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Article

Rigid, Fluoroarene-Containing Phosphonium Borates and Boranes: Syntheses and Reactivity Studies

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The reaction of $(C_6F_5)_2B(OEt)$ with $^t\mathrm{Bu_2P(CH_2Li)}$ yields the cyclic phosphonium ethoxyborate $(C_6F_5)(OEt)B(CH_2)(C_6F_4)P^t\mathrm{Bu}_2$ (**[1]OEt**) via B–C adduct formation and *ortho*-fluoride substitution. Treatment of **[1]OEt** with HCl in Et_2O gives the chloroborate **[1]Cl** in almost quantitative yield. The reaction of **[1]Cl** with $Li[AlH_4]$ leads not only to the reduction of the B–Cl bond but also to the selective substitution of one fluorine atom on the tetrafluorophenylene bridge (**[4]H**). **[1]Cl** is readily transformed into **[1]F**, **[1]OAc**, and **[1]OTf** upon reaction with $Tl[PF_6]$, AgOAc, and AgOTf, respectively (OAc = acetate; OTf = triflate). **[1]OTf** represents a convenient storage form of $[\mathbf{1}]^+$, because its B–O bond is highly labile. The free Lewis acid $[\mathbf{1}]^+$ was prepared in the form of its aluminate salt $[\mathbf{1}]^+[\mathbf{Al(O^{\mathit{t}}Bu^F)_4}]^-$. The phenyl derivative of **[1]OEt**, $(C_6H_5)(OEt)B(CH_2)(C_6F_4)P^t\mathrm{Bu}_2$ (**[5]OEt**), is also accessible and serves as starting material for the preparation of **[5]Cl** and $[\mathbf{5}]^+[\mathbf{Al(O^{\mathit{t}}Bu^F)_4}]^-$.

Introduction

Boron-based Lewis acids, in particular aryl boranes, are applied as anion sensors[1–4] and homogeneous (co)catalysts.[5–10] Recent developments in the field have shown that the acidity and thus the reactivity of these compounds can be improved by (i) the use of perfluorinated aryl substituents or (ii) the incorporation of a positive charge into the molecular framework. For example, Marder and Piers introduced the ditopic borane **[I]** (Figure 1) for use as an inverse chelator of F^- and OH^- ions.[11] In combination with $Ph_3C(OR)$ (R = Me, C_6F_5), **[I]** acts as an initiator for zirconocene-mediated ethylene polymerization reactions.[12] The Bourissou, Gabbaï, and Kawashima groups have employed the phosphonium borane $[\mathbf{II}]^+$ (Figure 1) as an efficient fluoride and azide scavenger, possessing an exceptionally high Lewis acidity.[1,13,14] Related *para*-configured phosphonium boranes have been described by Stephan et al.[15] With regard to organic synthetic transformations, Corey et al. reported cationic oxazaborolidinium triflates (**[III]OTf**; Figure 1) and triflimides (**[III]NTf$_2$**) to have an extraordinarily broad application profile as catalysts in (enantioselective) [4+2] and [3+2] cycloaddition reactions.[16–18] Stephan et al. coined the term “frustrated Lewis pair” (FLP) for electron-pair donor (e.g., $P^t\mathrm{Bu}_3$) and acceptor (e.g., $B(C_6F_5)_3$) molecules that are sterically incapable of adduct formation.[9,10] As a result, such systems possess a unique reactivity, which can be exploited for the activation of added molecules, the most prominent example being heterolytic H_2 splitting.[19] On the basis of this discovery, Erker et al. designed the ethylene-bridged compound $(C_6F_5)_2B{-}CH_2CH_2{-}PMes_2$ (Mes = mesityl), which turned out to be one of the most active metal-free hydrogenation catalysts described to date.[20]

Originally aiming at the preparation of the methylene-bridged FLP $(C_6F_5)_2B{-}CH_2{-}P^t\mathrm{Bu}_2$, we have recently obtained the cyclic phosphonium borate **[1]OEt** (Scheme 1), which can

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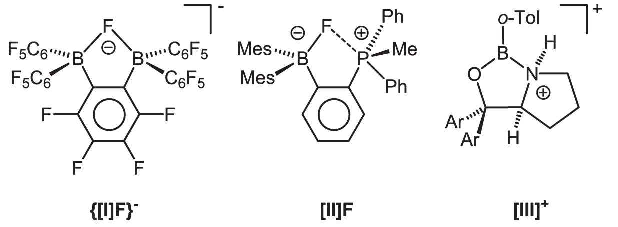
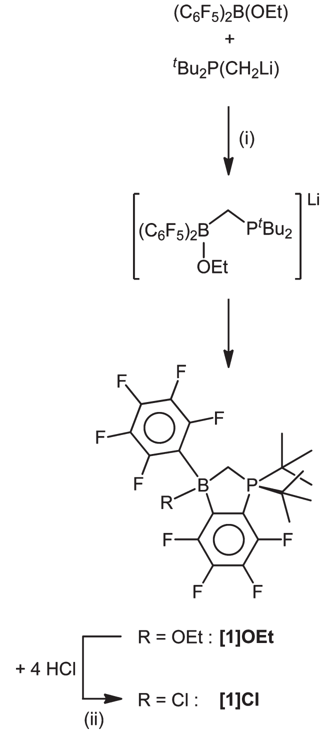


Figure 1. Boron-based Lewis acids can be applied as anion scavengers (e.g., [**I**], [**II**]$^+$) and homogeneous catalysts (e.g., [**III**]$^+$).

Scheme 1. Synthesis of the Zwitterionic Compound [1]OEt and Its Transformation into the Chloro Derivative [1]Cl[a]



[a] Conditions: (i) toluene, −78 °C → rt, 12 h. (ii) Et_2O, rt, 48 h.

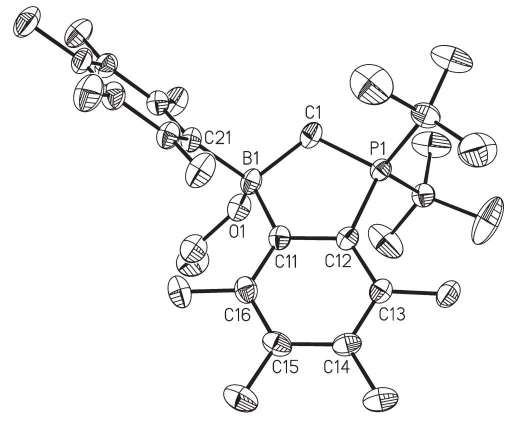


Figure 2. Molecular structure and numbering scheme of compound [**1**]**OEt**^{A}. H-atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B(1)−O(1) = 1.458(4), B(1)−C(1) = 1.659(5), B(1)−C(11) = 1.649(5), B(1)−C(21) = 1.651(4), P(1)−C(1) = 1.751(3), P(1)−C(12) = 1.804(3); B(1)−C(1)−P(1) = 109.4(2), C(1)−B(1)−C(11) = 104.0(3), C(1)−P(1)−C(12) = 98.5(2); C(1)−B(1)−C(11)−C(12) = −11.7(3), C(1)−P(1)−C(12)−C(11) = 0.5(2).

be viewed as the ethoxy adduct of a cationic Lewis acid [**1**]$^+$. [**1**]$^+$ combines perfluoroaryl substituents as well as a phosphonium group in the same molecule and is therefore likely to act as a particularly strong electron-pair acceptor for applications in the contexts mentioned above.

Given this background, we have investigated more closely the reactivity of [**1**]**OEt**, with a particular emphasis on the question of how the free cationic Lewis acid [**1**]$^+$ can be generated. [**1**]$^+$ should possess a comparably rigid and chemically inert framework and, with a view on [**III**]$^+$, can easily be turned into a chiral molecule by introducing two different substituents at the P atom.

Results and Discussion

Synthesis and Characterization of [1]OEt and [1]Cl. [1]OEt was synthesized from $(C_6F_5)_2B(OEt)$[21] and $^tBu_2P(CH_2Li)$[22] in toluene (Scheme 1) and recrystallized from a hot Et_2O−EtOH mixture (15:1). The compound is stable toward air and moisture for extended periods of time.

