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Article

Synthesis, Structure, and Stability of Adducts between Phosphide and Amide Anions and the Lewis Acids Borane, Tris(pentafluorophenyl)borane, and Tris(pentafluorophenyl)alane

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The phosphinoborane adduct $H_3P \cdot B(C_6F_5)_3$ can be deprotonated using $LiN(SiMe_3)_2$ to give the phosphidoborate salt $Li[H_2PB(C_6F_5)_3]$, which was converted to the phosphidodiborates $Li[H_2P\{B(C_6F_5)_3\}_2]$ and $Li[H_2P\{B(C_6F_5)_3\}\{BH_3\}]$ by treatment with an equivalent of $B(C_6F_5)_3$ or $Me_2S \cdot BH_3$, respectively. A series of anions of the form $[RR'P\{M(C_6F_5)_3\}\{BH_3\}]^-$, where R = R′ = Ph or R = ^{t}Bu, R′ = H, and M = B or Al, were prepared (through treatment of salts $Li[RR'P(BH_3)]$ with the corresponding Lewis acid) and characterized using multinuclear NMR, elemental analysis and X-ray crystallography. The solid state structures of $[Li(Et_2O)_x][Ph_2P\{M(C_6F_5)_3\}\{BH_3\}]$ exhibit η^2-bonding of the BH_3 group to the cationic lithium center. The attempted preparation of an analogous series with amide cores of the form $[R_2N\{B(C_6F_5)_3\}\{BH_3\}]^-$ proved unsuccessful; among the competing reaction pathways hydride abstraction occurred preferentially to yield $Li[HB(C_6F_5)_3]$ and dimers or higher oligomers with the composition $(R_2NBH_2)_n$.

Introduction

The complexation reaction between small dibasic anions and 2 equiv of perfluoroaryl-substituted group 13 Lewis acids has been demonstrated to be a highly effective method for the synthesis of large poorly coordinating anions.[1−6] For example, treatment of sodium amide with 2 equiv of tris(pentafluorophenyl)borane gives the sodium salt of the amidodiborate anion, $[H_2N\{B(C_6F_5)_3\}_2]^-$ (**I**).[4] This simple adduct formation reaction suggests that a family of anions of the general formula $[R_2E\{M(C_6F_5)_3\}_2]^-$ (where R is a hydrocarbon substituent, E = N or P and M = B or Al) should be readily accessible. On route to these anions the preparation of protic amine adducts of tris(pentafluorophenyl)-borane and -alane proved to be a relatively straightforward case of adduct formation, in which the compounds were further stabilized by intramolecular hydrogen-bonding.[7−9]

The first indication that tris(pentafluorophenyl)borane does not always form simple adducts came with the elegant investigation of its interaction with the tertiary amines dimethylaniline, diethylaniline, and triethylamine. Treatment of tris(pentafluorophenyl)borane with dimethylaniline yields a mixture of the adduct and the iminium salt $[PhCH_3N{=}CH_2][HB(C_6F_5)_3]$. In the case of diethylaniline no adduct was observed but as well as unreacted starting material the ionic $[Ph(Et)_2NH][HB(C_6F_5)_3]$ and zwitterionic $PhEtN^+{=}CH{-}CH_2B^-(C_6F_5)_3$ were identified.[10] The reaction between triethylamine and tris(pentafluorophenyl)borane proceeds similarly but to completion giving an equimolar mixture of $[Et_3NH][HB(C_6F_5)_3]$ and $Et_2N^+{=}CH{-}CH_2B^-(C_6F_5)_3$.[11]

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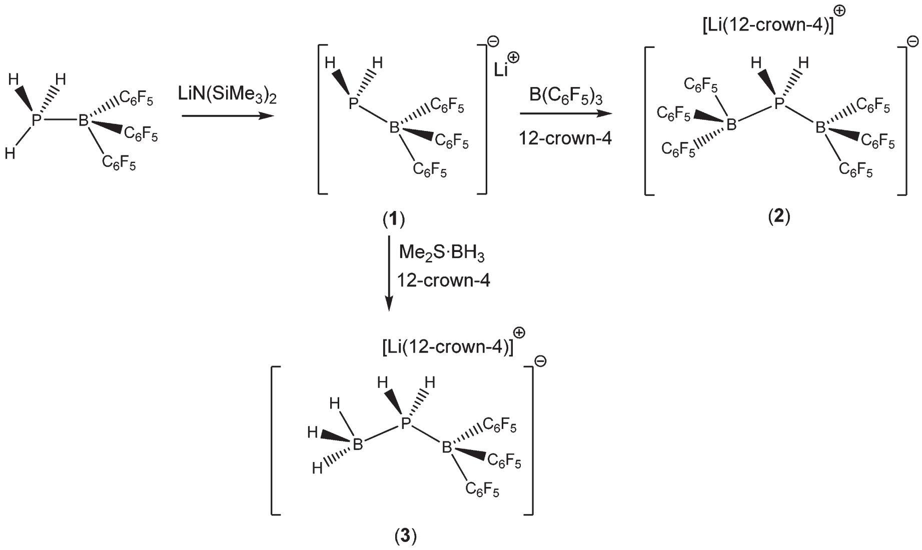
Scheme 1



There are somewhat fewer examples of isolated phosphine compared to amine adducts of tris(pentafluorophenyl)borane. The adduct $H_3P \cdot B(C_6F_5)_3$ was investigated by Bradley and co-workers and, in contrast to the ammonia adduct, found to be rather weakly bound, decomposing at approximately 50 °C under vacuum and when dissolved in basic solvents such as tetrahydrofuran (THF).[12,13] If a trialkyl phosphine of modest steric bulk is employed the complexes formed are unremarkable.[14] However, when sterically demanding phosphine ligands were employed by Stephan and co-workers this led to the landmark discovery of "frustrated Lewis pairs".[15] No adduct is formed if 1 equiv of $(^tBu)_3P$ or $(C_6H_2Me_3)_3P$ is combined with $B(C_6F_5)_3$. However, these mixtures react with dihydrogen to form the respective phosphonium hydridoborate salts.[16] The sterically hindered secondary phosphines $(^tBu)_2PH$ and $(C_6H_2Me_3)_2PH$ react, not by adduct formation, but through nucleophilic aromatic substitution at one of the *para*-carbons. The liberated fluoride anion coordinates to boron, and zwitterions of the form $[R_2P^+H(C_6F_4)B^-(C_6F_5)_2F]$ are generated.[17]

Attempts to prepare examples of anions $[R_2E\{M(C_6F_5)_3\}_2]^-$, either through direct complexation of the anionic core with 2 equiv of Lewis acid or by first deprotecting the protic adduct and treating it with a second equivalent of Lewis acid, employing anything other than R = H, lead only to complex product mixtures.[18] The presence of one or both of the $[B(C_6F_5)_4]^-$ and $[B(C_6F_5)_3H]^-$ anions suggests that in these systems abstraction reactions are successfully competing with adduct formation, but a detailed understanding of the competing reaction pathways remains elusive.

In contrast to the apparent instability of dialkylamido- and dialkylphosphido-di(tris(pentafluorophenyl))borate anions, the adducts between dialkyl amide anions and trihydridroborane are well-known. Lithium dimethylamidoborate, $LiMe_2NBH_3$, is available commercially as a reducing agent,[19] and the sodium salt of the dimethylamidodiborate anion, $NaMe_2N(BH_3)_2$ was first reported in 1971.[20,21] Primary and secondary phosphine adducts of BH_3 react with ^nBuLi to give the corresponding salts, in which there is competing Li−P and Li—H—B bonding.[22]

Herein the phosphidodiborate anion is reported and compared to the amidodiborate anion (**I**). The formation and stability of adducts between amido- and phosphido-trihydroborate anions and the Lewis acids tris(pentafluorophenyl)-borane and -alane are investigated and contrasted.

