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From $B(C_6F_5)_3$ to $B(OC_6F_5)_3$: Synthesis of $(C_6F_5)_2BOC_6F_5$ and $C_6F_5B(OC_6F_5)_2$ and Their Relative Lewis Acidity

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The pentafluorophenyl esters of bis(pentafluorophenyl)borinic acid $(C_6F_5)_2BOC_6F_5$ (**2**) and pentafluorophenylboronic acid $C_6F_5B(OC_6F_5)_2$ (**3**) have been prepared and characterized by multinuclear NMR and X-ray analysis. VT NMR studies have shown that restricted rotation around the B−O bond in **2** occurs below 193 K, corresponding to $\Delta G^{\ddagger} = 35$ kJ/mol for this process. This low barrier and the random torsion angles around the B−O bonds observed in the solid state structures of compounds **2**, **3**, and $B(OC_6F_5)_3$ (**4**) suggest that these torsion angles are not related to $p\pi-p\pi$ interactions between boron and oxygen, but more likely a consequence of the extensive intermolecular F−π interactions seen in the solid state structures. The Lewis acidity of **2**, **3**, and **4** has been compared with $B(C_6F_5)_3$ (**1**), using various Lewis bases. All compounds **1**−**4** appear to be strong Lewis acids, whereby **4** interacts more strongly with hard bases whereas **1** binds more strongly to softer bases.

Introduction

Four decades ago, Massey, Park, and Stone[1,2] reported the synthesis of tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ (**1**, Figure 1), a powerful Lewis acid comparable in acid strength to BF_3,[3,4] but much easier to handle. $B(C_6F_5)_3$ has found many applications, most notably as a cocatalyst in the polymerization of olefins,[5,6] but also in organic synthesis.[7−9] Several reactivity studies have shown that $B(C_6F_5)_3$ forms adducts with a range of Lewis bases, including those containing soft donors such as phosphorus[3,10,11] and sulfur[12,13] as well as hard donors, for example nitrogen[2,10,14−16] and oxygen.[12,17−19] The growing interest in $B(C_6F_5)_3$ has prompted us to prepare variations on $B(C_6F_5)_3$, to gain a better understanding and greater control over Lewis acid strength, with the aim to design Lewis acids for specific applications.

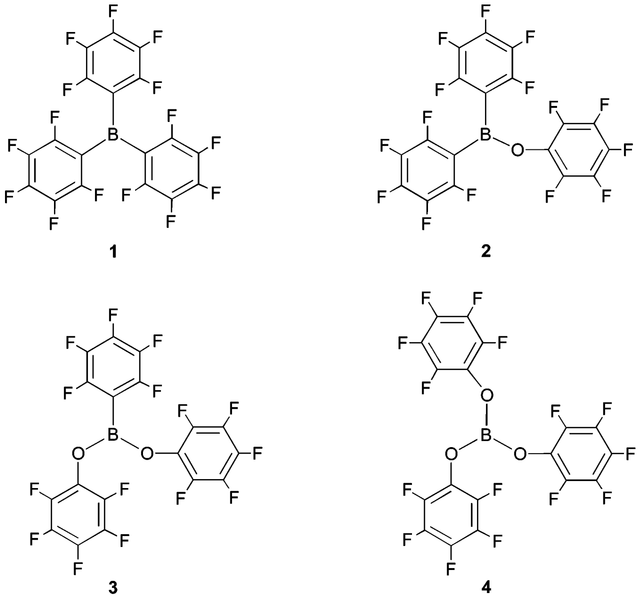

Figure 1. Perfluorophenyl boron Lewis acids **1**−**4**.

Borinic and boronic esters of the type $(C_6F_5)_2BOR$ or $C_6F_5B(OR)_2$ contain both electron-withdrawing C_6F_5 groups and electronegative oxygen substituents. These compounds are potentially alternative Lewis acids to $B(C_6F_5)_3$, with the advantage that the R substituents offer the possibility of tuning the Lewis acidity at the boron center; electron-withdrawing substituents, which are the subject of this study, will decrease $p\pi-p\pi$

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Table 1. ^{19}F and ^{11}B NMR Data for Compounds 1−4

compound	δ(^{19}F NMR)/ppm^a						δ(^{11}B NMR)/ppm^b
	C_6F_5			OC_6F_5			
	ortho	*meta*	*para*	*ortho*	*meta*	*para*	
1	−129.2	−160.1	−141.9				59
2	−131.1	−159.7	−144.1	−157.8	−161.4	−159.3	41.2
3	−131.1	−159.0	−145.2	−157.3	−161.9	−159.7	26.2
4				−157.7	−162.1	−159.7	14.8

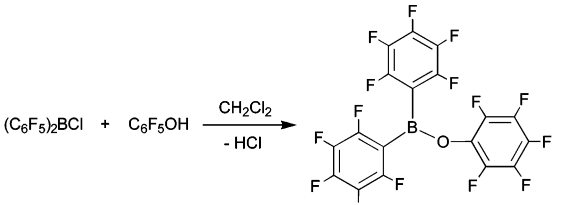
^{a} Solvent: C_6D_6; reference (external): $CFCl_3$. ^{b} Solvent: C_6D_6; reference (external): $BF_3{\cdot}OEt_2$.

interactions between oxygen and boron,[20−22] thereby increasing the Lewis acidity, whereas electron-donating substituents will have the opposite effect.