[**1**]**OEt** crystallizes with two crystallographically independent molecules in the asymmetric unit ([**1**]**OEt**^{A}, [**1**]**OEt**^{B}), of which only [**1**]**OEt**^{A} is discussed further (Figure 2). In addition to a B−C adduct bond (B(1)−C(1) = 1.659(5) Å),[23] [**1**]**OEt**^{A} contains a P−aryl bond (P(1)−C(12) = 1.804(3) Å). The OEt group is still present in the molecule (B(1)−O(1) = 1.458(4) Å), thus rendering the boron atom a four-coordinate chiral center and [**1**]**OEt**^{A} a phosphonium borate zwitterion. The B(1)−C(1)−P(1) bond angle of 109.4(2)° matches the ideal tetrahedral angle; the C(1)−B(1)−C(11) and C(1)−P(1)−C(12) angles possess values of 104.0(3)° and 98.5(2)°, respectively, thereby indicating a rather strain-free cyclic framework. [**1**]**OEt** adopts a slight envelope conformation in the solid state (dihedral angle C(11)C(12)P(1)C(1)//C(1)B(1)C(11) = 11.0°).

In [**1**]**OEt**, a five-membered heterocycle has been formed via the intramolecular nucleophilic substitution of an *ortho*-F atom by the phosphine moiety. It is reasonable to assume that the new B−C bond is created first (cf. the proposed intermediate in Scheme 1) and that the LiF liberation provides a driving force for the subsequent ring-closure reaction. Parallel to us, Stephan et al. investigated the reaction between $(C_6F_5)_2B(Cl)$ and $^tBu_2P(CH_2Li)$ and obtained a mixture of the fluoro- and chloroborate analogues of [**1**]**OEt** (i.e., [**1**]**F**, [**1**]**Cl**).[24] On the basis of DFT calculations, they concluded that the cyclization provides about 65 kcal mol^{-1} of thermodynamic

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[23] [**1**]**OEt**-type compounds can be viewed as neutral *intra*molecular adducts between a borane and a phosphorus ylide. Related *inter*molecular borane-ylide adducts have been described, i.e., H_3B−C(R^1)(R^2)−PPh_3 (Bestmann, H. J.; Sühs, K.; Röder, T. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1038–1039) and $(C_6F_5)_3B$−CH_2−PPh_3 (Döring, S.; Erker, G.; Fröhlich, R.; Meyer, O.; Bergander, K. *Organometallics* **1998**, *17*, 2183–2187). In $(C_6F_5)_3B$−CH_2−PPh_3, the B−C and P−C bond lengths amount to 1.675(2) and 1.792(1) Å, respectively; the B−C−P bond angle is 123.4(1)°.

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stabilization, which explains why the open-chain anion $[(C_6F_5)_2B(OEt)-CH_2-P^tBu_2]^-$ remains elusive.

In the $^{11}B\{^1H\}$ NMR spectrum, **[1]OEt** gives rise to a signal at 1.9 ppm, typical of tetracoordinate boron nuclei.[25] The $^{19}F\{^1H\}$ NMR spectrum reveals seven multiplet resonances. Two of them (−164.6, −134.8 ppm) possess an integral value of 2F, while each of the other signals integrates to 1F. This finding is in accord with the presence of one C_6F_5 substituent and one unsymmetrically substituted *ortho*-C_6F_4 ring in the molecule. The ^{t}Bu substituents are not magnetically equivalent ($\delta(^1H) = 0.60, 0.83$), and the same is true for the BCH_2P protons as well as the OCH_2CH_3 protons. We therefore conclude that the chiral ethoxy adduct remains intact in solution (C_6D_6) on the NMR time scale.

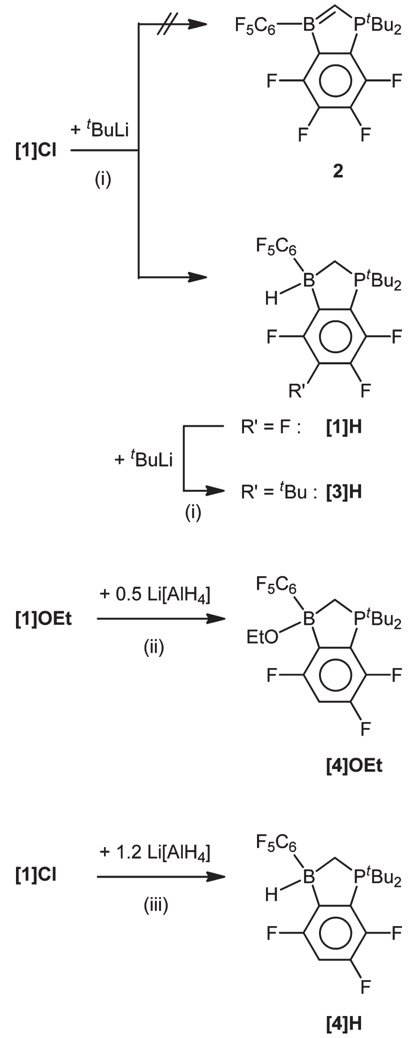
The most significant peak in the ESI^+ mass spectrum corresponds to the $[\mathbf{1}]^+$ cation ($m/z = 485.2$).

Since the latter observation indicated that it should indeed be possible to generate the free phosphonium borane without degradation of the molecular framework, we next decided to replace the ethoxy substituent of **[1]OEt** by a better leaving group. To this end, **[1]OEt** was treated with 4 equiv of HCl in Et_2O at rt. After 48 h, the chloro adduct **[1]Cl** had precipitated from the reaction mixture in 97% yield. The compound, which was characterized by an X-ray crystal structure analysis (see the Supporting Information (SI) for details) and by NMR spectroscopy, served as the starting material for most subsequent attempts at the preparation of free $[\mathbf{1}]^+$.

Reaction of [1]OEt and [1]Cl with Brønsted Bases and Hydride Donors. At first, we tried to deprotonate **[1]Cl** at the methylene bridge in order to temporarily neutralize the positive charge of the Lewis acid and thereby to facilitate the abstraction of the chloride anion (Scheme 2).

Since treatment of **[1]Cl** with $LiN(SiMe_3)_2$ in THF gave no reaction, the next experiment was conducted with ^{t}BuLi−pentane. After addition of approximately 1 equiv of the organolithium reagent, only one major product signal was visible in the $^{11}B\{^1H\}$ NMR spectrum (−17.1 ppm; C_6D_6); the signal split into a doublet in the proton-coupled ^{11}B NMR spectrum. The resonance of a corresponding B−H proton appeared as a broad 1:1:1:1 quartet at 3.71 ppm ($^1J_{BH} = 95$ Hz; 1H). Apart from that, the general signal pattern in the ^1H NMR spectrum, as well as in the $^{19}F\{^1H\}$ NMR spectrum, remained qualitatively the same. Thus, ^{t}BuLi had obviously not reacted as a base to give the phosphonium borane **2**, but as a hydride donor, producing the phosphonium hydridoborate **[1]H** (Scheme 2). Further addition of ^{t}BuLi−pentane to the reaction mixture, which still contained some starting material (**[1]Cl**), led not only to complete Cl/H exchange (^{11}B NMR spectroscopic control) but also to the formation of a second phosphonium hydridoborate species lacking one of the fluoride substituents at the phenylene bridge ($^{19}F\{^1H\}$ NMR spectroscopic control). The latter compound gave rise to a new doublet of doublets at $\delta(^1H) = 1.39$, thereby suggesting the introduction of a ^{t}Bu group into the phenylene fragment. Our proposal regarding the specific site of substitution (cf. **[3]H**; Scheme 2) is based on steric as well as electronic considerations and on the results of the reaction of **[1]Cl** with $Li[AlH_4]$ (see below).

Scheme 2. Attempts at the Deprotonation of [1]Cl; Cl/H Substitution at the Boron Center with Formation of [1]H and Subsequent F/^{t}Bu Substitution at the *ortho*-Phenylene Bridge Yielding [3]H; F/H Substitution at the *ortho*-Phenylene Bridge of [1]OEt with Formation of [4]OEt; Preparation of the Boron- and *ortho*-Phenylene-Substituted Compound [4]H[a]



[a] Conditions: (i) benzene−pentane, 5 °C → rt, 3 h. (ii) Et_2O, rt, 72 h. (iii) Et_2O−THF, rt, 14 d.

With the aim to prepare an authentic sample of the B−H product **[1]H**, we next studied the reaction of **[1]OEt** with 0.5 equiv of $Li[AlH_4]$ in Et_2O (Scheme 2). The transformation took 72 h to arrive at completion. According to NMR spectroscopy, the reaction product (87% yield) still contained the ethoxy substituent and a four-coordinate boron center. In the aromatic region of the ^1H NMR spectrum, a new multiplet appeared at 6.57 ppm (1H). Corresponding to that, one of the original seven resonances in the $^{19}F\{^1H\}$ NMR spectrum disappeared, thus pointing toward an F/H rather than an OEt/H exchange. X-ray crystallography (see the SI for details) finally revealed that the F atom in *para*-position to the phosphonium group on the bridging phenylene ring had been substituted by a hydrogen atom (cf. **[4]OEt**; Scheme 2). Both the reaction time and the product remained the same when 1 equiv of $Li[AlH_4]$ was employed.

