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Thermal Rearrangement of Phosphine−$B(C_6F_5)_3$ Adducts

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A series of tertiary and secondary phosphine−$B(C_6F_5)_3$ adducts are shown to undergo facile, thermal-induced rearrangement to give zwitterionic species of the form $R_3P(C_6F_4)BF(C_6F_5)_2$ and $R_2PH(C_6F_4)BF(C_6F_5)_2$, respectively.

The description of electron-deficient acceptors and electron-rich donors as Lewis acids and bases, respectively, is one of the axioms of inorganic chemistry. Indeed, the formation of simple Lewis acid–base adducts such as $NH_3 \cdot BH_3$ is a classic demonstration of this concept. Recently, we have been probing reactions of Lewis acids and bases in which steric congestion precludes adduct formation. Such sterically "frustrated Lewis pairs" result in unusual reactivity.[1–3] For example, reactions of most phosphines with tetrahydrofuran (THF)−$B(C_6F_5)_3$ result in simple donor exchange. In contrast, sterically demanding phosphines effect the nucleophilic ring opening of THF, giving the butoxy-tethered zwitterioinic species $R_2PHC_4H_8OB(C_6F_5)_3$ (Scheme 1).[4] In related reactions, simple amines, pyridines, and phosphines react with trityl borate to form the adducts $[LCPh_3][B(C_6F_5)_4]$.[5] In contrast, reactions of sterically encumbered phosphines (PR_3, R = *i*-Pr, Cy, and *t*-Bu) with $[CPh_3][B(C_6F_5)_4]$ resulted in nucleophilic attack at the para position of an aryl ring of the trityl cation, giving the species $[(R_3P(C_6H_4)CHPh_2][B(C_6F_5)_4]$ (Scheme 1).[5] Similarly, combination of the Lewis acid $B(C_6F_5)_3$ with sterically hindered tertiary or secondary phosphine, R_3P (R = *i*-Pr, Cy) or R_2PH (R = *t*-Bu, $C_6H_2Me_3$-2,4,6) showed no evidence of Lewis acid–base adducts. Instead, products of the form $R_3P(C_6F_4)BF(C_6F_5)_2$ or $R_2PH(C_6F_4)BF(C_6F_5)_2$ are obtained (Scheme 1).[6] These latter systems have proved particularly interesting because conversion to $[R_2PH(C_6F_4)BH(C_6F_5)_2]$ provides the first metal-free system capable of reversible activation of H_2.[2] Moreover, these species also provide a facile route to a family of Lewis acids that permits the facile tuning of the Lewis acidity of the borane derivatives.[6] In this report, we demonstrate that synthesis of the precursor compounds $R_3P(C_6F_4)BF(C_6F_5)_2$ or $R_2PH(C_6F_4)BF(C_6F_5)_2$ is not limited to sterically frustrated phosphine−borane combinations. Indeed, herein we show that classical Lewis phosphine−borane adducts rearrange readily upon heating, providing access to a range of phosphonium borate zwitterions (Table 1).

Table 1. Summary of ^{31}P, ^{11}B, and ^{19}F NMR Data for Phosphine−Borane Adducts and Phosphonium Borates

compound	δ ^{31}P	δ ^{11}B	^{19}F Δ_{p-m}[a]
$B(C_6F_5)_3$[24]		59	18.3
Cp_2PH[c]	−35.2		
Cy_2PH[e,25]	−27.5		
n Bu_3P[e]	−31.6		
Ph_3P[26]	−6.6		
$CyPH_2$[b]	−110.1		
Et_2PH[26]	−55.5		
Me_3P[26]	−62.0		
1[c]	11.2	−15.9	6.2
2[7]	9.3	−13.5	6.4
3[e]	−0.6	−13.5	7.0
4[8]	−5.2	−2.5	7.1
5[b]	−29.9	−17.5	7.0
6[b]	5.7	−16.2	7.3
7[b]	−6.1	−14.7	6.9
8[d]	12.7	−0.1	4.5
9[b]	11.5	−0.2	5.0
10[b]	33.1	−0.8	5.6
11[b]	15.1	−0.3	4.8
12[b]	41.6	−0.7	4.9

[a] Chemical shift difference for para and meta resonances in the ^{19}F NMR spectrum. [b] C_6D_5Br. [c] CD_2Cl_2. [d] THF-d_8. [e] C_6D_6.