Shortly after the first reports on $B(C_6F_5)_3$, the synthesis of bis(pentafluorophenyl)borinic acid, $(C_6F_5)_2BOH$, and pentafluorophenyl boronic acid, $C_6F_5B(OH)_2$, were reported by Chambers and Chivers, prepared by hydrolysis of the corresponding chloro compounds.[23] The borinic acid $(C_6F_5)_2BOH$ has been reported to exist as a trimer in the solid state,[22] which is in equilibrium with the monomeric form in solution.[24] Both acids have received renewed interest recently,[25] including applications in organic synthesis.[26,27] Only a few esters of these acids have been reported. The ethyl and butyl derivatives $(C_6F_5)_2BOEt$ and $(C_6F_5)_2BO^nBu$ were obtained upon thermal decomposition of $(C_6F_5)_2BF{\cdot}OEt_2$[28] and $(C_6F_5)_2BH{\cdot}thf$,[29] respectively. Di-*n*-propyl and di-isopropyl boronic esters $C_6F_5B(O^nPr)_2$ and $C_6F_5B(O^iPr)_2$ [30] and a few cyclic esters derived from catechol, naphthol, and pinacol have also been reported.[19,31] Here we report the first preparation of the pentafluorophenyl esters of bis(pentafluorophenyl)-borinic acid, $(C_6F_5)_2BOC_6F_5$ (**2**), and pentafluorophenyl-boronic acid, $C_6F_5B(OC_6F_5)_2$ (**3**). These two compounds form the missing links between $B(C_6F_5)_3$ and tris-(pentafluorophenyl)borate, $B(OC_6F_5)_3$ (**4**), which was first reported in 1992 by Naumann.[32] The complete series now in hand allows us to establish trends in the relative Lewis acidity of **1**−**4**.

Results and Discussion

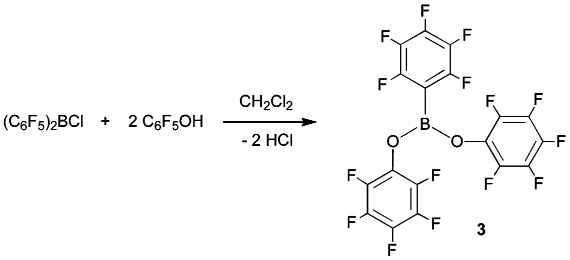
The reaction of $(C_6F_5)_2BCl$[23,29] with pentafluorophenol in dichloromethane leads to the clean formation of $(C_6F_5)_2BOC_6F_5$, **2** (eq 1). The boronic ester $C_6F_5B(OC_6F_5)_2$, **3**, is prepared by a similar procedure from $C_6F_5BCl_2$ (eq 3). The preparation of $C_6F_5BCl_2$ from $Me_3SnC_6F_5$ or $Me_2Sn(C_6F_5)_2$ and BCl_3 as previously reported[23,31] can be problematic, as the reaction products $C_6F_5BCl_2$ and Me_3SnCl or Me_2SnCl_2 are highly volatile and difficult to separate by distillation or sublimation. We found that $C_6F_5BCl_2$ is more conveniently prepared from $^nBu_3SnC_6F_5$ (eq 2). Both compounds **2** and **3** were purified by sublimation and have been characterized by ^{19}F NMR and ^{11}B NMR spectroscopy and single-crystal X-ray analysis. For comparison, we have also determined the structure of the previously reported compound $B(OC_6F_5)_3$ (**4**).



2

(1)

$$ {}^{n}Bu_3SnC_6F_5 \;+\; BCl_3 \longrightarrow (C_6F_5)_2BCl \;+\; {}^{n}Bu_3SnCl \qquad (2) $$



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(3)

NMR Spectroscopy. ^{19}F NMR and ^{11}B NMR spectroscopic data for compounds **1**−**4** have been collected in Table 1. The ^{11}B NMR chemical shift values decrease in the order from **1** to **4** with values in the typical range expected for compounds of the type BAr_3, Ar_2BOAr, $ArB(OAr)_2$, and $B(OAr)_3$.[33] This trend indicates an increased shielding of the boron center going from **1** to **4**. However, the ^{11}B chemical shift is not a direct measure for Lewis acidity. For example, the ^{11}B chemical shift values of $B(C_6H_5)_3$ and $B(OC_6H_5)_3$ have been reported as 68 and 16.5 ppm, respectively,[33] which are comparable to the values of 59 and 15 ppm reported for the much stronger Lewis acids $B(C_6F_5)_3$ and $B(OC_6F_5)_3$, respectively.[32,34] Moreover, BF_3 and $B(C_6F_5)_3$ have been reported to have similar Lewis acidities[3,4] but have completely different ^{11}B NMR values of 10 and 59 ppm, respectively.