Results and Discussion

The reaction between $H_3N \cdot B(C_6F_5)_3$ and ^nBuLi in THF solution proceeds cleanly giving the salt $[Li(THF)_2][H_2NB(C_6F_5)_3]$ in essentially quantitative yield.[23] However, this deprotonation protocol is not viable for the more labile $H_3P \cdot B(C_6F_5)_3$, even when THF was replaced with light petroleum; spectroscopic characterization revealed a complex mixture of products, suggesting competition between substitution and deprotonation reactions. In contrast, the reaction of the poorly nucleophilic base $Li[N(SiMe_3)_2]$ with $H_3P \cdot B(C_6F_5)_3$ proceeds cleanly in light petroleum solution precipitating $Li[H_2PB(C_6F_5)_3]$ (**1**) as a colorless solid (Scheme 1). Spectroscopic characterization was achieved by dissolution in an equal volume mixture of 1,2-difluorobenzene and benzene-d_6. The ^1H NMR spectrum of **1** consisted of a doublet at δ 2.25 ppm (J_{PH} = 247 Hz) versus δ 3.89 ppm (J_{PH} = 410 Hz) for $H_3P \cdot B(C_6F_5)_3$. In this instance coupling to phosphorus was observed in the ^{11}B spectrum with a doublet at δ −18.0 ppm (J_{BP} = 46 Hz), which is at somewhat lower frequency than that of the amidoborate salt

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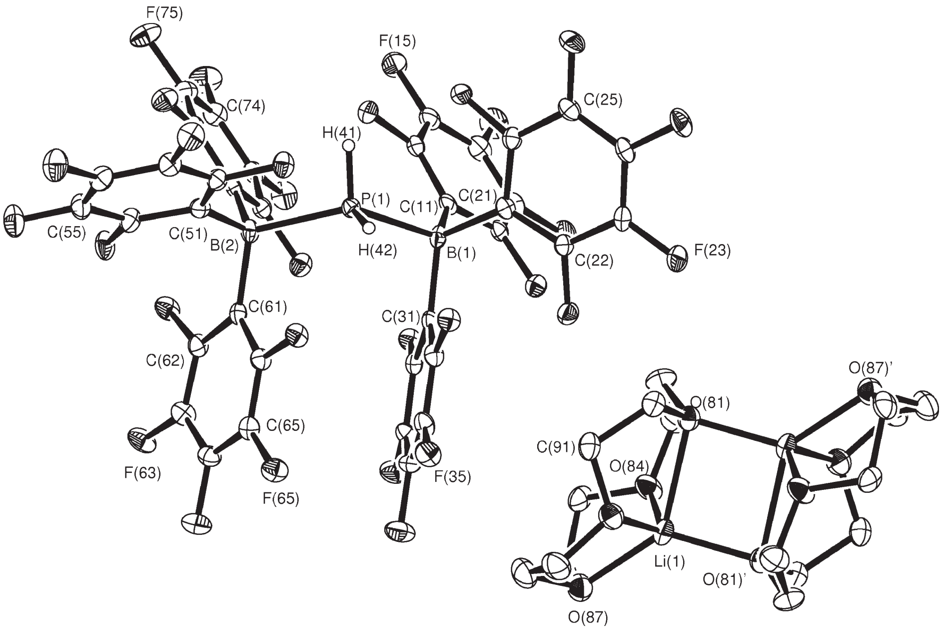

Figure 1. ORTEP of **2** with displacement ellipsoids drawn at the 30% probability level, hydrogen atoms on the 12-crown-4 ligand have been omitted for clarity. Selected bond lengths [Å] and angles [deg] P(1)—B(1) 2.056(6), P(1)—B(2) 2.058(6), P(1)—H(41) 1.22(4), P(1)—H(42) 1.28(4), B(1)—C(11) 1.640(7), B(1)—C(21) 1.664(7), B(1)—C(31) 1.647(7), B(2)—C(51) 1.661(7), B(2)—C(61) 1.637(7), B(2)—C(71) 1.647(7), Li(1)—O(81) 2.325(10), Li(1)—O(84) 1.975(9), Li(1)—O(87) 2.022(10), Li(1)—O(90) 2.011(9), Li(1)—O(81)′ 1.988(9). B(1)—P(1)—B(2) 129.8(2), P(1)—B(1)—C(11) 115.8(3), P(1)—B(1)—C(21) 107.7(3), P(1)—B(1)—C(31) 99.5(3), P(1)—B(2)—C(51) 111.0(3), P(1)—B(2)—C(61) 111.7(3), P(1)—B(2)—C(71) 102.8(3). ′ indicates symmetry operation $1 - x, 2 - y, 1 - z$.

$[Li(THF)_2][H_2NB(C_6F_5)_3]$, δ −9.1 ppm. The increased electron density at phosphorus on anion formation induces a low frequency shift of the ^{31}P resonance from that in $H_3P\cdot B(C_6F_5)_3$ (δ −99.6 ppm) to −155 ppm. Further evidence for anion formation is provided by the small chemical shift difference of the *para*- and *meta*-fluorine resonances ($\Delta\delta$ = 4.0 ppm), which is characteristic of anionic tris(pentafluorophenyl)boron species.[24,25] Compound **1** and derivatives in which the lithium salt was treated with THF or 12-crown-4 could not be induced to crystallize.

Treatment of **1** with a second equivalent of $B(C_6F_5)_3$ in THF solution gave a foam on removal of the solvents. A pure sample was successfully isolated only after the addition of 12-crown-4 and cooling a concentrated THF solution to −25 °C giving colorless crystals of $[Li(12\text{-crown-}4)][H_2P\{B(C_6F_5)_3\}_2]$ (**2**). The composition of **2** was confirmed by elemental analysis and multinuclear NMR. The PH_2 doublet in the ^1H NMR spectrum of **2** was found at δ 5.08 ppm (J_{PH} = 354 Hz), significantly higher frequency than that of **1** reflecting the decrease in electron density when coordinating the second borane. Accordingly, the ^{31}P chemical shift of **2** at δ −97 ppm is closer to that of the neutral adduct $H_3P\cdot B(C_6F_5)_3$ than the monoborate **1**. Here the ^{11}B NMR consisted of a broad peak at −12 ppm and the phosphorus−boron coupling was not resolved.

The solid-state structure of **2** was elucidated by X-ray crystallography (Figure 1). The lithium counterion is a centrosymmetric dimer $[Li_2(12\text{-crown-}4)_2]$ in which each lithium binds to the four oxygen atoms of a molecule of 12-crown-4 and has a fifth close Li···O contact to the second, symmetry-related, Li(12-crown-4) fragment. In the anion, the boron and phosphorus atoms have distorted tetrahedral coordination environments. The two boron atoms are essentially equidistant from the phosphorus atom at approximately 2.06 Å. The obtuse B—P—B angle of 129.8° minimizes the steric interactions between pentafluorophenyl groups, but is nevertheless smaller than the B—N—B angle of 134.3(2)° found in **I**, where the shorter B−N bonds would lead to greater steric interactions between the two $B(C_6F_5)_3$ groups. There is only one intramolecular H···F interaction with a separation less than 2.40 Å in the structure of **2** {(P(1)—H(42)···F(36) 2.39 Å, 120.56°}, which can be regarded as a weak hydrogen bond. There are three other intramolecular H···F contacts within the van der Waals radii; however, they are all somewhat long (2.43, 2.44, and 2.50 Å) with rather acute angles (98, 111, and 100°, respectively) and thus do not meet our interpretation of the Dunitz criteria for designation as a hydrogen bond.[7,26] This contrasts with the structure of **I**, which has a number of short N−H···F−C contacts.[4]

Treatment of **1** with $Me_2S\cdot BH_3$ in diethyl ether solution followed by removal of the solvents under reduced pressure yielded a colorless oil; recrystallization from dichloromethane/light petroleum in the presence of 2 equiv of 12-crown-4 provided the salt $[Li(12\text{-crown-}4)_2][H_2P\{B(C_6F_5)_3\}\{BH_3\}]$ (**3**) as a colorless crystalline solid. The quality of the X-ray analysis was suitable only for establishing connectivity. The bulk composition was confirmed by multinuclear NMR and elemental analysis. In the ^1H NMR spectrum the PH_2 signal was observed as a doublet at δ 3.78 (J_{PH} = 334 Hz), at higher frequency than **1** but lower frequency than that observed for **2**, reflecting the stronger Lewis acidity of $B(C_6F_5)_3$ versus BH_3. The BH_3 signal in the ^1H NMR is broad and unresolved. The ^{31}P resonance was found as a broad peak at δ −92 ppm, similar to that observed