Following a standard procedure, the phosphines Cp_2PH were combined in toluene with $B(C_6F_5)_3$ and stirred for 1 h at 25 °C. Concentration of the solvent afforded the near-quantitative yield of the adduct $(Cp_2PH)B(C_6F_5)_3$ (**1**). In a

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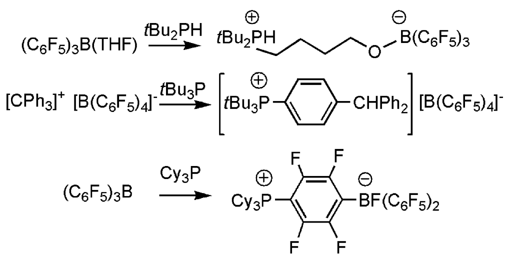
Scheme 1. Reactions of Sterically Demanding Phosphines



similar fashion, the species $(Cy_2PH)B(C_6F_5)_3$ (**2**),[7] $(Bu_3P)B(C_6F_5)_3$ (**3**), $(Ph_3P)B(C_6F_5)_3$ (**4**),[8,9] $(CyPH_2)B(C_6F_5)_3$ (**5**), $(Et_2PH)B(C_6F_5)_3$ (**6**) and $(Me_3P)B(C_6F_5)_3$ (**7**)[10–12] were also prepared. All of these compounds are easily characterized by ^1H, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, ^{19}F, and ^{31}P NMR spectroscopy.[13]These data are typical for such adducts, with each displaying a gap of the ^{19}F NMR resonances attributable to the *m*- and *p*-fluorine atoms and a $^{11}B\{^1H\}$ chemical shift that are characteristic of a four-coordinate boron center.[14–19] In addition, the species **1** was also characterized by X-ray crystallography (Figure 1).[20] As expected, the geometries at B and P are both pseudotetrahedral with a P−B distance of 2.024(3) Å. This compares to 2.0270(14), 2.180(6), 2.046(8), 2.039(3), and 2.061(4) Å previously reported for the adducts **2**,[7] **4**,[8] $(H_3P)B(C_6F_5)_3$,[21] $(PhPH_2)B(C_6F_5)_3$[22] and **7**, respectively. The remaining metric parameters were unexceptional.

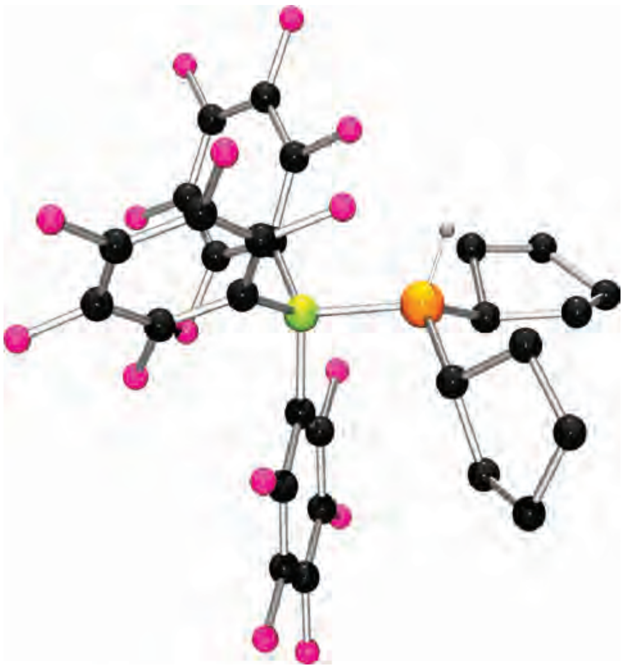


Figure 1. POV-ray drawing of **1**. All H atoms except P−H are omitted for clarity. Color code: F, pink; C, carbon; B, yellow-green; P, orange; H. gray.