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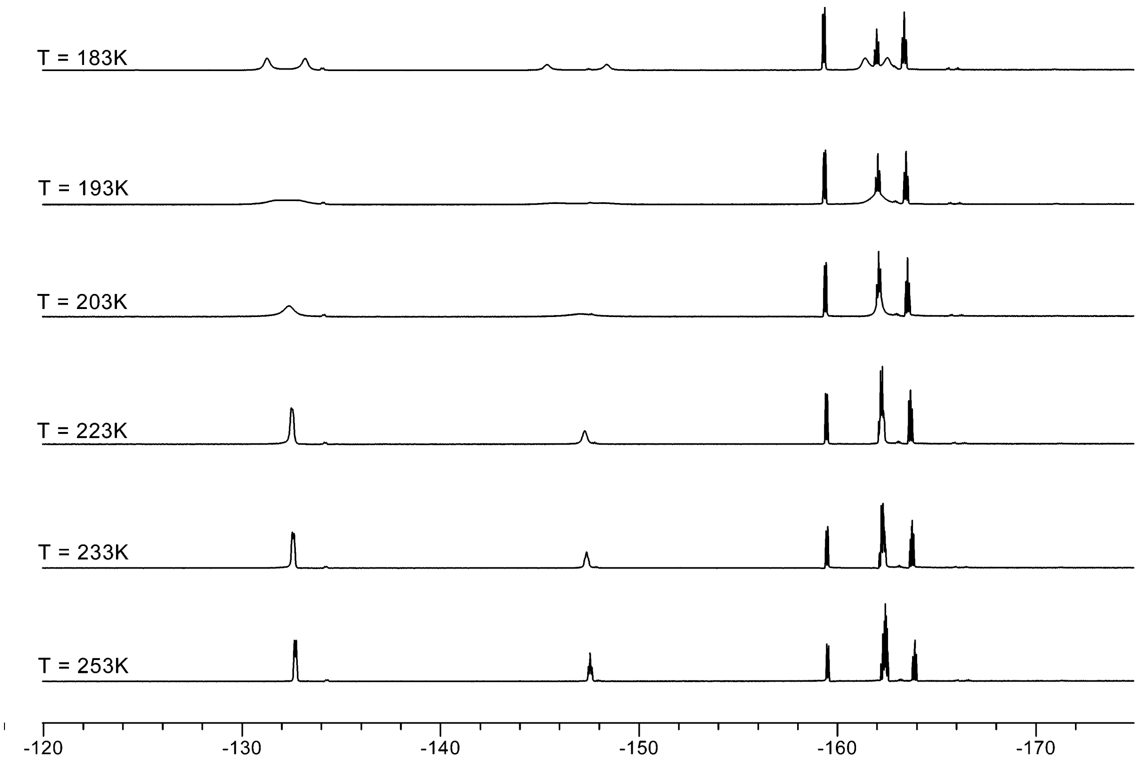
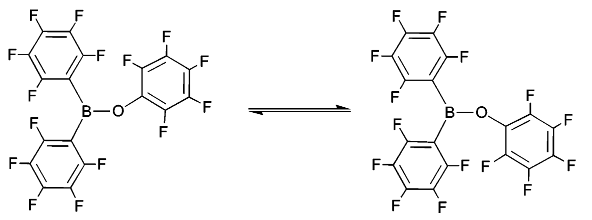


Figure 2. VT-^{19}F NMR of $(C_6F_5)_2BOC_6F_5$ (**2**) in CD_2Cl_2.

The ^{19}F NMR chemical shift values for the C_6F_5 fluorine atoms are generally found at higher frequency compared to the OC_6F_5 fluorine atoms and cover a larger shift range (ca. 30 ppm versus 5 ppm). For compounds **2** and **3**, two sets of *ortho*-, *meta-,* and *para*-fluorine signals for the C_6F_5 and OC_6F_5 groups are observed, indicating free rotation around all B−C and B−O bonds at room temperature. Restricted rotation around B−O bonds has been observed previously, and activation barriers have been determined using a variety of techniques.[35] Mislow and co-workers used dynamic ^{1}H NMR to determine activation barriers of $\Delta G^{\ddagger} = 54{-}58$ kJ/mol for alkyl esters of diarylborinic acids $Aryl_2BOR$ [Aryl = Mes (2,4,6-trimethylphenyl) or anthracenyl].[20] These values have been supported by theoretical calculations on H_2BOH[21,36,37] and by dynamic ^{13}C NMR spectroscopy studies on $Aryl_2BOR$ (where R = alkyl and aryl).[38] More recently, dynamic ^{19}F NMR has been used to measure the activation barrier in $(C_6F_5)_2BOH$, and a barrier for rotation around the B−O bond of $\Delta G^{\ddagger} = 39$ kJ/mol was determined.[22]

The Lewis acidity of the boron center in compounds **2**−**4** will be affected by pπ−pπ interactions between the lone pairs on the oxygen atoms and the empty p_z orbital on boron. On the other hand, the electron-withdrawing C_6F_5 substituents on oxygen will decrease the electron density at oxygen. To determine the B−O bond order in $(C_6F_5)_2BOC_6F_5$, **2**, we have carried out a VT ^{19}F NMR study in CD_2Cl_2, which is shown in Figure 2. It can be seen that free rotation around the B−O bond occurs down to 193 K. Cooling the sample beyond this coalescence temperature T_c results in freezing of the B−O bond rotation, and the rate of the interconversion of the two isomers, as shown in eq 4, will be slower than the NMR time scale. The two C_6F_5 groups become nonequivalent, giving rise to separate chemical shifts for the *ortho*, *meta*, and *para* fluorine atoms of these groups. The activation barrier for this process $\Delta G^{\ddagger} = 35$ kJ/mol (calculated from $T_c = 193$ K and $\delta\nu$(*ortho*-F) = 450 Hz at 183 K)[35] is the lowest value observed to date for a B−O bond rotation, indicating a rather weak pπ−pπ interaction and negligible B−O double-bond character in **2**. A VT ^{19}F NMR investigation of $C_6F_5B(OC_6F_5)_2$, **3**, did not show any coalescence down to 183 K in CD_2Cl_2. The activation barrier is likely to be even lower in this case, as the two oxygen donors, already weakened by the electron-withdrawing pentafluorophenyl substituents, will now have to compete for donation to the boron center, resulting in an even further weakening of the B−O double-bond character. A much lower barrier was also observed for $MesB(OMe)_2$, compared to Mes_2BOMe.[20]



(4)

