sample of $B(C_6F_5)_3$ (60 mg, 0.117 mmol) was treated with 0.45 mL of dry toluene-d_8, resulting in a rather turbid solution (due to incomplete dissolution of $B(C_6F_5)_3$). The solution became clear after addition of 2 μL of water (0.95 equiv). Further water was then added stepwise (2 + 2 + 0.5 + 0.5 μL, corresponding to an overall amount of 3.32 equiv) without causing any phase separation at room temperature or at 193 K. The addition of a further 0.5 μL (3.56 overall equiv) made the solution turbid at 193 K, while the formation of small droplets of water at room temperature was clearly detectable after addition of a further 0.5 μL (3.79 equiv). In a control experiment the same amount of toluene (without any $B(C_6F_5)_3$) was treated with 0.2 μL of water: after careful shaking, the solution showed microdroplets of water at room temperature and became turbid when cooled at 193 K. A further addition of 0.2 μL of water confirmed the saturation of the toluene, showing the formation of well-visible droplets of water.

Kinetics of the Exchange between $B(C_6F_5)_3$ (1) and $[B(C_6F_5)_3(OH_2)]$ (2) by Variable-Temperature ^{19}F NMR. As a check of the dissociative mechanism of the exchange, a solution of $B(C_6F_5)_3$ (26.8 mg, 0.052 mmol) in toluene-d_8 (0.68 mL) was treated with increasing amounts of water, to vary the [**2**]/[**1**] ratio, and successively with toluene, to vary the overall concentration. ^{19}F NMR spectra at 260 K were acquired after each addition, and the bandwidth of the signals was measured (in Table 2 the values for the *para* fluorines are reported). The bandwidths of the signals of **2** remained constant at all the concentrations, while those of **1** varied with the [**2**]/[**1**] ratio. The variation, however, was not linear, because at this temperature the bandwidth is affected also by the $^{19}F-^{19}F$ couplings. On the contrary, the values of the kinetic constants for the exchange from site **1** to **2** (k_{12} in Table 2), obtained by band shape analysis, gave a linear plot vs the [**2**]/[**1**] ratio, with intercept = 0 (R^2 0.998) and slope = 204 s^{-1} (Figure 4).

Variable-temperature ^{19}F NMR spectra were acquired on two samples, containing different concentrations of **1** and **2**. The first sample was prepared by dissolving 21.8 mg (0.0426 mmol) of $B(C_6F_5)_3$ in 0.60 mL of toluene-d_8 at room temperature. The ^1H NMR spectrum showed a weak signal at δ 4.75 ppm, attributable to some $[B(C_6F_5)_3(OH_2)]$, formed from adventitious water, whose amount was estimated (on using 0.5 μL of CH_2Cl_2 as an internal standard) as corresponding to 4.0 $\times 10^{-3}$ mmol (0.094 equiv). The composition of this sample was therefore as follows: overall concentration = 0.071 M, molar fraction of **1** (x_1) = 0.90, of **2** (x_2) = 0.10. ^{19}F spectra were then acquired at various temperatures, and their band shape analysis provided the following kinetic constants: k_{21}, s^{-1} (T, K) 6.7 (235), 23.5 (245), 92.8 (254.5), 385 (264.5), 1220 (273.5), 3300 (284), 11 100 (300).

The second sample was prepared by dissolving 32.9 mg of $B(C_6F_5)_3$ (0.0643 mmol) in 0.55 mL of toluene-d_8. Water was then added in order to have a higher **2**:**1** ratio, affording the following composition: overall concentration = 0.12 *M*, x_1 = 0.62, x_2 = 0.38. Band shape analysis of the ^{19}F spectra provided the following kinetic constants: k_{21}, s^{-1} (T, K) 7.4 (237), 21.4 (246.5), 75.9 (256), 229 (266), 774 (276), 1293 (281), 2250 (286), 6900 (295.5), 39700 (312).

Kinetics of the Exchange between $[B(C_6F_5)_3(OH_2)]$ (2) and $[(C_6F_5)_3B(OH_2)]\cdot H_2O$ (3) by Variable-Temperature ^1H NMR. A typical procedure was as follows. A sample of $B(C_6F_5)_3$ (35.0 mg, 0.068 mmol) in toluene-d_8 (0.470 g) was treated with different aliquots of water, to have in solution mixtures of **2** and **3**, whose exact relative amount was determined from the integration ratio between the ^1H signals of internal and external water (x_3 0.20, 0.37, 0.52). Two aliquots of toluene (0.488 and 0.744 g) were then added, to vary the overall concentration. After each addition, ^1H NMR spectra were recorded at 209 K. Band shape analysis of the signal of internal water, broadened by the **2** ⇔ **3** exchange, provided the kinetic constants k_{32} reported in Table S7. The experiment was repeated at two other temperatures (199, 214 K), and the results are reported in Tables S5 and S8, respectively. Tables S4 and S6 report the results of two experiments performed on using a lower initial concentration (ca. 0.05 M), at 194 and 206 K. In the experiment of Table S3 a slightly different procedure was followed: a 0.107 M solution of $B(C_6F_5)_3$ in toluene-d_8 (38.2 mg, 0.075 mmol, 0.70 mL of solvent) was treated with water to obtain mixtures of **2** and **3** with x_3 = 0.23, 0.59, and 0.76, respectively. ^1H NMR spectra at 188 K were acquired after each addition. Then, instead of diluting, further $B(C_6F_5)_3$ was added (18.8 mg, 0.037 mmol), leading to a 0.16 M solution, with x_3 = 0.40. ^1H and ^{19}F spectra were acquired at 188 K, and independent band shape analyses were performed on both the spectra, leading to identical values of k_{32} (2600 s^{-1}).