For its higher reactivity, **[1]Cl** was chosen as the next starting material. Its reaction with 0.5 equiv of $Li[AlH_4]$ in Et_2O−THF initially gave three different species together with some unconsumed starting material. The amount of added reducing agent was therefore increased to 1.2 equiv of $Li[AlH_4]$.

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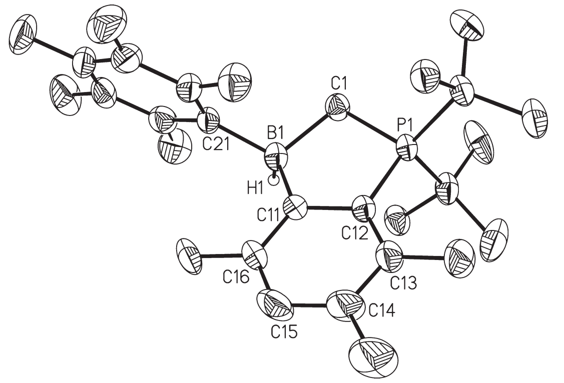


Figure 3. Molecular structure and numbering scheme of compound **[4]H**. H-atoms (except the atom on B(1)) have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B(1)−C(1) = 1.669(4), B(1)−C(11) = 1.626(5), B(1)−C(21) = 1.625(5), P(1)−C(1) = 1.790(3), P(1)−C(12) = 1.806(3); B(1)−C(1)−P(1) = 107.0(2), C(1)−B(1)−C(11) = 103.3(2), C(1)−P(1)−C(12) = 97.4(1); C(1)−B(1)−C(11)−C(12) = −16.6(4), C(1)−P(1)−C(12)−C(11) = 11.8(3).

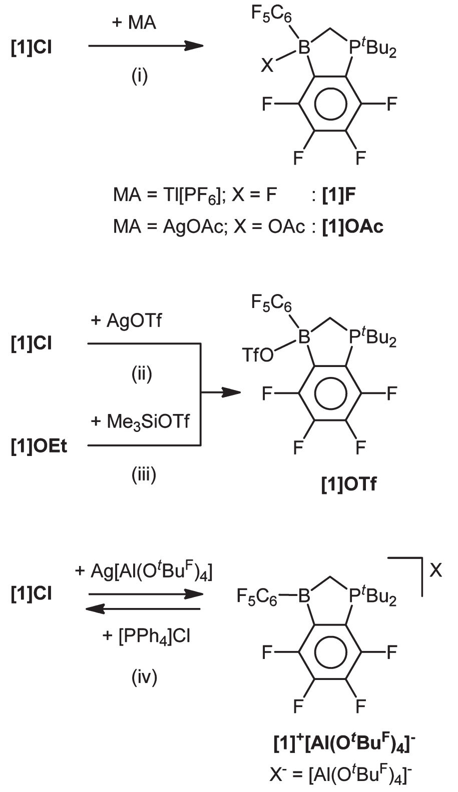
After 14 days, the reaction was finished and the double-substitution product **[4]H** (Scheme 2) could be isolated in 53% yield (the actual proportion of **[4]H** in the reaction mixture prior to workup was higher).

An NMR analysis of the stoichiometric ratio of the reaction intermediates (i.e., compounds where *either* the B−Cl *or* the C−F bond had been reduced) showed that the derivatization at the boron atom is significantly faster than that of the tetrafluorophenylene bridge. The presence of a B−H group in **[4]H** is evidenced by a sharp doublet in the ^{11}B NMR spectrum ($\delta(^{11}\mathrm{B}) = -17.4$; $^{1}J_{\mathrm{BH}} = 95$ Hz). Moreover, the $^{19}\mathrm{F}\{^{1}\mathrm{H}\}$ NMR resonance pattern is very similar to that of **[4]OEt** (and **[3]H**), but distinctly different from that of **[1]Cl**.

X-ray crystallography on **[4]H** confirmed the proposed molecular structure (Figure 3). The boron center indeed bears a hydrogen atom, and the site of tetrafluorophenylene substitution is the same as in **[4]OEt**. With regard to the selectivity of the fluoride substitution reaction, a directing effect of the OEt group during hydride attack (for example by complexation of the $\mathrm{Li}^{+}/\mathrm{Al}^{3+}$ counterion) can thus safely be excluded. We rather suggest that nucleophilic attack of a hydride ion at the *para*-position to the phosphonium substituent shifts π-electron density to the P−C_{ipso} carbon atom in the transition state. This accumulation of negative charge is then stabilized by the π-accepting properties of the phosphonium moiety by mechanisms similar to those operative in phosphonium ylides. For the same electronic reasons, we believe that the ^{t}Bu substituent of **[3]H** is also located in the *para*-position of the phosphorus atom.

Reaction of [1]Cl with Tl^{+} and Ag^{+} Salts of Weakly Coordinating Anions. In an attempt to prepare ionic species of the form $\mathbf{[1]}^{+}\mathbf{[anion]}^{-}$, **[1]Cl** was treated with $\mathrm{Tl[PF_6]}$, AgOAc, and AgOTf (Scheme 3).

Scheme 3. Substitution Reactions at the Boron Atom of [1]Cl with Formation of [1]F, [1]OAc, and [1]OTf; Preparation of the Free Phosphonium Borane in the Form of Its $[\mathrm{Al(O^{t}Bu^{F})_4}]^{-}$ Salt[a]



[a] Conditions: (i) **[1]F**: benzene, rt/ultrasonication, 48 h; **[1]OAc**: benzene, rt/ultrasonication, 36 h. (ii) benzene, rt, 30 d. (iii) $\mathrm{Et_2O}$, rt, 16 h. (iv) $\mathrm{CH_2Cl_2}$, rt, 1 h.

The reaction with $\mathrm{Tl[PF_6]}$ in benzene resulted in a clean product showing a doublet resonance in the $^{11}\mathrm{B}\{^{1}\mathrm{H}\}$ NMR spectrum ($\delta(^{11}\mathrm{B}) = 4.7$). The associated coupling constant of 72 Hz is in good agreement with literature-reported $^{1}J_{\mathrm{BF}}$ values of various fluoroborates.[25] In line with that, a broad, poorly resolved resonance was visible at $\delta(^{19}\mathrm{F}) = -176.8$, which can be assigned to a boron-coordinated fluorine atom. All other NMR data of the reaction product are closely similar to those of the starting material. Thus, after abstraction of a chloride ion from **[1]Cl**, the resulting strong Lewis acid $\mathbf{[1]}^{+}$ has obviously pulled off fluoride from the $[\mathrm{PF_6}]^{-}$ ion with formation of the derivative **[1]F** (for an X-ray crystal structure analysis of **[1]F** see the SI).[26]

Treatment of **[1]Cl** with the silver salts led to the exchange of chloride by coordinated acetate (**[1]OAc**) and triflate (**[1]OTf**; Scheme 3). Both compounds have been characterized by X-ray crystallography. A plot of the molecular structure of **[1]OTf** is presented in Figure 4 (see the SI for details of the solid-state structure of **[1]OAc**).

The B(1)−O(1) bond length of **[1]OTf** amounts to 1.589(3) Å, which is 0.075(3) Å longer than in **[1]OAc** and even 0.131(3) Å longer than in **[1]OEt**. This increase in bond length is paralleled by a decrease in the hydrolytic stability of the three derivatives (*note*: the molecular framework of $\mathbf{[1]}^{+}$ remains unaffected by hydrolysis).