Solid State Structures. Single-crystal X-ray structure determinations of compounds **2**, **3**, and **4** (Figures 3, 5, and 7, respectively) showed in each case the central boron atom to have a slightly distorted trigonal planar geometry, the boron atom lying only ca. 0.03, 0.01, and 0.03 Å out of the plane of its substituents in **2**, **3**, and **4**, respectively. As discussed in the previous section, the

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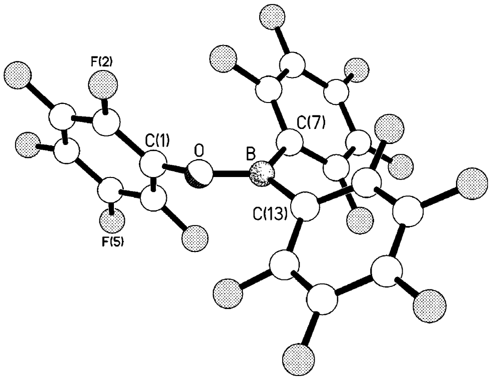

Figure 3. Molecular structure of $(C_6F_5)_2BOC_6F_5$ (**2**). Selected bond lengths (Å) and angles (deg): B−O 1.358(6), B−C(7) 1.587(7), B−C(13) 1.573(7), O−C(1) 1.392(5), O−B−C(7) 123.4(4), O−B−C(13) 113.9(4), C(7)−B−C(13) 122.6(4), B−O−C(1) 126.6(4).

Lewis acidity of boron compounds containing B−O bonds can be reduced due to pπ−pπ donation from oxygen to boron facilitated by a coplanar arrangement of the substituents at the two centers. In **2**, however, the B−O torsion angle of ca. 19° is relatively large, indicating a lesser degree of pπ−pπ donation, probably due to the electron-withdrawing effects of the pentafluorophenyl substituents. In **3**, while the B−O(1) torsion angle is small (ca. 5°), that for the B−O(2) bond is ca. 10°. In **4**, with three OC_6F_5 units, one of the B−O torsion angles [B−O(2) ca. 21°] is markedly larger than the other two [B−O(1) ca. 5°, B−O(3) ca. 7°]. It is noticeable that this correlates with an apparently longer B−O(2) bond length [1.371(9) Å], cf. those to O(1) and O(3) [1.357(10) and 1.346(9) Å, respectively], but this must be treated with caution as the relatively high esd's mean that the differences are not statistically significant. In the related complexes $(Mes)_2BOMe$ and $(Mes)_2BSMe$, the B−O and B−S torsion angles are ca. 5° and 4°, respectively.[21] In both **2** and **3**, all three C_6F_5 ring systems are inclined in the same sense (i.e., propeller-like) with respect to the BX_3 plane (by ca. 65°, 40°, 38° and ca. 63°, 75°, 49° for the C(1)-, C(7)-, and C(13)-based rings in **2** and **3**, respectively). In **4**, however, the C(1)-based ring is inclined in the opposite sense to the other two, the inclination angles being ca. 104°, 77°, and 52° for the C(1)-, C(7)-, and C(13)-based rings, respectively. In $(Mes)_2BOMe$ and $(Mes)_2BSMe$ the inclinations of the mesityl rings range between ca. 50° and 68°.[21]

Adjacent molecules along the *a* and *b* axis directions in the crystals of **2** are linked to form a sheet by F···π interactions between *ortho* and *meta* fluorines on the C(1) ring and the π-system of the C(7) ring (Figure 4). Such F···π interactions are not uncommon, and their occurrence has been recently reviewed.[39] The F···ring centroid separations are ca. 3.16 and 3.11 Å for interactions a and b, respectively, with associated C−F···π angles of ca. 155° and 130°. The F···π vectors are inclined by ca. 77° and 76° to the plane of the aromatic ring (for a and b, respectively), and the two vectors subtend an angle of ca. 154° at the ring centroid.

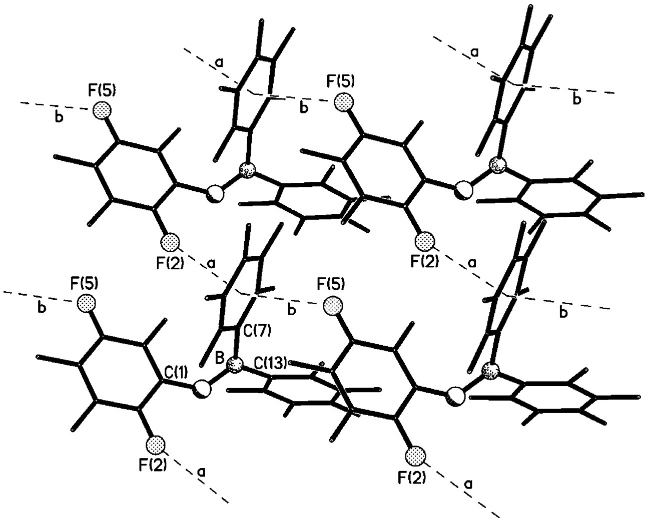

Figure 4. Part of the 2-D sheet of molecules linked by F···π interactions present in the crystals of $(C_6F_5)_2BOC_6F_5$ (**2**).