^{19}F and ^1H NMR Monitoring of a "Titration" of $B(C_6F_5)_3$ with Wet Toluene at 190 K. A sample of $B(C_6F_5)_3$ (3.4 mg, 0.00664 mmol), dissolved in 0.90 mL of toluene-d_8 (resulting in a 0.0074 M solution), was treated with different aliquots (30−200 μL) of toluene-d_8 saturated with H_2O, to realize the stepwise addition of very low aliquots of water and also to further dilute the solution (final overall concentration ca. 0.003 M). ^{19}F and ^1H NMR spectra were recorded after each addition, and the relative amounts of the species in solution were determined by integration of the ^{19}F *para* signals (and, above 2 equiv, by the position of the molar fraction weighted averaged resonances). Selected spectra are shown in Figure 7. Band shape analysis was performed on the ^{19}F and ^1H spectra of the mixtures containing both **2** and **3**, providing two independently estimated sets of kinetic constants k_{32}: ^{19}F 195, 155, 120 s^{-1}; ^1H 190, 170, 135 s^{-1}. A plot of the averaged kinetic constants vs [**2**] (0.0034, 0.0024, 0.0014 M) was satisfactorily linear, with slope 3.26(33) $\times 10^4$ and intercept 83(8).

Variable-Temperature ^{19}F NMR of a Very Diluted Mixture of 2 and 3 in Toluene-d_8. A diluted solution of **2** and **3** in toluene-d_8 was obtained by successive dilutions with anhydrous toluene-d_8 of a 0.08 M solution of $B(C_6F_5)_3$. The dilutions, controlled by weighing, afforded a 0.0084 M solution, and the water content was adjusted to give molar fractions x_2 = 0.57 and x_3 = 0.43. The ^{19}F NMR spectra acquired in the temperature range 187−210 K are shown in Figure S6.

Kinetics of the Exchange between B-Bonded and H-Bonded Water in $[(C_6F_5)_3B(OH_2)]\cdot H_2O$ (3) by Variable-Temperature ^1H NMR. A sample of $B(C_6F_5)_3$ (35.3 mg, 0.069 mmol) in toluene-d_8 (0.93 mL) was treated directly into the NMR tube with 1.7 μL (0.094 mmol) of water. ^1H NMR spectra revealed the presence in solution of a mixture of **2** and **3** ([**3**]/[**2**] 0.57:0.43). Variable-temperature ^1H NMR spectra were then acquired. The resonance of external water broadened at temperatures higher than 230 K. The bandwidth of this resonance in the range 223−273 K was as follows: ω, Hz (T, K) 6.8 (223), 8.9 (233), 14.5 (243), 29.0 (253), 69.7 (263), 161 (273). The experiment was repeated three other times, in the presence of amounts of water quite close to 2 equiv (the exact values were determined from the integration ratios), with the following results: experiment B, overall water 1.97 equiv, ω, Hz, (T, K): 6.4 (188), 5.9 (193), 5.6 (203), 6.1 (213), 12.9 (233), 42.5 (253), 166 (273); experiment C, overall water 2.08 equiv, ω, Hz, (T, K): 13 (188), 12 (193), 9.7 (199), 10.2 (204), 10.9 (208), 16.4 (218), 26.0 (227), 45.2 (237), 85.9 (247), 146.1 (256), 245 (266), 381 (275), 700 (285); experiment D, overall water 2.15 equiv, ω, Hz, (T, K): 12.9 (188), 14.2 (193), 17 (198), 30.4 (213), 49.7 (223), 84.8 (233), 151 (243), 240 (253), 341 (263), 492 (273), 660 (283). These data are reported in Figure S8b.

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Supporting Information Available: Tables S1−S8 (NMR literature data for $B(C_6F_5)_3\cdot(H_2O)_n$, n = 0, 1, 3; slopes of the ^{19}F titration curves; kinetic constants concerning the **2** ⇔ **3** exchange), Figures S1−S8 (observed and simulated ^{19}F NMR spectra of **1** and **2** at 223 K; ^{19}F titration curves at 300 K; ^{19}F NMR spectra taken at different stages of the titration at 196 K in toluene-d_8; ^1H titration curve at 300 K; plots of the kinetic constants for the exchange from **2** to **3**; variable-temperature ^{19}F NMR spectra of a solution containing 4.7 mM **2** and 3.7 mM **3**; variable-temperature ^1H NMR spectra of a sample of **3**; temperature and water concentration dependence of the bandwidth of the ^1H resonances of **3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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