The last experiment of the series was carried out using silver tetra(perfluoro-*tert*-butoxy)aluminate ($\mathrm{Ag[Al(O^{t}Bu^{F})_4]}$;[27,28] Scheme 3). Addition of this compound to **[1]Cl** in $\mathrm{C_6D_6}$ led to

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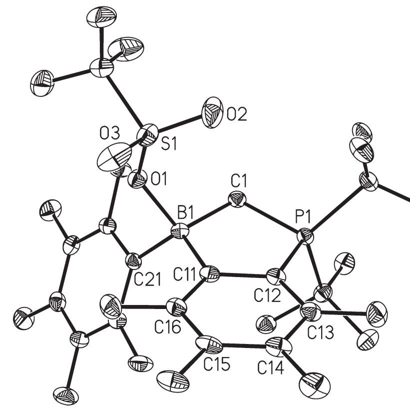
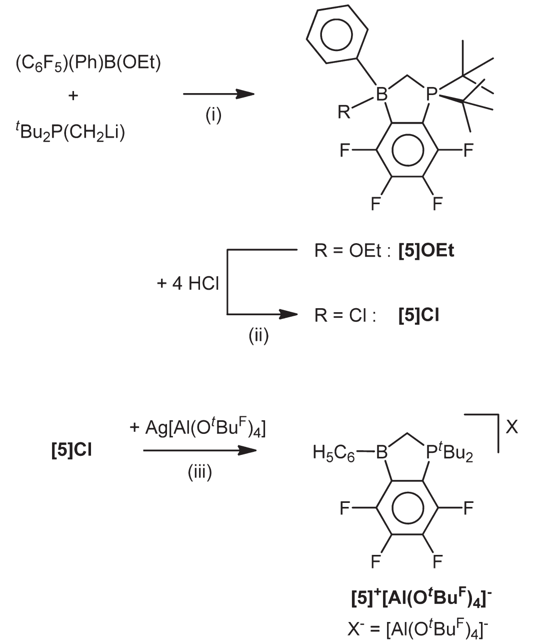


Figure 4. Molecular structure and numbering scheme of compound **[1]OTf**. H-atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B(1)−O(1) = 1.589(3), B(1)−C(1) = 1.646(4), B(1)−C(11) = 1.622(3), B(1)−C(21) = 1.625(4), P(1)−C(1) = 1.794(2), P(1)−C(12) = 1.807(2); B(1)−C(1)−P(1) = 107.9(2), C(1)−B(1)−C(11) = 105.5(2), C(1)−P(1)−C(12) = 96.9(1); C(1)−B(1)−C(11)−C(12) = −5.0(3), C(1)−P(1)−C(12)−C(11) = 12.7(2).

the formation of an insoluble sticky solid. An NMR spectroscopic investigation of the mother liquor showed no signals except the solvent signal, thereby confirming that the precipitation was quantitative. Subsequent addition of [Ph$_4$P]Cl (EtOH) to the precipitate regenerated **[1]Cl** (**[1]OEt**) (NMR spectroscopic control). The reaction was repeated in CH$_2$Cl$_2$ on a preparative scale. After mixing of **[1]Cl** and Ag[Al(O^{t}Bu^F)$_4$] (1:1) at rt, an off-white, voluminous precipitate immediately formed, which was removed by filtration. After the insoluble material had been dried in vacuo, its mass corresponded to 109% of the theoretically expected mass of AgCl. The clear yellow filtrate was evaporated to dryness under reduced pressure, redissolved in CD$_2$Cl$_2$, and investigated by NMR spectroscopy. The ^{11}B{^{1}H} NMR spectrum of the product showed only one signal; its chemical shift value (64.7 ppm) and large width at half-height (950 Hz) are characteristic of a three-coordinate boron compound (cf. (C$_6$F$_5$)$_3$B: $\delta(^{11}\mathrm{B}) = 59.4^{29}$ vs **[1]Cl**: $\delta(^{11}\mathrm{B}) = -2.1$ ($h_{1/2} = 135$ Hz)). The ^{t}Bu groups give rise to only one doublet in the ^{1}H NMR spectrum (1.43 ppm, $^3J_{\mathrm{PH}} = 17.7$ Hz), and the same applies to the BCH_2P protons (2.56 ppm, $^2J_{\mathrm{PH}} = 8.3$ Hz). We therefore conclude that the boron atom of $[\mathbf{1}]^+[\mathbf{Al(O}^t\mathbf{Bu}^\mathbf{F})_4]^-$ is no longer a chiral center and that the molecule possesses an average C_s symmetry. Further evidence for the presence of free $[\mathbf{1}]^+$ stems from the chemical shift value of the *para*-fluoro substituent in the C$_6$F$_5$ ring: The tetracoordinate starting material **[1]Cl** shows a corresponding signal at $\delta(^{19}\mathrm{F}) = -158.8$, significantly more shielded than in the three-coordinate compound (C$_6$F$_5$)$_3$B ($\delta(^{19}\mathrm{F}) = -143.0^{29}$). In comparison, the chemical shift of the *para*-fluorine atom in the C$_6$F$_5$ group of $[\mathbf{1}]^+[\mathbf{Al(O}^t\mathbf{Bu}^\mathbf{F})_4]^-$ ($\delta(^{19}\mathrm{F}) = -141.1$) fits almost perfectly to the latter value.[30]

Scheme 4. Synthesis of the Phenyl Derivative [5]OEt and Its Transformation into [5]Cl and $[\mathbf{5}]^+[\mathbf{Al(O}^t\mathbf{Bu}^\mathbf{F})_4]^-$ ^{a}



^{a} Conditions: (i) toluene, −78 °C → rt, 48 h. (ii) Et$_2$O, rt, 16 h. (iii) CD$_2$Cl$_2$, rt/ultrasonication, 5 min.

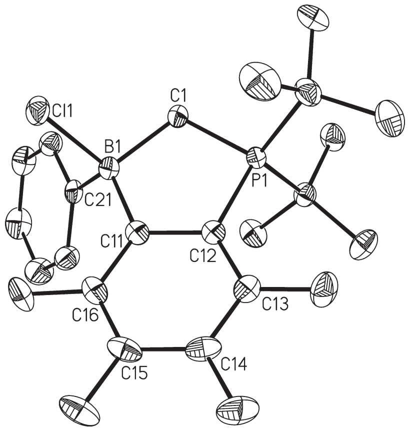


Figure 5. Molecular structure and numbering scheme of compound **[5]Cl**. H-atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): B(1)−Cl(1) = 1.944(2), B(1)−C(1) = 1.659(2), B(1)−C(11) = 1.620(2), B(1)−C(21) = 1.608(2), P(1)−C(1) = 1.788(1), P(1)−C(12) = 1.805(1); B(1)−C(1)−P(1) = 107.9(1), C(1)−B(1)−C(11) = 105.5(1), C(1)−P(1)−C(12) = 98.3(1); C(1)−B(1)−C(11)−C(12) = −3.9(2), C(1)−P(1)−C(12)−C(11) = 6.5(1).

Synthesis of a Less Lewis Acidic Analogue of $[\mathbf{1}]^+$. In order to modulate the Lewis acidity of $[\mathbf{1}]^+$-type phosphonium boranes, it is mandatory to exchange the C$_6$F$_5$ group for less electron-withdrawing substituents. For this reason, we prepared the C$_6$H$_5$ (Ph) derivative **[5]OEt** (Scheme 4). The required starting material, (C$_6$F$_5$)(Ph)B(OEt), is readily accessible from (Ph)(Cl)B(OEt) (see the SI) and C$_6$F$_5$MgBr in Et$_2$O. The reaction of (C$_6$F$_5$)(Ph)B(OEt) with ^{t}Bu$_2$P(CH$_2$Li) leads to **[5]OEt**, which can subsequently be transformed into **[5]Cl** using HCl in Et$_2$O.

The molecular structure of **[5]Cl** in the solid state was confirmed by X-ray crystallography (Figure 5). All key structural parameters are virtually the same as in **[1]Cl** with the exceptions

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(29) Sundararaman, A.; Jäkle, F. *J. Organomet. Chem.* **2003**, *681*, 134–142.

(30) $[\mathbf{1}]^+[\mathbf{Al(O}^t\mathbf{Bu}^\mathbf{F})_4]^-$ can be viewed as a phosphorus ylide adduct of a borenium ion. For reviews on related compounds, see: (a) Kölle, P.; Nöth, H. *Chem. Rev.* **1985**, *85*, 399–418. (b) Piers, W. E.; Bourke, S. C.; Conroy, K. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 5016–5036.

of the B(1)−Cl(1) bond, which is shorter by 0.015(2) Å, and the B(1)−C(21) bond, which is longer by 0.024(2) Å in the C_6F_5 derivative.

Similar to **[1]Cl**, **[5]Cl** can cleanly be converted into $\mathbf{[5]^+[Al(O^tBu^F)_4]^-}$ using $Ag[Al(O^tBu^F)_4]$ in CD_2Cl_2 (Scheme 4; see the SI for the NMR data of $\mathbf{[5]^+[Al(O^tBu^F)_4]^-}$).