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Scheme 2

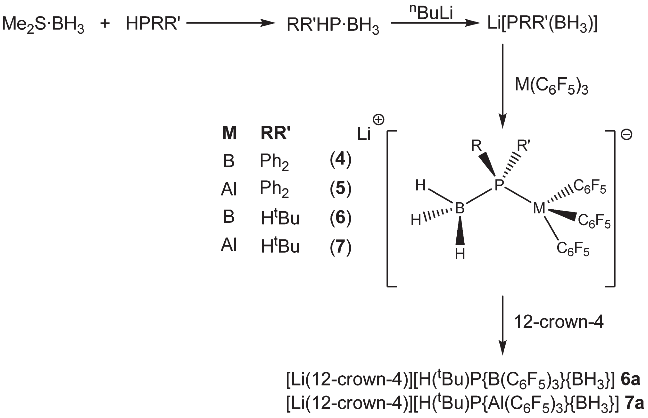

Table 1. ^{11}B, ^{19}F, and ^{31}P NMR data in Chloroform-d_1

	^{11}B	^{11}B	^{19}F	^{19}F	^{19}F	^{31}P
	BH_3	$B(C_6F_5)_3$	*o*-F	*p*-F	*m*-F	
1[a]		−18.0	−133.9	−161.5	−165.5	−154.6
2		−15.3	−129.7	−159.8	−165.8	−96.8
3	−41.3	−18.0	−130.2	−160.9	−165.7	−92.3
4	−32.3	−11.4	−126.2	−160.2	−166.5	0.3
5	−34.2		−120.0	−155.5	−163.3	−39.2
6	−40.5	−15.8	−128.2	−160.7	−165.6	−22.9
7	−40.8		−120.8	−155.6	−162.9	−54.9

[a] Run in benzene-d_6/1,2-difluorobenzene.

for **2**. The ^{11}B NMR spectrum revealed the expected pair of signals, with the $B(C_6F_5)_3$ boron at −18 ppm ($^1J_{BP} = 69$ Hz) and the ^{11}B BH_3 signal at δ −41 ppm, but the phosphorus−boron coupling was unresolved.

In contrast to the $[PH_2]^-$ chemistry, the reactions between either $LiPR_2$ and 1 or 2 equiv of $B(C_6F_5)_3$ or RR′(H)P·$B(C_6F_5)_3$ and ^nBuLi do not proceed cleanly, despite the stability of the analogous BH_3 adducts. The question therefore arose as to whether anions related to that in **3** utilizing 1 equiv of BH_3 and 1 equiv of $B(C_6F_5)_3$ would be accessible and stable. The reactions of Li[RR′P(BH_3)] with $M(C_6F_5)_3$ in diethyl ether resulted in the formation of $[Li(OEt_2)_n]$-[RR′P{$M(C_6F_5)_3$}{BH_3}] (where R = R′ = Ph, M = B (**4**), M = Al (**5**) and R = H, R′ = ^{t}Bu, M = B (**6**), M = Al (**7**)) (Scheme 2). The diphenylphosphide complexes were isolated as colorless solids, while the *tert*-butylphosphides were obtained as colorless oils.

All four compounds were soluble and stable in aromatic and chlorinated solvents facilitating spectroscopic characterization in chloroform-*d* (Table 1). The composition and number of diethyl ether molecules present were determined by integration of the signals in the ^1H NMR spectra and were in good agreement with the elemental analyses. Coincidentally the boron compounds **4** and **6** contained 3 equiv of diethyl ether, whereas the aluminum compounds **5** and **7** had 2 equiv. The BH_3 hydrogens in compounds **4**−**7** give very broad signals at δ 0.53 (**4**), 0.55 (**5**), −0.04 (**6**), and 0.06 (**7**) ppm, respectively. These chemical shift values suggest that substitution of aluminum for boron in the $M(C_6F_5)_3$ group has a very small effect on the BH_3 electron density. This is in contrast to the considerable difference observed when varying the phosphide substituent. The ^{11}B (BH_3) resonances δ −32.3, −34.2, −40.5, and −40.8 ppm for **4**−**7**, respectively, follow a similar trend. The ^{31}P resonances proved to be sensitive to both the alkyl and the Lewis acid substituents, with highest frequency resonances belonging to the $B(C_6F_5)_3$ complexes, suggesting that this group is more effectively removing electron density from the phosphorus center than $Al(C_6F_5)_3$. The normal pattern of ^{19}F resonances of aluminum-bonded pentafluorophenyl groups being found at higher frequency than the boron analogues was also found for these complexes.

Crystals of compound **4** were obtained by concentrating and cooling a diethyl ether solution, and the solid state structure was elucidated by X-ray crystallography (Figure 2). In the anion the B—P—B linkage is bent and at 117.06(7)° is significantly closer to the tetrahedral ideal than the corresponding angle in **2** (129.8(2)°), which is possible because of the reduced size of the BH_3 group. At 1.951(2) Å the P−BH_3 bond length is comparable to those in the previously reported phosphidoborate complexes $[(PEt_3)_2Pt(H)\{P(Ph)(H)(BH_3)\}]$ and $[CpFe(CO)_2\{PPh_2(BH_3)\}]$ at 1.953(7) and 1.949(7) Å, respectively.[27,28] Reflecting the greater steric requirement of the fragment, at 2.121(2) Å the P−$B(C_6F_5)_3$ bond is somewhat longer than the P−BH_3 bond and slightly longer than those found in $H_2(Ph)P{\cdot}B(C_6F_5)_3$ (2.039 Å) and **2**.[29] Three molecules of diethyl ether are coordinated to the lithium cation, which is closely associated with the anion. There are two short B−H···Li contacts of 2.02 and 2.17 Å.[30] The B(1)···Li(1) distance of 2.477(3) Å is similar to the value of 2.43 Å found for $Li[(Ph)(H)P(BH_3)_2]$, in which the BH_3 group also acts an η^2-donor.[31] There are two short intramolecular contacts between aromatic hydrogens and organofluorines which are within the range for designation as hydrogen bonds: H(42)···F(12) 2.17 Å, C(42)—H(42)···F(12) 148° and H(52)···F(22) 2.26 Å, C(52)—H(52)···F(22) 147°. However, while these parameters are reminiscent of the dimensions found in primary and secondary amine adducts of $B(C_6F_5)_3$,[7] here they do not complete the six-membered rings favored by Etter's rules[32], and their strength and significance are not clear.

Crystals of compound **5**, $[Li(OEt_2)_2][Ph_2P\{Al(C_6F_5)_3\}\{BH_3\}]$, suitable for study by X-ray diffraction, were obtained following recrystallization from diethyl ether (Figure 3). There are two diethyl ether molecules coordinated to the lithium cation, which also associates with the anion through two B−H···Li interactions slightly shorter than those present in **4**, B(2)—H(2b)···Li(1) 1.95 Å (96.6°) and B(2)—H(2c)···Li(1) 1.96 Å (94.4°) with a B(2)···Li(1) distance of 2.346(4) Å.[33] At 112.19(8)° the central Al(1)—P(1)—B(2) angle is more acute than the central B(1)—P(1)—B(2) angles observed in **2** and **4** (Table 2) because of the relief in steric strain associated with the greater P—Al bond length. The $H_3B(2)$—P(1) bond length at 1.949(2) Å is comparable to that

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(33) As in **4**, the B—H bond length of the non-interacting hydrogen in **5** is marginally shorter than the other two, (1.08(3) versus 1.10(3) and 1.16(2) Å).