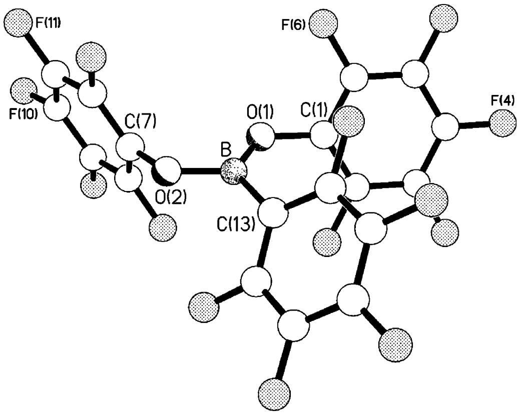

Figure 5. Molecular structure of $C_6F_5B(OC_6F_5)_2$ (**3**). Selected bond lengths (Å) and angles (deg): B−O(1) 1.371(4), B−O(2) 1.367(4), B−C(13) 1.561(4), O(1)−C(1) 1.379(3), O(2)−C(7) 1.381(4), O(1)−B−O(2) 116.9(3), O(1)−B−C(13) 126.0(3), O(2)−B−C(13) 117.1(3), B−O(1)−C(1) 125.0(2), B−O(2)−C(7) 123.0(2).

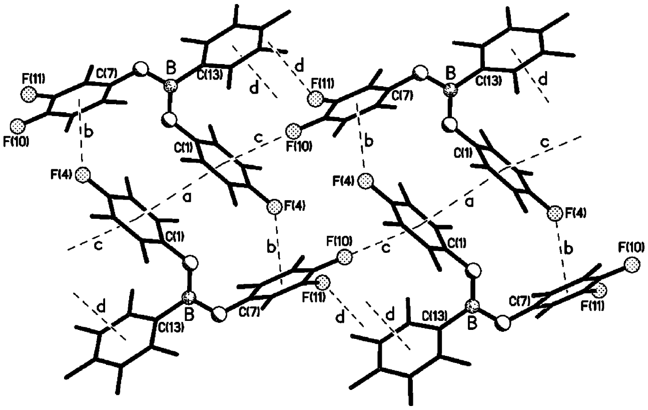

Figure 6. Portion of the 3-D network of F···π and π···π linked molecules present in the crystals of $C_6F_5B(OC_6F_5)_2$ (**3**).

The dominant feature of the packing in the solid state structure of **3** is a π···π stacking interaction (or a double F···π interaction) between the C(1)-based ring and its centrosymmetrically related counterpart (interaction a in Figure 6). The centroid···centroid and mean interplanar separations are ca. 4.15 and 3.33 Å, respectively,

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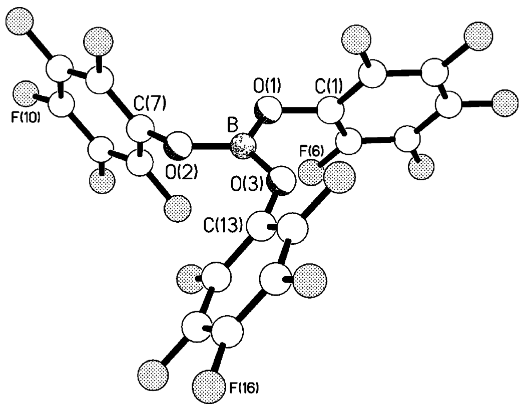

Figure 7. Molecular structure of $B(OC_6F_5)_3$ (**4**). Selected bond lengths (Å) and angles (deg): B−O(1) 1.357(10), B−O(2) 1.371(9), B−O(3) 1.346(9), O(1)−C(1) 1.386(7), O(2)−C(7) 1.372(8), O(3)−C(13) 1.350(8), O(1)−B−O(2) 118.7(6), O(1)−B−O(3) 120.7(6), O(2)−B−O(3) 120.5(7), B−O(1)−C(1) 122.1(5), B−O(2)−C(7) 122.4(5), B−O(3)−C(13) 126.3(5).

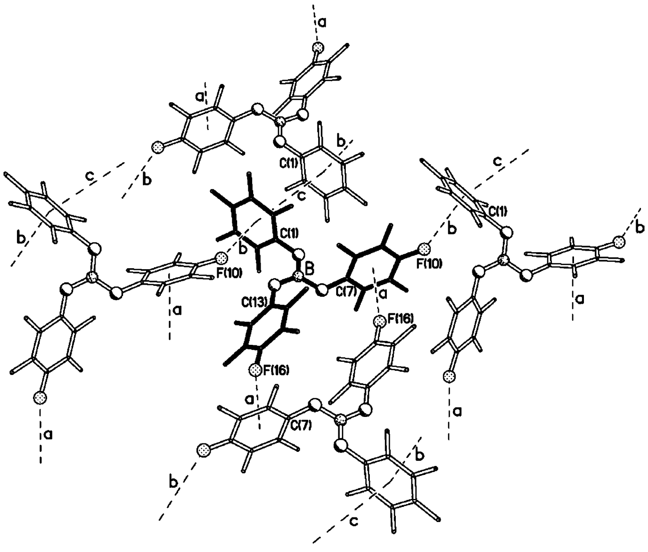

Figure 8. F···π and π···π interactions linking to neighboring molecules in the crystals of $B(OC_6F_5)_3$ (**4**).

and the overlap is such that the F(6) fluorine atom of one ring is placed almost directly above the centroid of the other and vice versa (F···centroid 3.30 Å, vector inclined by ca. 86° to the ring plane). This interaction is supplemented by three relatively weak F···π contacts (b, c, and d in Figure 6) with F···π distances (Å) and C−F···π angles (deg) of b 3.25, 130; c 3.35, 163; d 3.31, 145. The F···π vectors are inclined by ca. 74°, 68°, and 77° to their associated ring planes for b, c, and d, respectively. Interactions a and c subtended an angle of ca. 144° at the C(1) ring centroid.