Conclusion

Decoration of an aryl borane with (i) fluorine substituents and (ii) peripheral cationic groups enhances its Lewis acidity, which can be exploited for anion sensing and Lewis acid catalysis. In this paper, we report on the facile synthesis of the cyclic phosphonium chloroborate $(C_6F_5)(Cl)B(CH_2)(C_6F_4)P^tBu_2$ (**[1]Cl**) and its transformation into the derivatives **[1]OTf** and $\mathbf{[1]^+[Al(O^tBu^F)_4]^-}$, both of them representing convenient storage forms of the free fluorinated phosphonium borane $\mathbf{[1]}^+$.

$\mathbf{[1]}^+$ is able to abstract a fluoride ion from $[PF_6]^-$ and forms a covalent bond to the triflate ion, which testifies to an extraordinarily high Lewis acidity. Thus, from our experiences with the various counterions employed in this work, we come to the conclusion that only the most weakly coordinating specimen allows the successful preparation of the free Lewis acid $\mathbf{[1]}^+$.

We have shown that the phenyl analogue of $\mathbf{[1]}^+$, i.e., $[(C_6H_5)B(CH_2)(C_6F_4)P^tBu_2]^+$ ($\mathbf{[5]}^+$), can also be synthesized. This provides an important set-screw for a fine-tuning of the Lewis acidity of this class of compounds. Moreover, the tetrafluorophenylene bridge of $\mathbf{[1]}^+$ undergoes nucleophilic substitution in *para*-position to the phosphorus atom when treated with hydride or alkyl sources, which offers another way of derivatizing the basic phosphonium borane framework. Finally, the use of mixed-substituted phosphinomethanides $^tBu(R)P(CH_2Li)$ instead of $^tBu_2P(CH_2Li)$ in combination with $(C_6F_5)_2B(OEt)$ should give rise to chiral $\mathbf{[1]}^+$-type Lewis acids.

Experimental Section

General Remarks. All reactions were carried out under an N_2 atmosphere using Schlenk tube techniques and carefully dried solvents. NMR: Bruker AM 250, Avance 300, and Avance 400. Chemical shifts are referenced to residual solvent signals (^1H, $^{13}C\{^1H\}$) or external $BF_3\cdot Et_2O$ ($^{11}B\{^1H\}$), $CFCl_3$ ($^{19}F\{^1H\}$), and 85% H_3PO_4 ($^{31}P\{^1H\}$). Abbreviations: s = singlet, d = doublet, tr = triplet, q = quartet, vtr = virtual triplet, m = multiplet, br = broad, n.r. = multiplet expected in the ^1H NMR spectrum but not resolved, n.o. = signal not observed. The compounds $(C_6F_5)_2B(OEt)$[21], $^tBu_2P(CH_2Li)$,[22] and $Ag[Al(O^tBu^F)_4]\cdot CH_2Cl_2$[27,28] were synthesized according to literature procedures. Compound (Ph)(Cl)B(OEt) is also known in the literature;[31,32] an optimized synthesis and full NMR characterization are described in the SI.

Synthesis of [1]OEt. $^tBu_2P(CH_2Li)$ (0.47 g, 2.83 mmol) was suspended in toluene (25 mL) and the resulting slurry cooled to −78 °C. A solution of $(C_6F_5)_2B(OEt)$ (1.10 g, 2.83 mmol) in toluene (10 mL) was added dropwise with stirring. The reaction mixture was gradually warmed to rt and stirred for 12 h. After addition of deionized H_2O, the resulting two phases were separated and the aqueous layer was extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and filtered, and the solvent was removed from the filtrate in vacuo. The slightly yellow crude product was dissolved in a refluxing mixture of Et_2O (15 mL) and EtOH (1 mL). X-ray quality crystals of **[1]OEt** grew slowly upon storage of the solution at 5 °C for 14 days. Yield: 0.80 g (1.52 mmol, 54%).

Table 1. Selected Crystallographic Data for [1]OEt and [4]H

	[1]OEt	[4]H
formula	$C_{23}H_{25}BF_9OP$	$C_{21}H_{22}BF_8P$
fw	530.21	468.17
color, shape	colorless, plate	colorless, plate
temp (K)	173(2)	173(2)
radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/n$
a (Å)	10.2630(6)	8.4845(13)
b (Å)	20.5092(9)	15.6453(15)
c (Å)	45.270(2)	16.591(2)
α (deg)	90	90
β (deg)	90	101.627(12)
γ (deg)	90	90
V (Å^3)	9528.7(8)	2157.2(5)
Z	16	4
D_{calcd} (g cm^{-3})	1.478	1.442
$F(000)$	4352	960
μ (mm^{-1})	0.200	0.201
cryst size (mm^3)	0.34 × 0.27 × 0.11	0.24 × 0.19 × 0.08
no. of rflns collected	35 845	9021
no. of indep rflns (R_{int})	8398 (0.0648)	4000 (0.0628)
data/restraints/params	8398/0/632	4000/0/280
GOOF on F^2	0.952	0.862
R_1, wR_2 ($I > 2\sigma(I)$)	0.0529, 0.1266	0.0508, 0.1033
R_1, wR_2 (all data)	0.0866, 0.1398	0.1018, 0.1176
largest diff peak and hole (e Å^{-3})	0.817, −0.354	0.503, −0.310

^1H NMR (300.0 MHz, C_6D_6): δ 0.60 (d, 9H, $^3J_{PH}$ = 15.2 Hz; $C(CH_3)_3$), 0.81 (n.r., 1H; BCH_2P), 0.83 (d, 9H, $^3J_{PH}$ = 15.6 Hz; $C(CH_3)_3$), 1.29 (n.r., 1H; BCH_2P), 1.37 (tr, 3H, $^3J_{HH}$ = 6.9 Hz; OCH_2CH_3), 3.42 (m, 1H; OCH_2CH_3), 3.82 (m, 1H; OCH_2CH_3). $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ 1.9 ($h_{1/2}$ = 20 Hz). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ 12.5 (m; BCH_2P), 18.0 (OCH_2CH_3), 27.6 (m; $C(CH_3)_3$), 28.0 (m; $C(CH_3)_3$), 35.0 (m; $C(CH_3)_3$), 35.6 (m; $C(CH_3)_3$), 59.4 (m; OCH_2CH_3), n.o. (CF). $^{19}F\{^1H\}$ NMR (282.3 MHz, C_6D_6): δ −164.6 (m, 2F; C_6F_5), −160.2 (tr, 1F, $^3J_{FF}$ = 21 Hz; C_6F_5), −155.6 (m, 1F), −146.4 (m, 1F), −134.8 (m, 2F; C_6F_5), −125.2 (m, 1F), −123.9 (m, 1F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 84.8 (m). MS (ESI$^+$): *m*/*z* (%) 485.2 (100) [M − OEt]$^+$. Anal. Calcd for $C_{23}H_{25}BF_9OP$ [530.21]: C, 52.10; H, 4.75. Found: C, 52.34; H, 4.66.

Synthesis of [1]Cl. A solution (0.91 M) of HCl in Et_2O (4.9 mL, 4.46 mmol) was added at rt via syringe to a stirred solution of **[1]OEt** (0.59 g, 1.12 mmol) in Et_2O (30 mL). Stirring was continued for 48 h, whereupon **[1]Cl** gradually precipitated. All volatiles were driven off from the reaction mixture under reduced pressure to give **[1]Cl** as a colorless solid in analytically pure form. Yield: 0.56 g (1.08 mmol, 97%). Single crystals suitable for X-ray crystallography were grown by slow evaporation of a CH_2Cl_2 solution of **[1]Cl** at rt.

^1H NMR (300.0 MHz, C_6D_6): δ 0.43 (d, 9H, $^3J_{PH}$ = 15.6 Hz; $C(CH_3)_3$), 0.70 (d, 9H, $^3J_{PH}$ = 15.9 Hz; $C(CH_3)_3$), 1.30 (dd, 1H, $^2J_{HH}$ = 16.4 Hz, $^2J_{PH}$ = 8.8 Hz; BCH_2P), 1.86 (dd, 1H, $^2J_{HH}$ = 16.4 Hz, $^2J_{PH}$ = 11.9 Hz; BCH_2P). $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ −2.1 ($h_{1/2}$ = 135 Hz). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$): δ 14.8 (m; BCH_2P), 26.8 (m; $C(CH_3)_3$), 27.8 (m; $C(CH_3)_3$), 35.1 (m; $C(CH_3)_3$), 35.6 (m; $C(CH_3)_3$), n.o. (CF). $^{19}F\{^1H\}$ NMR (282.3 MHz, C_6D_6): δ −164.4 (m, 2F; C_6F_5), −158.8 (tr, 1F, $^3J_{FF}$ = 21 Hz; C_6F_5), −154.4 (m, 1F), −145.3 (m, 1F), −132.0 (m, 2F; C_6F_5), −125.6 (m, 1F), −123.7 (m, 1F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 88.3 (m). MS (ESI$^+$): *m*/*z* (%) 485.2 (100) [M − Cl]$^+$. Anal. Calcd for $C_{21}H_{20}BClF_9P$ [520.60]: C, 48.45; H, 3.87. Found: C, 48.51; H, 3.67.