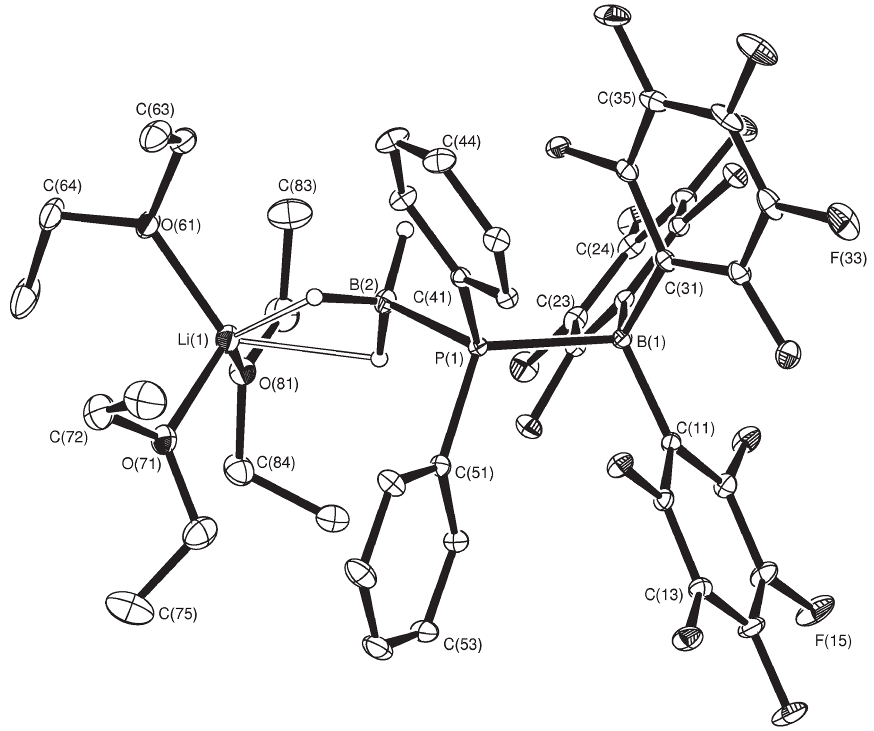


Figure 2. ORTEP of **4** with displacement ellipsoids drawn at the 30% probability level; aromatic protons and those on the diethyl ether have been omitted for clarity. Selected distances [Å] and angles [deg] P(1)—B(1) 2.1206(15), P(1)—B(2) 1.9509(16), P(1)—C(41) 1.8375(14), P(1)—C(51) 1.8329(14), B(1)—C(11) 1.6480(19), B(1)—C(21) 1.646(2), B(1)—C(31) 1.6381(19), Li(1)—O(61) 1.992(3), Li(1)—O(71) 1.977(3), Li(1)—O(81) 1.983(3). B(1)—P(1)—B(2) 117.06(7), B(1)—P(1)—C(41) 108.58(6), B(1)—P(1)—C(51) 113.31(6), B(2)—P(1)—C(41) 106.82(7), B(2)—P(1)—C(51) 105.86(7), C(41)—P(1)—C(51) 104.30(6), C(11)—B(1)—P(1) 110.07(9), C(21)—B(1)—P(1) 106.67(9), C(31)—B(1)—P(1) 103.54(9), O(61)—Li(1)—O(71) 106.79(13), O(61)—Li(1)—O(81) 109.18(13), O(71)—Li(1)—O(81) 112.38(13).

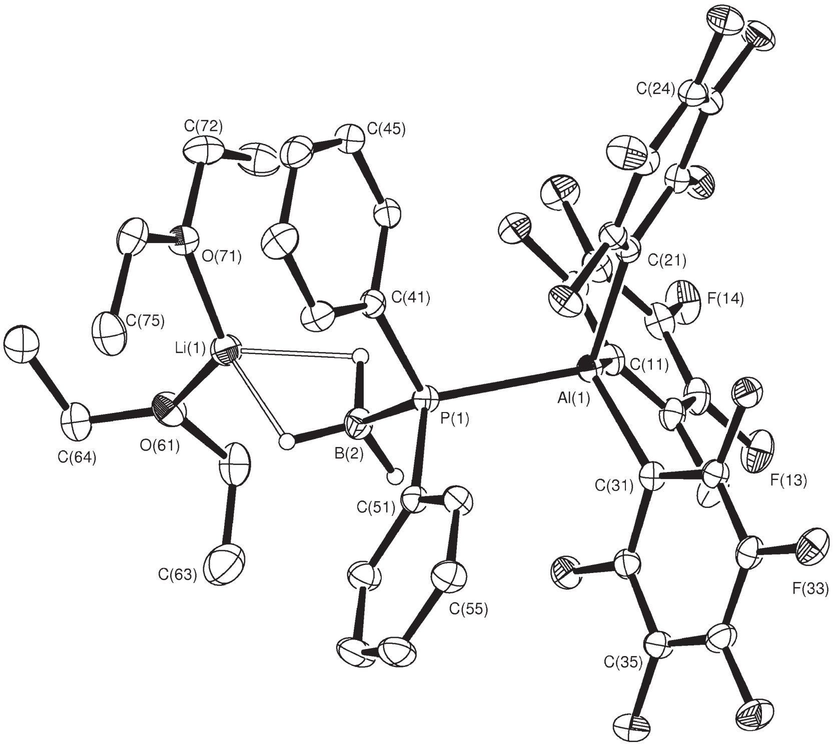


Figure 3. ORTEP of **5** with displacement ellipsoids drawn at the 30% probability level, aromatic hydrogen atoms and those of the diethyl ether have been omitted for clarity. Selected bond lengths [Å] and angles [deg] P(1)—Al(1) 2.4538(9), P(1)—B(2) 1.949(2), P(1)—C(41) 1.831(2), P(1)—C(51) 1.834(2), Al(1)—C(11) 2.008(2), Al(1)—C(21) 2.009(2), Al(1)—C(31) 2.007(2), Li(1)—O(61) 1.887(4), Li(1)—O(71) 1.891(4). Al(1)—P(1)—B(2) 112.19(8), Al(1)—P(1)—C(41) 110.55(7), Al(1)—P(1)—C(51) 109.31(7), B(2)—P(1)—C(41) 110.73(10), B(2)—P(1)—C(51) 109.00(10), C(41)—P(1)—C(51) 104.78(9), C(11)—Al(1)—P(1) 109.11(6), C(21)—Al(1)—P(1) 110.77(6), C(31)—Al(1)—P(1) 103.01(6), O(61)—Li(1)—O(71) 124.7(2).

observed in **4**. The pattern of C−H$\cdots$F contacts in compound **5** resembles that in compound **4**, but here there is one intramolecular and one intermolecular interaction and, presumably because of the greater P—M separation, the distances are greater H(56)$\cdots$F(26) 2.39 and H(53)$\cdots$F(36)′ 2.39 Å.

Crystals of $[Li(OEt_2)_2][H(^tBu)P\{Al(C_6F_5)_3\}\{BH_3\}]$ (**7**) suitable for X-ray diffraction could not be obtained despite repeated attempts, including the addition of 12-crown-4 (**7a**); however, X-ray diffraction quality crystals of the $B(C_6F_5)_3$ analogue $[Li(OEt_2)_3][H(^tBu)P\{B(C_6F_5)_3\}\{BH_3\}]$ (**6**) as $[Li(12\text{-crown-}4)_2][H(^tBu)P\{B(C_6F_5)_3\}\{BH_3\}]$ (**6a**) could be obtained through the addition of 2 equiv of 12-crown-4 to a diethyl ether solution and cooling to −25 °C (Figure 4). The phosphorus centers in **6a** are bonded to four different substituents in an approximately tetrahedral geometry and are therefore chiral, but crystallize as a racemic mixture. The $H_3B(2)$—P(1) (1.946(3) Å) and $(C_6F_5)_3B(1)$—P(1) (2.040(3) Å) distances are comparable to those found for **4**. The B—P—B angle of 116.00(12)° suggests that the *tert*-butyl and hydrogen combination presents a similar requirement to the two phenyl substituents in **4**, where the corresponding angle is 117.06(7)°. Since the Li cation is coordinated to two 12-crown-4 molecules, effectively encapsulating the ion, there are no close interactions with the BH_3 hydrogen atoms and all three B−H distances are comparable. The P−H bond length was experimentally determined to be 1.32(2) Å, and the hydrogen is engaged in hydrogen bonding to an *o*-F of one of the C_6F_5 rings (H(51)$\cdots$F(12) 2.30(2) Å, P−H$\cdots$F 114.4(14)°). Related H$\cdots$F interactions have been observed in the primary phosphine adduct $H_2(^tBu)P\cdot B(C_6F_5)_3$, but were notably absent in the secondary phosphine adducts $H(R)_2P\cdot B(C_6F_5)_3$ (where R = phenyl and cyclohexyl).[13,34,35]

Table 2. Selected Bond Lengths (Å) and Angles (deg)

	M(1)—P(1)	P(1)—B(2)	M(1)—P(1)—B(2)
2	2.056(6)	2.058(6)	129.8(2)
4	2.121(2)	1.951(2)	117.06(7)
5	2.4538(9)	1.949(2)	112.19(8)
6a	2.040(3)	1.946(3)	116.00(12)

Evidently there are close parallels between anion formation chemistry in the case of the $[EH_2]^-$ cores, and, like phosphidoborates, there are many known examples of amidoborates. It might therefore be expected that the chemistry and stability of the $[R_2N\{M(C_6F_5)_3\}\{BH_3\}]^-$ anions would reflect the pattern observed for the phosphorus analogues. However, the reaction between $LiNH^tBu\{BH_3\}$ and $B(C_6F_5)_3$ does not proceed cleanly and when monitored by ^{19}F NMR at least two unidentified products are observed. In this instance there is no indication for the formation of $[HB(C_6F_5)_3]^-$. The isolation of the constituents by fractional crystallization methods was attempted, including the addition of 12-crown-4, but was not successful. The analogous reaction between $Li[N(CH_3)_2(BH_3)]$ and $B(C_6F_5)_3$ yields two fluorine-containing products, one of which was identified as $[HB(C_6F_5)_3]^-$. Treatment of Li $[(cyclo\text{-}NC_5H_{10})(BH_3)]$ with $B(C_6F_5)_3$ in THF solution gave a product mixture from which $(cyclo\text{-}NC_5H_{10})_2(\mu\text{-}BH_2)_2$ (**8**) and $[Li(12\text{-crown-}4)_2][HB(C_6F_5)_3]$ (**9**) were subsequently fractionally crystallized (Scheme 3). The identity of both components was definitively established by diffraction methods. Compound **8** has been reported,[36] while the data for the salt **9** was only of sufficient quality to establish connectivity; the anion has been previously crystallographically characterized.[16,37] The reaction of $Li[NH_2(BH_3)]$ with $B(C_6F_5)_3$ proceeds similarly and cleanly giving $[HB(C_6F_5)_3]^-$, which was identified by multinuclear NMR; however the second component of this mixture, presumed to be an oligomer of the form $[(H_2N)(\mu\text{-}BH_2)]_n$, could not be isolated. The crude ^{11}B solution NMR spectrum did not show the signals around −10 ppm recently observed for such species,[38,39] but this may be because of precipitation from the reaction medium.