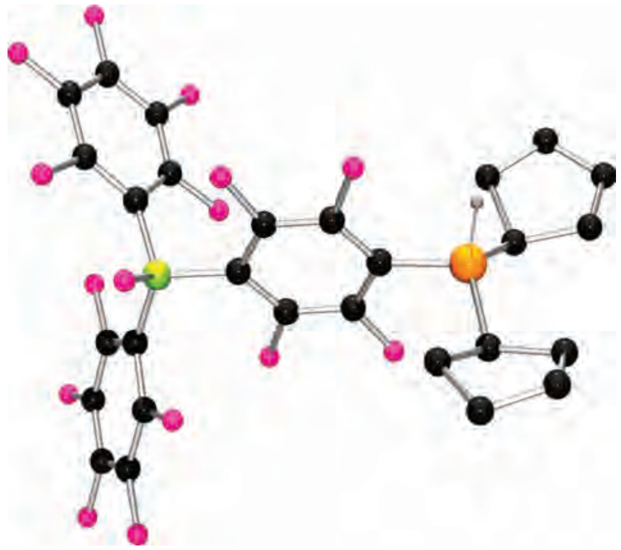


Figure 2. POV-ray drawing of **8**. All H atoms except P−H are omitted for clarity. COlor code: F, pink; C, carbon; B, yellow-green; P, orange; H, gray.

Heating of **1** in a Teflon-capped, sealed reaction bomb to 130 °C for 24 h in a toluene solution resulted in the formation of a white precipitate. The addition of pentane and filtration allowed isolation of the white solid **8** in 73% yield.[13] The $^{11}B\{^1H\}$ NMR signal was observed to shift from 13.50 ppm in the adduct to –0.21 ppm in **8**, while the ^{31}P NMR resonance shifted downfield slightly to 11.50 ppm. Notably this latter signal exhibits a $^1J_{PH}$ coupling constant of 480 Hz typical of phosphonium salts. A new ^{19}F NMR signal was observed at –191.47 ppm[2,6] typical of a B−F unit, while resonances at –129.22 and –131.87 ppm confirmed the presence of a disubstituted C_6F_4 aryl ring. Collectively, these data are consistent with the formulation of **8** as $Cp_2PH(C_6F_4)BF(C_6F_5)_2$. An X-ray crystallographic study[20] of **8** (Figure 2) confirmed the zwitterionic nature, in which a fluoroborate center is linked to a phosphonium center by a C_6F_4 unit. The metric parameters are similar to those previous reported for $R_2R'P(C_6F_4)BF(C_6F_5)_2$ (R = R′, *i*-Pr, Cy; R = *t*-Bu, $C_6H_2Me_3$-2,4,6, R′ = H) derived from sterically frustrated Lewis pairs. The molecules of **8** pack in the solid state such that the closest approach between the PH and BF fragments is 2.099. These head-to-tail interactions forms an extended hydrogen-bonded structure.

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(20) X-ray data for **1**: space group $P2_1/n$, $a = 9.8263(11)$ Å, $b = 12.5957(14)$ Å, $c = 22.117(2)$ Å, $\beta = 96.3620(10)°$, $V = 2720.5(5)$ Å^3, $R = 0.0431$, $R_w = 0.1019$, GOF = 1.038. X-ray data for **8**: space group $P2_1/n$, $a = 11.321(4)$ Å, $b = 8.895(3)$ Å, $c = 28.018(10)$ Å $\beta = 100.216(6)°$, $V = 2776.6(17)$ Å^3, $R = 0.0812$, $R_w = 0.1237$, GOF = 0.985.
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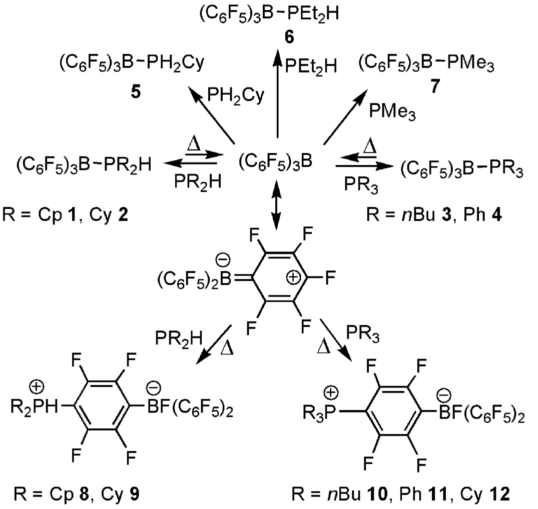
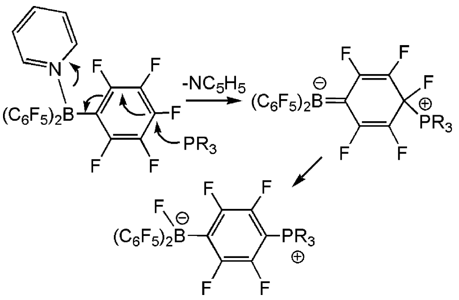
Scheme 2. Formation of Adducts **1**–**7** and Zwitterions **8**–**12**