In **4**, neighboring molecules are linked by a combination of F···π and π···π interactions (Figure 8) to form a complex 3-D network. The F···π interaction a has an F···ring centroid separation of ca. 3.17 Å and a C−F···π angle of ca. 164°; the F···π vector is inclined by ca. 72° to the plane of the π system. For interaction b the respective values are 3.23 Å, 143°, and 82°. The π···π or double F···π contact c has a centroid···centroid distance of ca. 4.40 Å with a mean interplanar separation of ca. 3.49 Å. Being related to each other by a center of symmetry, the two ring systems are perfectly parallel and, as was seen for the π···π interaction in **3**, one of the fluorine atoms [F(6)] on one ring is placed almost directly above the centroid of the other ring, and vice versa (F···centroid 3.50 Å, vector inclined by ca. 84° to the ring plane).

The low barrier for rotation around the B−O bond determined by ^{19}F NMR for compounds **2** and **3**, combined with the extensive F···π interactions seen in the solid state structures, indicates that the observed and rather random torsion angles in compounds **2**−**4** are probably not related to pπ−pπ interactions between B and O, but simply a result of crystal packing.[39]

Trends in Relative Lewis Acidity. Since Lewis first proposed his acid−base theory in 1923, many attempts have been made to quantify Lewis acidity, for example by correlating Lewis acid strength with thermodynamic data,[40−43] chemical reactivity,[44,45] or spectroscopic data.[46,47] To evaluate the relative Lewis acid strength of the series of pentafluorophenyl boron compounds **1**−**4**, we have chosen two NMR spectroscopic methods, which have been previously employed by others. The first method is based on Gutmann's classification of solvents by acceptor numbers,[48,49] which measures the change in ^{31}P NMR chemical shift ($\Delta\delta$) between Et_3PO and its adduct. This method has been modified by Beckett for Lewis acids.[4,18,50] We have changed the solvent in this method from thf to benzene. The same changes in chemical shift ($\Delta\delta$) were observed in both solvents and also in $CDCl_3$. Thf was avoided because slow polymerization of thf was observed with some Lewis acids.[51] The second method, developed by Childs, measures the change in ^1H NMR chemical shift of the proton H_3 in crotonaldehyde (CA) upon binding of a Lewis acid to the carbonyl oxygen atom.[52] Our results are summarized in Table 2 and Figure 9. For comparison, we have also included two nonfluorinated boron compounds, triphenylborane $B(C_6H_5)_3$ and triphenylborate $B(OC_6H_5)_3$, in our evaluation.

The difference in chemical shift ($\Delta\delta$ ^{31}P NMR) observed upon reaction of Et_3PO with a Lewis acid (Figure 9, left-hand *Y*-axis) increases in the order **1** < **2** < **3** < **4**. The strongest interaction is observed for $B(OC_6F_5)_3$ (**4**), indicating that this is the strongest Lewis acid in the case of Et_3PO. A similar trend is observed for Ph_3PO as the reference base,[53] albeit with an overall

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Table 2. NMR Data for Lewis Acid–Base Adducts between 1–4 and R_3PX (R = Et, Ph; X = O, S)

Lewis acid	Et_3PO ^{31}P ppm^a	Et_3PO $\Delta\delta$ ppm^a	Et_3PO ^{11}B ppm^a	Ph_3PO ^{31}P ppm^a	Ph_3PO $\Delta\delta$ ppm^a	Et_3PS ^{31}P ppm^a	Et_3PS $\Delta\delta$ ppm^a	Et_3PS ^{11}B ppm^a	CA ^1H ppm^b	CA $\Delta\delta$ ppm^b
none	46.4			25.5		53.6			6.85	
BPh_3	65.9	19.6		25.5	0	53.6	0		6.90	0.05
$B(OPh)_3$	69.4	23.0		27.0	1.5	53.6	0		6.88	0.03
1	76.6	30.2	−2.8	45.8	20.3	57.8	4.2	0.0	7.90	1.05
2	80.0	33.6	3.5	46.1	20.6	53.6	0	41.4	7.85	1.00
3	80.5	34.1	2.6	46.2	20.7	53.6	0		7.35	0.50
4	80.9	34.5	0.0	46.6	21.1	53.6	0		7.25	0.40

^{a} In C_6D_6 at room temperature. ^{b} In CD_2Cl_2 at room temperature.

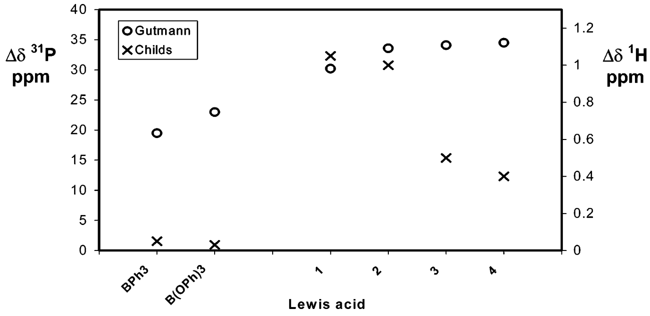

Figure 9. Evaluation of relative Lewis acidities.

lowermagnitude of $\Delta\delta$, which could be due to steric factors or to the difference in basicity. The much softer base Et_3PS, which is sterically comparable to Et_3PO, shows only a weak interaction with $B(C_6F_5)_3$ (**1**) and no interaction with the Lewis acids **2**–**4**. Noteworthy, it has been reported that the soft base PH_3 interacts strongly with $B(C_6F_5)_3$, but not with $B(OC_6F_5)_3$.[11] The formation of Lewis acid–base adducts between Et_3PO and compounds **1**–**4** and between Et_3PS and **1** is confirmed by the changes in the ^{11}B NMR spectra. In all cases a chemical shift value around 0 ppm is observed, characteristic for tetracoordinate boron compounds of this type.[4,10,33]

The evaluation of the Lewis acidity by Childs' method, using crotonaldehyde as the reference base, resulted in a different trend (Figure 9, right-hand *Y*-axis). In this case, the largest difference in chemical shift ($\Delta\delta$ ^1H NMR) is seen for $B(C_6F_5)_3$ (**1**) and the relative order is reversed: **1** > **2** > **3** > **4**. As might be expected, the nonfluorinated boron compounds $B(C_6H_5)_3$ and $B(OC_6H_5)_3$, which are much less Lewis acidic, show much weaker interactions. Although analogous trends are seen for these Lewis acids in both methods, the observed changes in chemical shift are too small to draw any firm conclusions.