While, where R = R′ = Me or R = H, R′ = ^tBu, one of the sets of signals we observe may indicate the competing formation of an anion of the type $[RR'N\{B(C_6F_5)_3\}\{BH_3\}]^-$, the predominant fluorine-containing product in this series is the hydridoborate anion. Where RR′ completes

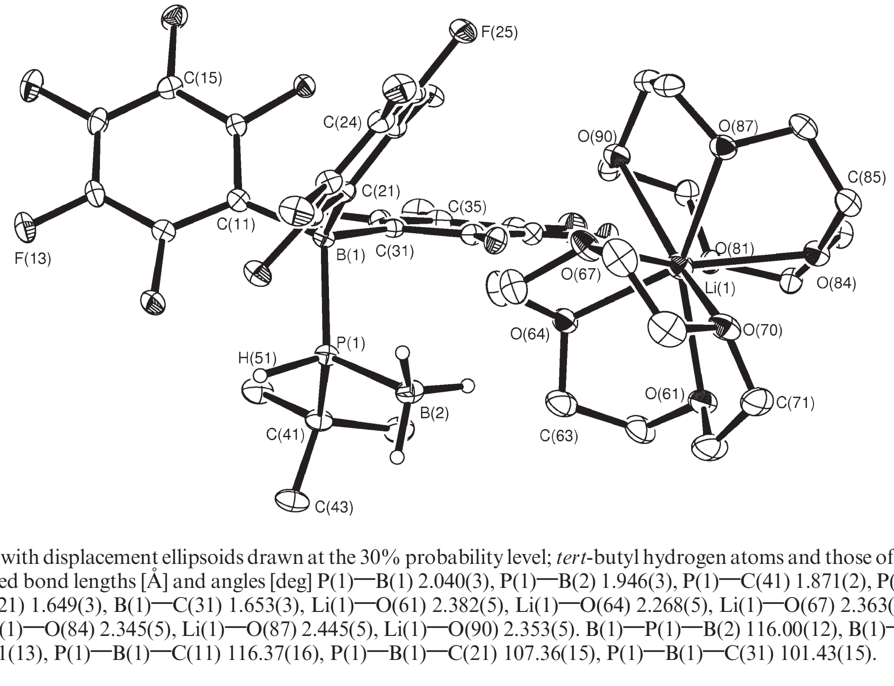
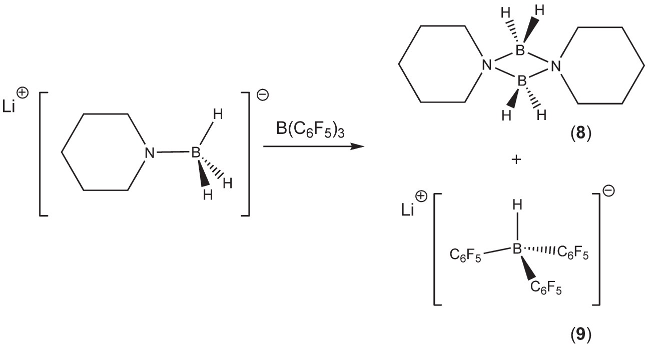


Figure 4. ORTEP of **6a** with displacement ellipsoids drawn at the 30% probability level; *tert*-butyl hydrogen atoms and those of the crown ether have been omitted for clarity. Selected bond lengths [Å] and angles [deg] P(1)—B(1) 2.040(3), P(1)—B(2) 1.946(3), P(1)—C(41) 1.871(2), P(1)—H(51) 1.32(2), B(1)—C(11) 1.650(3), B(1)—C(21) 1.649(3), B(1)—C(31) 1.653(3), Li(1)—O(61) 2.382(5), Li(1)—O(64) 2.268(5), Li(1)—O(67) 2.363(5), Li(1)—O(70) 2.359(5), Li(1)—O(81) 2.291(5), Li(1)—O(84) 2.345(5), Li(1)—O(87) 2.445(5), Li(1)—O(90) 2.353(5). B(1)—P(1)—B(2) 116.00(12), B(1)—P(1)— C(41) 115.87(11), B(2)—P(1)—C(41) 110.61(13), P(1)—B(1)—C(11) 116.37(16), P(1)—B(1)—C(21) 107.36(15), P(1)—B(1)—C(31) 101.43(15).

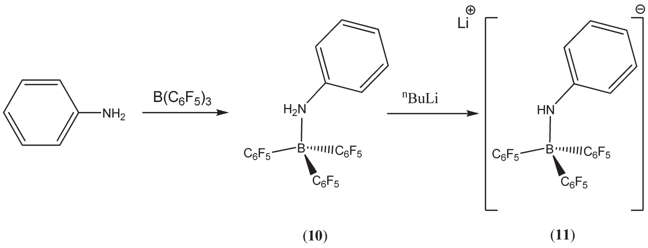
Scheme 3



the piperidinyl ring, the reaction proceeds fairly selectively giving almost exclusively the hydridoborate anion and the concomitant isolation of [(*cyclo*-NC_5H_{10})(μ-BH_2)]$_2$ (**8**) indicates that the hydridoborate anion is formed by abstraction of hydride from the BH_3 group of the amidoborate anion, giving a neutral aminoborane which subsequently dimerizes.

To determine whether the failure to isolate $[R_2N\{B(C_6F_5)_3\}\{BH_3\}]^-$ anions was a consequence of inherent instability or the favorable competition of the abstraction reaction resulting from the synthetic procedure being employed, reactions between $Li[R_2N\{B(C_6F_5)_3\}]$ and $Me_2S\cdot BH_3$ were considered. However, the NH_2 and N(Ph)H derivatives are the only two known examples of isolable $[R_2N\{B(C_6F_5)_3\}]^-$ anions.[18,23] The imidazolium salt $[^tBu_2N_2C_3H_3][(Ph)HN\{B(C_6F_5)_3\}]$ was recently reported by Stephan and co-workers.[37] Treatment of tris(pentafluorophenyl)borane with 1 equiv of aniline yields the Lewis adduct $(Ph)H_2N\cdot B(C_6F_5)_3$ (**10**) (Scheme 4). The lithium salt $[Li(12\text{-crown-}4)_2][(Ph)HN\{B(C_6F_5)_3\}]$ (**11**) was prepared by the deprotonation of **10** followed by precipitation with 12-crown-4, and characterized by X-ray diffraction methods.[40] Treatment of this amidoborate anion with 1 equiv of $Me_2S\cdot BH_3$ yielded only intractable mixtures with multiple ^{11}B resonances, none of which had the characteristic quartet coupling expected for the BH_3 group of a $[R_2N\{B(C_6F_5)_3\}\{BH_3\}]^-$ anion. The failure to isolate examples of $[R_2N\{B(C_6F_5)_3\}\{BH_3\}]^-$ anions despite utilizing two distinct synthetic approaches suggests an intrinsic instability at odds with that of the analogous phosphido anions and particularly surprising in the case of the $[NH_2]^-$ core where anion **I** has been demonstrated to show excellent stability. However, it is consistent with earlier observations on the instability of the $Li[NH_2(BH_3)_2]$ anion, which was shown to be unstable with respect to the formation of $Li[BH_4]$ and $(BH_2NH_2)_n$.[41]

Scheme 4



Conclusion

The chemistry of the phosphidodiborate anion $[H_2P\{B(C_6F_5)_3\}_2]^-$ closely resembles that of the amidodiborate analogue. Whether this anion will prove to be as useful in polymerization catalysis and the isolation of reactive electrophiles as the amidodiborate remains to be established.[1-5] The seemingly straightforward extension of this anion complexation chemistry to derivatives with alkyl-amide and -phosphide cores is frustrated by the existence of competing reaction pathways and their apparent lack of stability.