Synthesis of [3]H. A solution (1.9 M) of ^tBuLi in pentane (0.21 mL, 0.40 mmol) was added with stirring at 5 °C to a solution

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(31) Dandegaonker, S. H.; Gerrard, W.; Lappert, M. F. *J. Chem. Soc.* **1957**, 2872–2877.

(32) Dandegaonker, S. H.; Gerrard, W.; Lappert, M. F. *J. Chem. Soc.* **1957**, 2893–2897.

of **[1]Cl** (0.095 g, 0.18 mmol) in benzene (11 mL). The mixture was allowed to warm to rt, and stirring was continued for 3 h. An aqueous solution of NaOH (10%, 1 mL) was added in one portion, and the resulting mixture was filtered through Na_2SO_4. The solid was washed with benzene (1 × 5 mL, 3 × 3 mL), and the combined organic phases were evaporated to dryness in vacuo. The crude product thus obtained formed a pale yellow microcrystalline solid.

^{1}H NMR (300.0 MHz, C_6D_6): δ 0.74 (d, 9H, $^3J_{PH}$ = 15.2 Hz; $PC(CH_3)_3$), 0.81 (d, 9H, $^3J_{PH}$ = 15.2 Hz; $PC(CH_3)_3$), 0.80−0.89 (m, 1H; BCH_2P), 1.13−1.19 (m, 1H; BCH_2P), 1.39 (dd, 9H; $C(CH_3)_3$), 3.77 (br q, 1H, $^1J_{BH}$ = 95 Hz; BH). $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ −17.0 ($h_{1/2}$ = 50 Hz). ^{11}B NMR (96.3 MHz, C_6D_6): δ −17.0 (d, $^1J_{BH}$ = 95 Hz). $^{19}F\{^1H\}$ NMR (282.3 MHz, C_6D_6): δ −165.3 (br, 2F; C_6F_5), −161.9 (tr, 1F, $^3J_{FF}$ = 21 Hz; C_6F_5), −135.4 (m, 1F), −133.1 (br, 2F; C_6F_5), −129.3 (m, 1F), −97.2 (m, 1F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 89.0 (m). MS (ESI$^+$): *m*/*z* (%) 523.7 (100) $[M - H]^+$.

Synthesis of [1]F. Neat $Tl[PF_6]$ (0.13 g, 0.38 mmol) was added in one portion at rt to a stirred solution of **[1]Cl** (0.10 g, 0.19 mmol) in benzene (20 mL). The resulting suspension was agitated in an ultrasonic bath for 48 h, after which time all starting material had been consumed (NMR spectroscopic control). After filtration, the insoluble material was washed with benzene (3 × 3 mL), and the organic phases were combined and freeze-dried in vacuo. The obtained colorless product was further purified by column chromatography (silica gel, hexane−EtOAc, 4.5:1) to obtain **[1]F** as a colorless solid. Yield: 0.044 g (0.087 mmol, 45%). Single crystals suitable for X-ray crystallography were grown by slow evaporation of an Et_2O solution of **[1]F** at rt.

^{1}H NMR (300.0 MHz, C_6D_6): δ 0.64 (d, 9H, $^3J_{PH}$ = 15.5 Hz; $C(CH_3)_3$), 0.75 (d, 9H, $^3J_{PH}$ = 15.7 Hz; $C(CH_3)_3$), 0.85−0.98 (m, 1H; BCH_2P), 1.17−1.35 (m, 1H; BCH_2P). $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ 4.7 (d, $^1J_{BF}$ = 72 Hz). $^{19}F\{^1H\}$ NMR (282.3 MHz, C_6D_6): δ −176.8 (m, 1F; BF), −164.6 (m, 2F; C_6F_5), −159.8 (tr, 1F, $^3J_{FF}$ = 21 Hz; C_6F_5), −154.5 (m, 1F), −145.4 (m, 1F), −134.4 (m, 2F; C_6F_5), −128.8 (m, 1F), −124.5 (m, 1F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 86.8 (m). MS (ESI$^+$): *m*/*z* (%) 485.2 (100) $[M - F]^+$. Anal. Calcd for $C_{21}H_{20}BF_{10}P$ [504.15]: C, 50.03; H, 4.00. Found: C, 49.92; H, 3.91.

Synthesis of [1]OAc. A mixture of **[1]Cl** (0.10 g, 0.19 mmol) and AgOAc (0.045 g, 0.27 mmol) was suspended in benzene (15 mL) at rt. Under exclusion of light, the slurry was agitated in an ultrasonic bath for 36 h, after which time all starting material had been consumed (NMR spectroscopic control). After filtration, the insoluble material was washed with benzene (5 mL), and the organic phases were combined and freeze-dried in vacuo. **[1]OAc** was obtained as a colorless flaked solid. Yield: 0.093 g (0.17 mmol, 89%). Single crystals suitable for X-ray crystallography were grown by slow evaporation of an Et_2O solution of **[1]OAc** at rt.

^{1}H NMR (300.0 MHz, C_6D_6): δ 0.20 (d, 9H, $^3J_{PH}$ = 15.3 Hz; $C(CH_3)_3$), 0.66 (d, 9H, $^3J_{PH}$ = 15.8 Hz; $C(CH_3)_3$), 0.92 (dd, 1H, $^2J_{HH}$ = 15.5 Hz, $^2J_{PH}$ = 6.9 Hz; BCH_2P), 1.76 (s, 3H; $(CO)CH_3$), 1.95 (vtr, 1H, $^2J_{HH}$ = $^2J_{PH}$ = 15.5 Hz; BCH_2P). $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ 0.5 ($h_{1/2}$ = 75 Hz). $^{19}F\{^1H\}$ NMR (282.3 MHz, C_6D_6): δ −164.5 (m, 2F; C_6F_5), −159.3 (tr, 1F, $^3J_{FF}$ = 21 Hz; C_6F_5), −155.0 (m, 1F), −146.7 (m, 1F), −133.6 (m, 2F; C_6F_5), −129.7 (m, 1F), −126.1 (m, 1F). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 84.1 (m). MS (ESI$^+$): *m*/*z* (%) 485.2 (70) $[M - OAc]^+$. Anal. Calcd for $C_{23}H_{23}BF_9O_2P$ [544.19]: C, 50.76; H, 4.26. Found: C, 50.84; H, 4.24.

Synthesis of [1]OTf. **[1]OEt** (0.21 g, 0.40 mmol) was placed in a Schlenk vessel and cooled to −196 °C. Et_2O (10 mL), dried over potassium, was vacuum-transferred into the reaction flask. The vessel was purged with N_2 and then allowed to warm to rt. Neat Me_3SiOTf (0.077 mL, 0.094 g, 0.42 mmol) was added, and the resulting clear solution was stirred at rt for 16 h, whereupon a colorless crystalline precipitate formed. All volatiles were driven off under reduced pressure to obtain **[1]OTf** in pure form. Yield: 0.25 g (0.39 mmol, 98%). For the synthesis of **[1]OTf** from **[1]Cl** and AgOTf, see the SI.