A linear correlation between Gutmann's method and Child's method was previously observed for a selection of Lewis acids.[4] From our results, we suggest that such a linear correlation does not strictly apply to all Lewis acids, but that different bases can give different trends. Drago and Matwiyoff stated already in 1968 that, "Any order of donor or acceptor strengths must be established relative to a given donor or acceptor. Reversals may be expected when orders toward different donors (or acceptors) are compared."[54] The results obtained here for the Lewis acid series **1**–**4**, when compared with different Lewis bases, show that this is indeed the case. Different trends in Lewis acidity when using different reference bases were also seen by Graham and Stone[55] and more recently by Marks and Luo.[42] The observation of different orders can be rationalized in terms of Pearson's *hard soft acid base* (HSAB) classification,[56] whereby the hardness or softness of a particular Lewis acidic or Lewis basic center is affected by the nature of the other atoms attached to it and the type of bonding between them. BF_3 is generally regarded as a harder acid than BH_3, because the B–F bond is more ionic in character, whereas the B–H bond is more covalent. For the same reasons, B–O bonds are more ionic than B–C bonds, and therefore $B(OC_6F_5)_3$ will be a harder Lewis acid than $B(C_6F_5)_3$. The oxygen atom in crotonaldehyde is attached to a carbon atom, and the C=O pπ–pπ double bond is largely covalent in character. The P=O double bond in R_3P=O is a pπ–dπ bond, which is much more ionic in character, making the oxygen atom harder in this case. The combination of a hard Lewis acid with a hard Lewis base, or a soft Lewis acid with a soft Lewis base, results in a stronger interaction than the mixed hard–soft interaction.

In conclusion, compared to $B(C_6F_5)_3$ (**1**), the pentafluorophenyl boron compounds **2**, **3**, and **4** are progressively harder Lewis acids, which form increasingly stronger interactions with a hard Lewis base such as Et_3PO, whereas the interaction with softer Lewis bases such as Et_3PS or crotonaldehyde is strongest in the case of $B(C_6F_5)_3$ (**1**). VT NMR studies have shown that there is no significant pπ–pπ interaction between B and O in compounds **2**–**4**, resulting in free rotation around the B–O bond at room temperature. In the solid state structures of **2**–**4** extensive intermolecular F···π interactions are observed. We are currently exploring applications of these new Lewis acids in synthesis and catalysis.

Experimental Section

General Procedures. All moisture-sensitive compounds were manipulated using standard vacuum line, Schlenk, or cannula techniques, or in a conventional nitrogen-filled glovebox. ^1H, ^{19}F, ^{31}P, and ^{11}B NMR spectra were recorded on a Bruker AC-250 or a JEOL JNM-EX270 spectrometer; chemical shifts for ^1H NMR are referenced to the residual protio impurity of the deuterated solvent. ^{19}F, ^{31}P, and ^{11}B chemical shifts are reported relative to $CFCl_3$, H_3PO_4 (85%), and $BF_3 \cdot OEt_2$, respectively.

Solvents and Reagents. Pentane was dried by passing through a column, filled with commercially available Q-5 reagent (13 wt % CuO on alumina) and activated alumina (pellets, 3 mm). Diethyl ether and tetrahydrofuran were dried over sodium metal with a benzophenone ketyl indicator,

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whereas dichloromethane and acetonitrile were dried over CaH_2. Pentafluorophenol was dried over molecular sieves (4 Å) and distilled prior to use. The syntheses of $(C_6F_5)_2BCl$,[29] $^nBu_3SnC_6F_5$,[57] Et_3PS,[58] and $B(OC_6F_5)_3$ (**4**)[32] have been reported previously. Crystals of **4** suitable for X-ray diffraction were grown from a pentane solution at −20 °C. All other chemicals and NMR solvents were obtained commercially and used as received. Elemental analyses were performed by the Science Technical Support Unit at London Metropolitan University.

Pentafluorophenyl Boron Dichloride, $C_6F_5BCl_2$. $^nBu_3SnC_6F_5$ (17.56 g, 38.42 mmol) was placed in a 50 mL glass ampule containing a magnetic stirrer bar. The ampule was evacuated and sealed, and it was placed in a NaCl/ice bath at −10 °C. After 30 min, BCl_3 (6.75 g, 57.62 mmol) was condensed into the flask. The clear yellow solution was left stirring at −10 °C for 1 h and then at room temperature overnight. The next day, the ampule was put again in a NaCl/ice bath at −10 °C and opened to dynamic vacuum for 30 min, to remove the excess BCl_3. The product was subsequently distilled at 40 °C/0.05 mbar. Yield = 2.6 g (27%). Spectroscopic data were identical to the reported data.[34]