Although anions of the form $[RR'P\{B(C_6F_5)_3\}_2]^-$ have proven elusive, the analogous species in which the phosphide core is complexed by a combination of BH_3 and either $B(C_6F_5)_3$ or $Al(C_6F_5)_3$ are both stable and isolable. These $[RR'P\{M(C_6F_5)_3\}\{BH_3\}]^-$ anions are conveniently prepared from $Li[RR'P(BH_3)]$ and the corresponding Lewis acid. However, in the special (stable) case of the $Li[H_2P\{B(C_6F_5)_3\}]$ precursor, the $[H_2P\{B(C_6F_5)_3\}\{BH_3\}]^-$ anion can be prepared by addition of BH_3. In the solid state structures of the salts $[Li(OEt_2)_n][RR'P\{M(C_6F_5)_3\}\{BH_3\}]$ (M = B, $n = 3$ and M = Al, $n = 2$) the lithium counterion is η^2-coordinated to the BH_3 group. The coordination chemistry of these species awaits further investigation.

The analogous anions built on amide cores could not be prepared. Despite the stability of the $[H_2N\{B(C_6F_5)_3\}_2]^-$ and $[R_2N(BH_3)]^-$ salts all attempts, regardless of the order of reagent addition, at the isolation of salts of the form $[Li(OEt_2)_n][RR'N\{B(C_6F_5)_3\}\{BH_3\}]$ proved unsatisfactory. In several instances $Li[HB(C_6F_5)_3]$ was observed, which coupled with the isolation of an example of an aminoborane dimer is strongly consistent with the supposition that these anions are unstable with respect to hydride abstraction by tris(pentafluorophenyl)borane. This is essentially the same pathway that accounts for the instability of tertiary amine adducts of tris(pentafluorophenyl)borane; however, in this instance the more hydridic B−H is preferentially abstracted.

Experimental Section

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques in pre-dried glassware. Solvents were dried using an appropriate drying agent and distilled under nitrogen prior to use: dichloromethane (CaH_2), light petroleum (Na/K alloy or sodium/dyglyme/benzophenone), diethylether and THF (sodium/benzophenone) and toluene (sodium). Samples for NMR analysis were prepared using degassed deuterated solvents dried over activated 4 Å molecular sieves. NMR spectra were obtained using a Bruker Avance DPX300 spectrometer at 23 °C. Chemical shifts are reported in parts per million and referenced to residual solvent resonances (^1H, $^{13}C\{^1H\}$); ^{19}F is relative to $CFCl_3$; ^{11}B is relative to $Et_2O\cdot BF_3$; $^{31}P\{^1H\}$ is relative to an 85% solution of H_3PO_4. Elemental analyses were carried out at Medac Ltd. and at the Department of

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(34) Lancaster, S. J.; Mountford, A. J.; Hughes, D. L.; Schormann, M.; Bochmann, M. *J. Organomet. Chem.* **2003**, *680*, 193.

(35) In **6a**, there is also a close interaction between one of the ^tBu hydrogen atoms and an *o*-F of a second C_6F_5 ring (C(44)−H(44a)···F(36) 2.31 Å).

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(37) (a) Chase, P. A.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7433. (b) Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, 1701.

(38) Dietrich, B. L.; Goldberg, K. I.; Heinekey, D. M.; Autrey, T.; Linehan, J. C. *Inorg. Chem.* **2008**, *47*, 8583.

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(40) The anionic part of **11** is essentially the same as that reported in reference 37; our results are reported in the Electronic Supporting Information.

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Health and Human Sciences, London Metropolitan University. The syntheses of $B(C_6F_5)_3$ and $Al(C_6F_5)_3\cdot$toluene were conducted according to the literature procedures.[42,43]

Li[H$_2$PB(C$_6$F$_5$)$_3$] (1). A suspension of $H_3P\cdot B(C_6F_5)_3$ (0.72 g, 1.3 mmol) in light petroleum (10 mL) was treated with a solution of $Li[N(SiMe_3)_2]$ (0.22 g, 1.3 mmol) in light petroleum (10 mL) at −78 °C. The resulting suspension was warmed to room temperature and stirred for a further 30 min before the solid was isolated by filtration (0.67 g, 1.2 mmol, 93%). Elem. Anal. Calcd (found) for $C_{18}H_2BF_{15}LiP$: C, 39.17 (39.90); H, 0.37 (0.96). The slightly elevated C and H values are due to the presence of persistent traces of solvent, which were not removed on drying. ^{1}H NMR ($C_6D_6/C_6H_4F_2$ 50:50): δ 2.25 (2H, d, $^1J_{PH} = 250$ Hz, PH$_2$). ^{11}B NMR (96.3 MHz; $C_6D_6/C_6H_4F_2$ 50:50): δ −18.0 (d, $^1J_{BP} = 46$ Hz). ^{19}F NMR ($C_6D_6/C_6H_4F_2$ 50:50): δ −133.9 (6F, m, *o*-F), −161.5 (3F, t, $^3J_{FF} = 20$ Hz, *p*-F), −165.5 (6F, m, *m*-F). ^{31}P NMR ($C_6D_6/C_6H_4F_2$ 50:50): δ −154.6 (br).

[Li$_2$(12-crown-4)$_2$][H$_2$P{B(C$_6$F$_5$)$_3$}$_2$]$_2$ (2). A suspension of Li[H$_2$PB(C$_6$F$_5$)$_3$] (0.32 g, 0.6 mmol) in toluene (10 mL) was cooled (−78 °C) and treated with $B(C_6F_5)_3$ (0.30 g, 0.6 mmol). The reaction mixture became homogeneous momentarily but proceeded to precipitate a colorless oil. The emulsion was stirred at room temperature for 30 min before the solvent was removed under vacuum yielding a foam which was washed with light petroleum affording a fine powder (0.24 g, 0.2 mmol, 33%). ^{1}H NMR ($C_6D_6/C_6H_4F_2$ 50:50): δ 5.08 (2H, d, $^1J_{PH} = 350$ Hz, PH$_2$). ^{11}B NMR ($C_6D_6/C_6H_4F_2$ 50:50): δ −15.3. ^{19}F NMR ($C_6D_6/C_6H_4F_2$ 50:50): δ −129.7 (12F, m, *o*-F), −159.8 (6F, m, *p*-F), −165.8 (12F, m, *m*-F). ^{31}P NMR ($C_6D_6/C_6H_4F_2$ 50:50): δ −96.8 (br). The crude solid was treated with a THF (10 mL) solution of 12-crown-4 (0.1 mL, 0.6 mmol), concentration afforded block-shaped crystals. Elem. Anal. Calcd (found) for $C_{36}H_2B_2F_{30}P\cdot O_4C_8H_{16}Li$: C, 42.62 (43.27); H, 1.46 (1.44). ^{1}H NMR ($C_6D_6/C_6H_4F_2$ 50:50): δ 5.08 (2H, d, $^1J_{PH} = 354$ Hz, PH$_2$), 3.07 (32H, s, CH$_2$). ^{11}B NMR ($C_6D_6/C_6H_4F_2$ 50:50): δ −15.8. ^{19}F NMR ($C_6D_6/C_6H_4F_2$ 50:50): δ −129.1 (6F, br, *o*-F), −159.6 (3F, m, *p*-F), −165.4 (6F, m, *m*-F). ^{31}P ($C_6D_6/C_6H_4F_2$ 50:50): δ −100.8.

[Li(12-crown-4)$_2$][H$_2$P{B(C$_6$F$_5$)$_3$}{BH$_3$}] (3). Borane-dimethyl sulfide (0.1 mL, 1 mmol) was added to a solution of Li[H$_2$PB(C$_6$F$_5$)$_3$] (0.56 g, 1.0 mmol) in diethyl ether (10 mL) at −78 °C. The solution was then allowed to warm to room temperature before the addition of 12-crown-4 (0.3 mL, 2 mmol) resulting in the precipitation of impurities, which were separated by filtration. The filtrate was reduced to dryness, and the pure product precipitated from dichloromethane/light petroleum solution at −25 °C. Elem. Anal. Calcd (found) for $C_{34}H_{37}B_2F_{15}LiO_8P$: C, 44.48 (44.28); H, 4.06 (4.15). ^{1}H NMR (CDCl$_3$): δ 3.78 (2H, d, $^1J_{PH} = 334$ Hz, PH$_2$), 3.65 (32H, s, CH$_2$), 0.20 (3H, br, BH$_3$). ^{13}C NMR (CDCl$_3$): δ 66.52 (CH$_2$). ^{11}B NMR (CDCl$_3$): δ −18.0 (1B, d, $^1J_{BP} = 69$ Hz, B(C$_6$F$_5$)$_3$), −41.3 (1B, br, BH$_3$). ^{19}F NMR (CDCl$_3$): δ −130.2 (6F, br, *o*-F), −160.9 (3F, t, $^3J_{FF} = 21$ Hz, *p*-F), −165.7 (6F, m, *m*-F). ^{31}P NMR (CDCl$_3$): δ −92.33.