Table 2. Selected Crystallographic Data for [1]OTf and [5]Cl

	[1]OTf	**[5]Cl**
formula	$C_{22}H_{20}BF_{12}O_3PS$	$C_{21}H_{25}BClF_4P$
fw	634.22	430.64
color, shape	colorless, block	colorless, block
temp (K)	173(2)	173(2)
radiation	Mo Kα, 0.71073 Å	Mo Kα, 0.71073 Å
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	*Pbca*
a (Å)	10.8970(7)	12.3167(5)
b (Å)	14.7165(7)	17.5802(6)
c (Å)	16.2526(10)	19.4216(7)
α (deg)	90	90
β (deg)	92.259(5)	90
γ (deg)	90	90
V (Å^3)	2604.3(3)	4205.4(3)
Z	4	8
D_{calcd} (g cm^{-3})	1.618	1.360
F(000)	1280	1792
μ (mm^{-1})	0.296	0.296
cryst size (mm^3)	0.22 × 0.21 × 0.17	0.32 × 0.25 × 0.13
no. of rflns collected	28 528	55 248
no. of indep rflns (R_{int})	4883 (0.0855)	4302 (0.0818)
data/restraints/params	4883/0/362	4302/0/253
GOOF on F^2	0.948	1.055
R_1, wR_2 ($I > 2\sigma(I)$)	0.0401, 0.0821	0.0332, 0.0797
R_1, wR_2 (all data)	0.0695, 0.0903	0.0445, 0.0841
largest diff peak and hole (e Å^{-3})	0.569, −0.305	0.293, −0.328

^{1}H NMR (300.0 MHz, C_6D_6): δ 0.34 (d, 9H, $^3J_{PH}$ = 15.8 Hz; $C(CH_3)_3$), 0.81 (d, 9H, $^3J_{PH}$ = 16.3 Hz; $C(CH_3)_3$), 1.23 (dd, 1H, $^2J_{HH}$ = 16.3 Hz, $^2J_{PH}$ = 7.0 Hz; BCH_2P), 2.27 (vtr, 1H, $^2J_{HH}$ = $^2J_{PH}$ = 16.3 Hz; BCH_2P). $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ 4.4 ($h_{1/2}$ = 300 Hz). $^{19}F\{^1H\}$ NMR (282.3 MHz, C_6D_6): δ −163.3 (m, 2F; C_6F_5), −156.0 (tr, 1F, $^3J_{FF}$ = 21 Hz; C_6F_5), −150.8 (m, 1F), −144.2 (m, 1F), −133.7 (m, 2F; C_6F_5), −125.2 (m, 1F), −124.8 (m, 1F), −78.2 (s, 3F; OSO_2CF_3). $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 84.3 (m).

Synthesis of $[1]^+[Al(O^tBu^F)_4]^-$. CH_2Cl_2 (6 mL) was added at rt to a solid mixture of **[1]Cl** (0.050 g, 0.096 mmol) and $Ag[Al(O^tBu^F)_4]\cdot CH_2Cl_2$ (0.111 g, 0.096 mmol). The resulting suspension was stirred for 1 h. All insolubles were collected on a frit and washed with CH_2Cl_2 (2 × 1 mL). The combined organic phases were evaporated to dryness in vacuo to obtain $[1]^+[Al(O^tBu^F)_4]^-$ as a colorless solid. Yield: 0.14 g (0.096 mmol, 100%).

^{1}H NMR (300.0 MHz, CD_2Cl_2): δ 1.43 (d, 18H, $^3J_{PH}$ = 17.7 Hz; $C(CH_3)_3$), 2.56 (d, 2H, $^2J_{PH}$ = 8.3 Hz; BCH_2P). $^{11}B\{^1H\}$ NMR (96.3 MHz, CD_2Cl_2): δ 64.7 ($h_{1/2}$ = 950 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 18.3 (very br; BCH_2P), 27.2 (m; $C(\mathit{C}H_3)_3$), 36.5 (d, $^1J_{PC}$ = 29 Hz; $\mathit{C}(CH_3)_3$), n.o. (CF). $^{19}F\{^1H\}$ NMR (282.3 MHz, CD_2Cl_2): δ −159.3 (m, 2F; C_6F_5), −141.1 (tr, 1F; C_6F_5), −138.4 (m, 1F), −133.7 (m, 1F), −126.6 (m, 2F; C_6F_5), −117.7 (m, 1F), −114.7 (m, 1F), −75.8 (s, 36F; $Al(O^tBu^F)_4$). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 82.5 (m).

Synthesis of [4]OEt. A solution (1.0 M) of $Li[AlH_4]$ in Et_2O (0.19 mL, 0.19 mmol) was added via syringe at rt to a stirred solution of **[1]OEt** (0.20 g, 0.38 mmol) in Et_2O (15 mL). The reaction mixture was stirred for 72 h, during which time the initially clear colorless solution turned slightly turbid. Deionized H_2O was added dropwise under an inert atmosphere until the hydrogen evolution ceased. A voluminous colorless microcrystalline solid precipitated, which was transformed into a more coarse-grained material by the addition of a saturated aqueous solution of Na_2SO_4 (2 mL). The reaction mixture was filtered through Na_2SO_4. The solid was washed with a toluene−Et_2O mixture (1:1, 3 × 5 mL), and the combined organic phases were evaporated to dryness in vacuo to obtain analytically pure **[4]OEt**. Yield: 0.17 g (0.33 mmol, 87%). Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a CH_2Cl_2 solution of **[4]OEt** at rt.

^{1}H NMR (300.0 MHz, C_6D_6): δ 0.63 (d, 9H, $^{3}J_{PH} = 15.1$ Hz; $C(CH_3)_3$), 0.87 (d, 10H, $^{3}J_{PH} = 15.5$ Hz; $C(CH_3)_3$, BCH_2P), 1.30−1.39 (m, 1H; BCH_2P), 1.40 (tr, 3H, $^{3}J_{HH} = 6.9$ Hz; OCH_2CH_3), 3.46 −3.57 (m, 1H; OCH_2CH_3), 3.84 −3.93 (m, 1H; OCH_2CH_3), 6.57 (m, 1H; Ar−H). ^{11}B{^{1}H} NMR (96.3 MHz, C_6D_6): δ 1.6 ($h_{1/2}$ = 20 Hz). ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): δ 12.5 (m; BCH_2P), 18.0 (OCH_2CH_3), 27.6 (m; $C(CH_3)_3$), 28.1 (m; $C(CH_3)_3$), 34.9 (m; $C(CH_3)_3$), 35.5 (m; $C(CH_3)_3$), 59.2 (m; OCH_2CH_3), 109.8 (m; Ar−C), n.o. (CF). ^{19}F{^{1}H} NMR (282.3 MHz, C_6D_6): δ −164.9 (m, 2F; C_6F_5), −160.7 (tr, 1F, $^{3}J_{FF} = 21$ Hz; C_6F_5), −136.2 (m, 1F), −134.6 (m, 2F; C_6F_5), −129.7 (m, 1F), −100.2 (m, 1F). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 84.1 (m). MS (ESI^{+}): *m*/*z* (%) 467.4 (100) $[M - OEt]^{+}$. Anal. Calcd for $C_{23}H_{26}BF_8OP$ [512.22]: C, 53.93; H, 5.12. Found: C, 53.79; H, 4.98.

Synthesis of [4]H. [1]Cl (0.15 g, 0.29 mmol) was dissolved in a mixture of Et_2O (10 mL) and THF (6 mL). A solution (1.0 M) of $Li[AlH_4]$ in Et_2O (0.36 mL, 0.36 mmol) was added quickly via syringe. The resulting mixture was stirred at rt and continuously monitored by NMR spectroscopy. After 14 days the reaction was complete. An alkaline (NaOH) saturated aqueous Na_2SO_4 solution was purged with argon and then added dropwise under an inert atmosphere to the reaction vessel until hydrogen evolution ceased. The resulting suspension was filtered through Na_2SO_4. The solid was washed with a toluene−Et_2O mixture (1:1, 3 × 5 mL), and the combined organic phases were evaporated to dryness in vacuo to obtain **[4]H** as a colorless solid. Yield: 0.072 g (0.15 mmol, 53%). The X-ray crystal structure analysis was carried out with crystalline material obtained by slow evaporation of an Et_2O solution of **[4]H** at rt under an N_2 atmosphere.

^{1}H NMR (300.0 MHz, C_6D_6): δ 0.70 (d, 9H, $^{3}J_{PH} = 15.1$ Hz; $C(CH_3)_3$), 0.77 (d, 9H, $^{3}J_{PH} = 15.2$ Hz; $C(CH_3)_3$), 1.08−1.18 (m, 1H; BCH_2P), 1.25−1.40 (m, 1H; BCH_2P), 3.70 (br q, 1H, $^{1}J_{BH} =$ 95 Hz; BH), 6.46 (m, 1H; Ar−H). ^{11}B{^{1}H} NMR (96.3 MHz, C_6D_6): δ −17.4 ($h_{1/2}$ = 50 Hz). ^{11}B NMR (96.3 MHz, C_6D_6): δ −17.4 (d, $^{1}J_{BH} = 95$ Hz). ^{19}F{^{1}H} NMR (282.3 MHz, C_6D_6): δ −165.2 (br, 2F; C_6F_5), −161.5 (tr, 1F, $^{3}J_{FF} = 21$ Hz; C_6F_5), −138.2 (m, 1F), −133.0 (br, 2F; C_6F_5), −131.3 (m, 1F), −103.5 (m, 1F). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 89.7 (m). MS (ESI^{+}): *m*/*z* (%) 467.4 (100) $[M - H]^{+}$. Anal. Calcd for $C_{21}H_{22}BF_8P$ [468.17]: C, 53.87; H, 4.74. Found: C, 53.98; H, 4.86.