Scheme 3. Proposed Mechanism for Zwitterion Formation from $(C_5H_5N)B(C_6F_5N)$



In a similar fashion, heating of the adducts **2**–**4** to 125 °C for 48 h resulted in rearrangement to give the para-substituted zwitterions $Cy_2PH(C_6F_4)BF(C_6F_5)_2$ (**9**) and $R_3P(C_6F_4)BF(C_6F_5)_2$ [R = Bu (**10**), Ph (**11**); Scheme 2].[13] While the phosphonium borate salts **9**–**11** are soluble in chloroalkane solvents and bromobenzene to some extent, **8** was only soluble in THF. NMR spectroscopy confirmed the nature of these products. Interestingly, the ^{31}P NMR chemical shifts for **8** and **9** were similar to those seen for the adducts **1** and **2** ($\Delta = 1$–2 ppm). In contrast, the ^{31}P NMR chemical shifts for **10** and **11** are approximately 30 and 20 ppm, respectively, downfield of the precursor adducts. These observations may reflect the greater steric congestion for the tertiary phosphine adducts.

Mechanistically the rearrangement reactions require phosphine dissociation from boron. Attack at the *p*-carbon is consistent with a zwitterionic resonance structure of $B(C_6F_5)_3$ (Scheme 2). A related rearrangement was reported by Erker and co-workers,[23] who described the thermal rearrangement of the ylide−borane adduct $(Ph_3PCHPh)B(C_6F_5)_3$ to the extended zwitterionic phosphonium borate salt $(Ph_3PCHPh)C_6F_4BF(C_6F_5)_2$.

Heating of the solutions of adducts **5**–**7** under conditions similar to those described above resulted in no reaction. Even after prolonged heating in bromobenzene to 140 °C for several days, no evidence of reaction was observed. The inability of the adducts **5**–**7** to undergo thermal rearrangement suggests that small, highly basic phosphines form strong P−B bonds with $B(C_6F_5)_3$. In the case of the primary phosphines, it may be that secondary H•••F interactions analogous to those seen for amine adducts[7] also strengthen the Lewis acid–base interaction.

The zwitterions **8**–**11** are air- and moisture-stable, although the preparations in toluene require anerobic conditions as a result of the high reactivity of the borane with moisture. Interestingly, we have found that employing dry coordinating solvents allows the preparation of these zwitterions without strict anaerobic precautions. For example, heating pyridine or acetonitrile solutions of $(Base)B(C_6F_5)_3$ (Base = NC_5H_5[27] or CH_3CN[8]) with Cy_3P to 100 °C for 12 h gave $Cy_3P(C_6F_4)BF(C_6F_5)_2$ **12**[6] in good yield.[28] This finding suggests a distinct mechanistic possibility in which nucleophilic para attack is concurrent with ligand displacement from boron (Scheme 3), although thermal generation of free borane cannot be excluded.

In summary, the zwitterionic phosphonium borates $R_3P(C_6F_4)BF(C_6F_5)_2$ are readily available from thermal rearrangement of classical Lewis donor−borane adducts. The chemistry of these unique species continues to be the subject of study in our laboratories.

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Supporting Information Available: Crystallographic data in CIF format and preparative details and full spectroscopic and analytical characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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