[Li(OEt$_2$)$_3$][Ph$_2$P{B(C$_6$F$_5$)$_3$}{BH$_3$}] (4). Li[Ph$_2$P(BH$_3$)] (0.27 g, 1.3 mmol), freshly prepared by the treatment of H(Ph)$_2$PBH$_3$ with ^{n}BuLi, was treated with a solution of $B(C_6F_5)_3$ (0.68 g, 1.3 mmol) in diethyl ether (15 mL) at −78 °C. The reaction mixture dissolved at 0 °C, before precipitating a colorless solid approaching room temperature, which in turn redissolved after further stirring for several minutes. After stirring for 30 min, all volatiles were removed under vacuum. The product was purified by slow evaporation of a concentrated diethyl ether solution, which was cooled to −25 °C at the first sign of nucleation yielding crystals of **4** (0.73 g, 0.8 mmol, 60%). Elem. Anal. Calcd (found) for $C_{42}H_{43}B_2F_{15}LiO_3P$: C, 53.65 (53.72); H, 4.61 (4.32). ^{1}H NMR (CDCl$_3$): δ 7.28 (10H, m, C$_6$H$_5$), 3.47 (12H, q, $J_{HH} = 7.1$ Hz, CH$_2$), 1.15 (18H, t, $J_{HH} = 7.1$ Hz, CH$_3$), 0.53 (3H, br, BH$_3$). ^{13}C NMR (CDCl$_3$): δ 66.4 (CH$_2$), 15.0 (CH$_3$). ^{11}B NMR (CDCl$_3$): δ −11.4 (1B, br, B(C$_6$F$_5$)$_3$), −32.3 (1B, br, BH$_3$). ^{19}F NMR (CDCl$_3$): δ −126.2 (6F, d, $^3J_{FF} = 20$ Hz, *o*-F), −160.2 (3F, t, $^3J_{FF} = 20$ Hz, *p*-F), −166.5 (6F, t, $^3J_{FF} = 20$ Hz, *m*-F). ^{31}P NMR (CDCl$_3$): δ 0.3.

[Li(OEt$_2$)$_2$][Ph$_2$P{Al(C$_6$F$_5$)$_3$}{BH$_3$}] (5). A solution of freshly prepared Li[Ph$_2$P(BH$_3$)] (0.46 g, 2.2 mmol) in diethyl ether (15 mL) was cooled to −78 °C and treated with $Al(C_6F_5)_3\cdot$toluene (1.38 g, 2.2 mmol). The resulting solution was stirred at room temperature for 30 min before the solvent was removed under vacuum affording a sticky colorless solid. The product was washed with light petroleum to give a fine powder, which was recrystallized by diffusion of light petroleum through a diethyl ether solution at −25 °C affording needle-shaped crystals (0.93 g, 1.1 mmol, 48%). Elem. Anal. Calcd (found) for $C_{38}H_{33}AlBF_{15}LiO_2P$: C, 51.73 (51.64); H, 3.77 (3.69). ^{1}H NMR (CDCl$_3$): δ 7.30 (10H, m, C$_6$H$_5$), 3.53 (8H, q, $J_{HH} = 7.1$ Hz, CH$_2$), 1.17 (12H, t, $J_{HH} = 7.1$ Hz, CH$_3$), 0.55 (3H, br, BH$_3$). ^{11}B NMR (CDCl$_3$): δ −34.2 (br). ^{19}F NMR (CDCl$_3$): δ −120.0 (6F, m, *o*-F), −155.5 (3F, t, $^3J_{FF} = 20$ Hz, *p*-F), −163.3 (6F, m, *m*-F). ^{31}P NMR (CDCl$_3$): δ −39.2 (br).

[Li(OEt$_2$)$_3$][H(^{t}Bu)P{B(C$_6$F$_5$)$_3$}{BH$_3$}] (6). Li[H(^{t}Bu)P(BH$_3$)] (0.18 g, 1.6 mmol) in diethyl ether (20 mL) was treated with $B(C_6F_5)_3$ (0.83 g, 1.6 mmol) at −78 °C. The homogeneous reaction mixture was allowed to warm to room temperature where it was stirred for 30 min before all solvents were removed under reduced pressure affording an oily material. ^{1}H NMR (CDCl$_3$): δ 4.78 (1H, d, $^1J_{PH} = 360$ Hz, PH), 3.59 (12H, q, $J_{HH} = 7.1$ Hz, CH$_2$), 1.19 (18H, t, $J_{HH} = 7.1$ Hz, CH$_3$), 0.94 (9H, d, $^3J_{PH} = 13$ Hz, C(CH$_3$)$_3$), −0.04 (3H, br, BH$_3$). ^{11}B NMR (CDCl$_3$): δ −15.8 (1B, d, $^1J_{BP} = 76$ Hz, B(C$_6$F$_5$)$_3$), −40.5 (1B, br, BH$_3$). ^{19}F NMR (CDCl$_3$): δ −128.2 (6F, br, *o*-F), −160.7 (3F, br, *p*-F), −165.6 (6F, br, *m*-F). ^{31}P NMR (CDCl$_3$): δ −22.9. Needle shaped crystals of [Li(12-crown-4)] [H(^{t}Bu)P{B(C$_6$F$_5$)$_3$}{BH$_3$}] **6a** were grown by dissolving the product in a minimum volume of diethyl ether and adding 2 equiv of 12-crown-4 before cooling the solution to −25 °C for several hours (0.73 g, 0.9 mmol, 54%). Elem. Anal. Calcd (found) for $C_{22}H_{13}B_2F_{15}P\cdot C_{16}H_{32}O_8Li$: C, 46.85 (46.72); H, 4.66 (4.90). ^{1}H NMR (CDCl$_3$): δ 4.60 (1H, d, $^1J_{PH} = 356$ Hz, PH), 3.55 (32H, s, CH$_2$), 0.84 (9H, d, $^3J_{PH} = 12$ Hz, C(CH$_3$)), 0.28 (3H, br, BH$_3$). ^{13}C NMR (CDCl$_3$): δ 66.3 (CH$_2$), 29.2 (CH$_3$). ^{11}B NMR (CDCl$_3$): δ −16.0 (1B, d, $^1J_{BP} = 75$ Hz, B(C$_6$F$_5$)$_3$), −41.0 (1B, br, BH$_3$). ^{19}F NMR (CDCl$_3$): δ −127.5 (6F, v br, *o*-F), −161.5 (3F, m, *p*-F), −166.0 (6F, m, *m*-F). ^{31}P NMR (CDCl$_3$): δ −18.7 (br).

[Li(OEt$_2$)$_2$][H(^{t}Bu)P{Al(C$_6$F$_5$)$_3$}{H$_3$B}] (7). A solution of $Al(C_6F_5)_3\cdot$toluene (0.58 g, 0.9 mmol) in diethyl ether was treated with freshly prepared Li[PH(^{t}Bu)(BH$_3$)] (0.10 g, 0.93 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and was then stirred for 30 min before the solvent was removed under vacuum affording a colorless oil. ^{1}H NMR (CDCl$_3$): δ 3.68 (1H, d, $^1J_{PH} = 320$ Hz, PH), 3.61 (8H, q, $J_{HH} = 7.1$ Hz, CH$_2$), 1.21 (12H, t, $J_{HH} = 7.1$ Hz, CH$_3$), 1.08 (9H, d, $^3J_{PH} = 23$ Hz, C(CH$_3$)$_3$), 0.06 (3H, br, BH$_3$). ^{11}B NMR (CDCl$_3$): δ −40.8. ^{19}F NMR (CDCl$_3$): δ −120.8 (6F, m, *o*-F), −155.6 (3F, m, *p*-F), −162.9 (6F, m, *m*-F). ^{31}P NMR (CDCl$_3$): δ −54.9. Light petroleum was layered over a dichloromethane solution containing 12-crown-4 and cooled to −25 °C overnight affording small block-shaped crystals of [Li(12-crown-4)][H(^{t}Bu)P{Al(C$_6$F$_5$)$_3$}{BH$_3$}] **7a** (0.42 g, 0.5 mmol, 57%). Elem. Anal. Calcd (found) for $C_{22}H_{13}AlBF_{15}P\cdot C_{16}H_{32}O_8Li$: C, 46.08 (45.43); H, 4.58 (4.96). The discrepancy in the elemental analyses results for **7a** is presumably due to the highly sensitive nature of this compound and the resulting difficulties with its manipulation. ^{1}H NMR (CDCl$_3$): δ 3.59 (1H, d, $^1J_{PH} = 315$ Hz, PH), 3.64