Bis(pentafluorophenyl)borinic Acid Pentafluorophenyl Ester, $(C_6F_5)_2BOC_6F_5$ (2). C_6F_5OH (0.63 g, 3.4 mmol) and $(C_6F_5)_2BCl$ (1.31 g, 3.4 mmol) were placed in two separate Schlenk flasks and dissolved in 15 mL of dichloromethane. The flask containing the $(C_6F_5)_2BCl$ solution was placed in an ice bath at 0 °C. The C_6F_5OH solution was added dropwise via cannula. When the addition was complete, the mixture was left at 0 °C for 30 min and then allowed to warm to room temperature, at which it was left stirring for 2 h. The solvent was removed by vacuum, leaving an off-white solid. The compound was purified by sublimation at 90 °C/0.1 mbar. Yield = 64%. Crystals suitable for X-ray diffraction were grown from a pentane solution at −20 °C. ^{19}F NMR (C_6D_6, 235 MHz): C_6F_5 group −131.1 (o, 4F) −144.1 (p, 2F) −159.7 (m, 4F) ppm; OC_6F_5 group −157.8 (o, 2F) −159.3 (p, F) −161.4 (m, 2F) ppm. ^{11}B NMR (C_6D_6, 83 MHz): 41.2 ppm. Anal. Calcd for $C_{18}BF_{15}O$: C, 40.95. Found: C, 40.91.

Pentafluorophenylboronic Acid Bis(pentafluorophenyl) Ester, $C_6F_5B(OC_6F_5)_2$ (3). $C_6F_5BCl_2$ (2.6 g, 10.45 mmol) and C_6F_5OH (3.85 g, 20.9 mmol) were placed under N_2 in two Schlenk flasks and dissolved in 20 mL of dry CH_2Cl_2. The $C_6F_5BCl_2$ solution was placed in an ice bath at 0 °C, and the pentafluorophenol solution was added dropwise via cannula. The clear, colorless solution was left stirring overnight at room temperature. The day after, the solvent was removed by high vacuum, leaving an off-white solid, which was purified by sublimation at 90 °C/0.1 mbar. Yield = 62%. Crystals suitable for X-ray diffraction were grown from a pentane solution at −20 °C. ^{19}F NMR (C_6D_6, 235 MHz): C_6F_5 group −131.1 (2F, o), −145.2 (1F, p), −159.0 (2F, m) ppm; OC_6F_5 group −157.3 (4F, o), −159.7 (2F, p), −161.9 (4F, m) ppm. ^{11}B NMR (C_6D_6, 83 MHz): 26.2 ppm. Anal. Calcd for $C_{18}BF_{15}O_2$: C, 39.74. Found: C, 39.84.

Structure Determinations. Crystal data for 2: $C_{18}BF_{15}O$, $M = 527.99$, triclinic, $P\bar{1}$ (no. 2), $a = 6.6111(16)$ Å, $b = 8.6330(19)$ Å, $c = 15.917(4)$ Å, $\alpha = 83.18(2)°$, $\beta = 78.31(3)°$, $\gamma = 89.39(2)°$, $V = 883.2(3)$ Å^3, $Z = 2$, $D_c = 1.985$ g cm^{-3}, μ(Mo Kα) = 0.231 mm^{-1}, $T = 173$ K, colorless thin plates; 3071 independent measured reflections, F^2 refinement, $R_1 = 0.067$, $wR_2 = 0.161$, 1881 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 317 parameters. CCDC 255626.

Crystal data for 3: $C_{18}BF_{15}O_2$, $M = 543.99$, triclinic, $P\bar{1}$ (no. 2), $a = 6.0687(13)$ Å, $b = 10.5527(19)$ Å, $c = 14.722(3)$ Å, $\alpha = 83.699(15)°$, $\beta = 84.364(18)°$, $\gamma = 79.853(11)°$, $V = 919.5(3)$ Å^3, $Z = 2$, $D_c = 1.965$ g cm^{-3}, μ(Mo Kα) = 0.229 mm^{-1}, $T = 203$ K, colorless plates; 3249 independent measured reflections, F^2 refinement, $R_1 = 0.044$, $wR_2 = 0.090$, 2043 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 326 parameters. CCDC 255627.

Crystal data for 4: $C_{18}BF_{15}O_3$, $M = 559.99$, monoclinic, $P2_1/c$ (no. 14), $a = 16.611(5)$ Å, $b = 5.618(6)$ Å, $c = 20.090(7)$ Å, $\beta = 93.620(19)°$, $V = 1871(2)$ Å^3, $Z = 4$, $D_c = 1.988$ g cm^{-3}, μ(Mo Kα) = 0.232 mm^{-1}, $T = 203$ K, colorless needles; 3276 independent measured reflections, F^2 refinement, $R_1 = 0.087$, $wR_2 = 0.224$, 1645 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 335 parameters. CCDC 255628.

Determination of Lewis Acidity. Gutmann's Method. This method was performed as described by Beckett et al.,[50] except that C_6D_6 was used as the solvent rather than tetrahydrofuran, as slow polymerization of thf was observed with certain Lewis acids. The Lewis acid and the phosphine oxide (or phosphine sulfide) were placed together in 1:1 ratio in a small glass vial and dissolved in the minimum amount of dry C_6D_6. The solution was placed in an NMR tube, and the ^{31}P NMR chemical shift was recorded at room temperature.

Childs' Method. This method was performed as described by Childs et al.,[52] except that the NMR measurement was carried out at room temperature rather than at −20 °C. The Lewis acid and crotonaldehyde were mixed together in a glass vial and dissolved in CD_2Cl_2. The resulting mixture was then placed into an NMR tube, and the ^1H NMR chemical shift of the H_3 proton of crotonaldehyde was recorded.

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Supporting Information Available: For **2**−**4**, figures giving molecular structures and ClF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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