Synthesis of (C_6F_5)(Ph)B(OEt). (Ph)(Cl)B(OEt) (1.51 g, 9.0 mmol) was dissolved in Et_2O (20 mL), and the solution was cooled to 0 °C. Freshly prepared C_6F_5MgBr (9.08 mmol) in Et_2O (20 mL) was added dropwise with stirring over a period of 30 min, whereupon a colorless solid precipitated from the light brown solution. The reaction mixture was allowed to warm to rt and stirred for 12 h. The solvent was removed in vacuo, and the residue was extracted with benzene (1 × 20 mL, 2 × 10 mL). The extracts were combined, and the solvent was removed by distillation at ambient pressure. (C_6F_5)(Ph)B(OEt) was obtained by subsequent distillation of the oily residue at lower pressure (0.1 Torr, 79−81 °C) as a slightly viscous colorless liquid. Yield: 1.89 g (6.30 mmol, 70%).

^{1}H NMR (300.0 MHz, C_6D_6): δ 0.99 (tr, 3H, $^{3}J_{HH} = 7.1$ Hz; OCH_2CH_3), 3.68 (q, 2H, $^{3}J_{HH} = 7.1$ Hz; OCH_2CH_3), 7.12−7.25 (m, 3H; Ph-H), 7.69−7.72 (m, 2H; Ph-H). ^{11}B{^{1}H} NMR (96.3 MHz, C_6D_6): δ 43.1 ($h_{1/2}$ = 140 Hz). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ 17.0 (OCH_2CH_3), 65.2 (OCH_2CH_3), 128.3 (Ph−C), 133.0 (Ph−C), 135.6 (Ph−C), n.o. (CF, BC). ^{19}F{^{1}H} NMR (282.3 MHz, C_6D_6): δ −160.6 (m, 2F; F_m), −151.9 (tr, 1F, $^{3}J_{FF} = 21$ Hz; F_p), −131.9 (m, 2F; F_o). Anal. Calcd for $C_{14}H_{10}BF_5O$ [300.03]: C, 56.04; H, 3.36. Found: C, 55.86; H, 3.13.

Synthesis of [5]OEt. $^{t}Bu_2P(CH_2Li)$ (0.10 g, 0.60 mmol) was suspended in toluene (10 mL), and the slurry was cooled to −78 °C. A solution of (C_6F_5)(Ph)B(OEt) (0.18 g, 0.60 mmol) in toluene (5 mL) was added dropwise with stirring over 10 min. The reaction mixture was allowed to warm to rt, stirred for 48 h, and evaporated to dryness in vacuo. The residue was extracted with hexane (1 × 10 mL, 1 × 5 mL). All volatiles were removed from the combined extracts under reduced pressure to obtain crude **[5]OEt** (0.14 g, 54%) as a yellow oil. Subsequent column chromatography (silica gel, hexane−EtOAc, 1:2) gave analytically pure **[5]OEt** as a colorless solid. Yield: 0.074 g (0.17 mmol, 28%). *Note*: **[5]OEt** partly decomposes on silica gel.

^{1}H NMR (300.0 MHz, C_6D_6): δ 0.59 (d, 9H, $^{3}J_{PH} = 15.0$ Hz; $C(CH_3)_3$), 0.78−0.83 (m, 1H; BCH_2P), 0.88 (d, 9H, $^{3}J_{PH} = 15.3$ Hz; $C(CH_3)_3$), 1.18−1.26 (m, 1H; BCH_2P), 1.42 (tr, 3H, $^{3}J_{HH} =$ 6.9 Hz; OCH_2CH_3), 3.47−3.58 (m, 1H; OCH_2CH_3), 4.01−4.12 (m, 1H; OCH_2CH_3), 7.33 (m, 1H; Ph-H_p), 7.51 (vtr, 2H; Ph-H_m), 7.74 (d, 2H, $^{3}J_{HH} = 7.2$ Hz; Ph-H_o). ^{11}B{^{1}H} NMR (96.3 MHz, C_6D_6): δ 5.0 ($h_{1/2}$ = 50 Hz). ^{19}F{^{1}H} NMR (282.3 MHz, C_6D_6): δ −156.3 (m, 1F), −146.4 (m, 1F), −123.7 (m, 1F), −121.8 (m, 1F). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 85.7 (m). MS (ESI^{+}): *m*/*z* (%) 395.4 (100) $[M - OEt]^{+}$. Anal. Calcd for $C_{23}H_{30}BF_4OP$ [440.26]: C, 62.75; H, 6.87. Found: C, 62.61; H, 6.86.

Synthesis of [5]Cl. [5]OEt (0.090 g, 0.20 mmol) was dissolved in Et_2O (7 mL), and a solution (0.91 M) of HCl in Et_2O (0.90 mL, 0.82 mmol) was added via syringe at rt. The reaction mixture was stirred for 16 h, whereupon a colorless precipitate formed. All volatiles were driven off under reduced pressure to obtain analytically pure **[5]Cl** as a colorless solid. Yield: 0.084 g (0.19 mmol, 95%). Single crystals suitable for X-ray crystal structure analysis were grown by slow evaporation of a CH_2Cl_2 solution of **[5]Cl** at rt.

^{1}H NMR (300.0 MHz, C_6D_6): δ 0.52 (d, 9H, $^{3}J_{PH} = 15.4$ Hz; $C(CH_3)_3$), 0.82 (d, 9H, $^{3}J_{PH} = 15.7$ Hz; $C(CH_3)_3$), 1.22 (dd, 1H, $^{2}J_{HH} = 16.1$ Hz, $^{2}J_{PH} = 9.7$ Hz; BCH_2P), 1.64 (dd, 1H, $^{2}J_{HH} =$ 16.1 Hz, $^{2}J_{PH} = 10.5$ Hz; BCH_2P), 7.27 (m, 1H; Ph-H_p), 7.43 (vtr, 2H; Ph-H_m), 7.84 (d, 2H, $^{3}J_{HH} = 7.7$ Hz; Ph-H_o). ^{11}B{^{1}H} NMR (96.3 MHz, C_6D_6): δ 2.5 ($h_{1/2}$ = 180 Hz). ^{19}F{^{1}H} NMR (282.3 MHz, C_6D_6): δ −155.2 (m, 1F), −144.8 (m, 1F), −124.6 (m, 1F), −123.7 (m, 1F). ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 88.8 (m). MS (ESI^{+}): *m*/*z* (%) 395.4 (100) $[M - Cl]^{+}$. Anal. Calcd for $C_{21}H_{25}BClF_4P$ [430.64]: C, 58.57; H, 5.85. Found: C, 58.63; H, 5.82.

X-ray Crystal Structure Analysis of [1]OEt, [1]Cl, [1]F, [1]OAc, [1]OTf, [4]H, [4]OEt, (C_6F_5)$_2$B(OEt), and [5]Cl. Data were collected on a Siemens CCD three-circle diffractometer (**[1]Cl**) and on a STOE IPDS II two-circle diffractometer (all other structures) with graphite-monochromated Mo Kα radiation. Empirical absorption corrections were performed for all structures except (C_6F_5)$_2$B(OEt) using the MULABS[33] option in PLATON.[34] The structures were solved by direct methods using the program SHELXS[35] and refined against F^2 with full-matrix least-squares techniques using the program SHELXL-97.[36]

The compounds **[1]OEt** and **[4]OEt** crystallize with two crystallographically independent molecules in the asymmetric unit.

CCDC reference numbers: 787432 (**[1]OEt**), 787433 (**[1]Cl**), 787435 (**[1]F**), 787436 (**[1]OAc**), 787437 (**[1]OTf**), 787434 (**[4]H**), 787438 (**[4]OEt**), 787439 ((**C_6F_5)$_2$B(OEt)**), and 787440 (**[5]Cl**).

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Supporting Information Available: Synthesis of **[1]OTf** from **[1]Cl** and AgOTf; synthesis details and NMR spectroscopic characterization of (Ph)(Cl)B(OEt); plots of the NMR spectra of **[1]$^{+}$[Al(O^{t}Bu^{F})$_4$]$^{-}$** and NMR data of **[5]$^{+}$[Al(O^{t}Bu^{F})$_4$]$^{-}$**. Crystallographic data of **[1]OEt**, **[1]Cl**, **[1]F**, **[1]OAc**, **[1]OTf**, **[4]H**, **[4]OEt**, **(C_6F_5)$_2$B(OEt)**, and **[5]Cl** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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