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Table 3. Crystallographic Data

	2	**4**	**5**	**6a**
chemical formula	$[Li_2(12\text{-crown-}4)_2][H_2P\{B(C_6F_5)_3\}_2]_2$	$[Li(OEt_2)_3][\{H_3B\}PPh_2\{B(C_6F_5)_3\}]$	$[Li(OEt_2)_2][\{H_3B\}PPh_2\{Al(C_6F_5)_3\}]$	$[Li(12\text{-crown-}4)][\{H_3B\}PH^tBu\{B(C_6F_5)_3\}]$
M	1240.11	940.29	882.34	974.27
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	12.465(13)	12.9559(9)	12.277(2)	8.545(2)
b/Å	14.37(3)	13.0944(7)	12.334(2)	15.851(5)
c/Å	14.461(14)	14.6714(6)	14.628(3)	16.004(3)
α/deg	62.10(13)	79.742(4)	84.969(12)	99.750(17)
β/deg	84.68(10)	80.895(5)	71.244(13)	96.41(2)
γ/deg	89.27(10)	61.807(4)	73.580(14)	91.167(17)
V/Å^3	2279(5)	2150.7(2)	2011.8(6)	2121.4(9)
T/K	120(2)	120(2)	120(2)	120(2)
Z	1	2	2	2
reflections measured	42972	46149	41196	48265
unique reflections, R_{int}	10370, 0.1233	9827, 0.0279	9117, 0.0603	9718, 0.0649
observed data	5853	8260	7606	6586
wR_2, R_1 (observed data)	0.1373, 0.0919	0.0955, 0.0381	0.1422, 0.0573	0.1117, 0.0577
wR_2, R_1 (all data)	0.1620, 0.1821	0.1016, 0.0481	0.1501, 0.0684	0.1270, 0.1019
Largest difference peak	0.630	0.808	0.780	0.725

(32H, s, CH_2), 1.06 (9H, d, $^3J_{PH} = 14$ Hz, $C(CH_3)$), 0.39 (3H, br, BH_3). ^{13}C NMR ($CDCl_3$): δ 66.1 (CH_2), 28.1 (CH_3). ^{11}B NMR ($CDCl_3$): δ −40.9. ^{19}F NMR ($CDCl_3$): δ −119.7 (6F, d, $J_{FF} = 20$ Hz, *o*-F), −156.4 (3F, t, $J_{FF} = 20$ Hz, *p*-F), −163.2 (6F, m, *m*-F). ^{31}P NMR ($CDCl_3$): δ −50.5 (br).

[(*cyclo*-NC_5H_{10})$_2$(*μ*-BH_2)$_2$] and [Li(12-crown-4)$_2$][HB(C_6F_5)$_3$] (8 and 9). To a solution of $[Li(THF)_n]$[*cyclo*-$NC_5H_{10}(BH_3)$] (prepared according to the literature method[44]) (5 mmol) in THF (2 mL) was added $B(C_6F_5)_3$ (2.56 g, 5 mmol) at room temperature. The resultant solution was cooled to −25 °C, affording colorless X-ray quality plates of [(*cyclo*-NC_5H_{10})$_2$(*μ*-BH_2)$_2$], which were separated by filtration. ^1H NMR (C_6D_6): δ 3.33 (8H, d, $^3J_{HH} = 4.7$ Hz, CH_2), 1.38 (8H, m, CH_2), 1.12 (4H, m, CH_2). ^{13}C NMR (C_6D_6): δ 68.2, 23.7, 23.5. ^{11}B NMR (C_6D_6): δ 2.5 (t, $^1J_{BH} = 112$ Hz, BH_2).

To the filtrate was added 12-crown-4 (0.2 mL, 1.2 mmol) at room temperature before being cooled to −25 °C to afford small colorless crystals of $[Li(12\text{-crown-}4)_2][(C_6F_5)_3BH]$; X-ray analysis of these crystals produced a poor quality result suitable only to establish connectivity. ^1H NMR ($CDCl_3$): δ 3.66 (32H, s, CH_2), 1.88 (1H, br, BH). ^{13}C NMR ($CDCl_3$): δ 66.2. ^{11}B NMR ($CDCl_3$): δ −25.3 (d, $^1J_{BH}$ = 88 Hz). ^{19}F NMR ($CDCl_3$): δ −134.0 (6F, m, *o*-F), −146.4 (3F, t, $^3J_{FF} = 20$ Hz, *p*-F), −167.5 (6F, m, *m*-F).

$H_2PhNB(C_6F_5)_3$ (10). A solution of $(C_6F_5)_3B \cdot OEt_2$ (2.75 g, 4.7 mmol) in toluene (50 mL) was treated with aniline (0.43 mL, 4.7 mmol). Addition of light petroleum (150 mL) followed by cooling to −25 °C afforded a colorless solid. Elem. Anal. Calcd (found): C, 47.64 (47.76); H, 1.17 (1.16); N, 2.31 (2.30). ^1H NMR ($CDCl_3$): δ 7.28 (4H, m, CH), 7.02 (1H, m, CH), 6.79 (2H, br, NH). ^{13}C NMR ($CDCl_3$): δ 134.0 (*i*-C), 130.0 (CH), 129.2 (CH), 122.3 (CH). ^{11}B NMR ($CDCl_3$): δ −5.3. ^{19}F NMR ($CDCl_3$): δ −133.3 (6F, m, *o*-F), −155.1 (3F, t, $^3J_{FF} = 20$ Hz, *p*-F), −162.1 (6F, m, *m*-F).

[Li(12-crown-4)$_2$][HPhNB(C_6F_5)$_3$] (11). A solution of $H_2PhNB(C_6F_5)_3$ (1.15 g, 1.9 mmol) in diethyl ether (10 mL) was cooled to 0 °C before the addition of ^{n}BuLi (1.9 mmol). After warming to room temperature 12-crown-4 (0.6 mL, 3.8 mmol) was added, resulting in the precipitation of the pure product as a colorless solid which was separated by filtration. Colorless crystals suitable for X-ray analysis were obtained by cooling the filtrate to 0 °C. Elem. Anal. Calcd (found) for $C_{40}H_{38}BF_{15}LiNO_8$: C, 49.87 (49.80); H, 3.98 (3.85); N, 1.45 (1.45). ^1H NMR ($CDCl_3$): δ 3.60 (s, 32H, C*H*$_2$), 3.78 (s, 1H, N*H*), 6.25 (t, 1H, $J_{HH} = 7.2$ Hz, *p*-H), 6.30 (d, 2H, $J_{HH} = 7.8$ Hz, *o*-H), 6.82 (m, 2H, *m*-H). ^{11}B NMR ($CDCl_3$): δ −9.9. ^{19}F NMR ($CDCl_3$): δ −134.0 (m, 6F, *o*-F), −162.6 (t, 3F, $^3J_{FF}$ = 20 Hz, *p*-F), −166.4 (m, 6F, *m*-F).

Crystal Structure Analyses. Diffraction data for **2**, **4**, **5**, and **6** were collected by the EPSRC Crystallography Service at the University of Southampton on a Bruker-Nonius KappaCCD diffractometer, and the data were processed using the DENZO/SCALEPACK programs.[45] Diffraction data for **3**, **8**, **9**, and **11** were collected at UEA on an Oxford Diffraction Xcalibur-3 CCD diffractometer, and processed using the CrysAlis-CCD and RED programs.[46] Compound **8** has been reported previously.[36] The anion of **11** has been described,[37] and the structural data for **11** are in the Supporting Information. Crystals of **3** and **9** gave poor quality intensity data; the identities of these compounds were established, but full analyses were not feasible. In each case, the structure was determined by direct method routines in the SHELXS program and refined by full-matrix least-squares methods on F^2 in SHELXL[47] within the WinGX program suite.[48] The results are collated in Table 3. Scattering factors for neutral atoms were taken from literature values.[49]

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Supporting Information Available: Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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