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Phosphonium–Borate Zwitterions, Anionic Phosphines, and Dianionic Phosphonium–Dialkoxides via Tetrahydrofuran Ring-Opening Reactions

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Sterically demanding secondary phosphines and phosphides react with (THF)B(C_6F_5)$_3$ (THF = tetrahydrofuran) to give the THF ring-opened compounds [$R_2PHC_4H_8OB(C_6F_5)_3$] and [$Mes_2PC_4H_8OB(C_6F_5)_3Li(THF)_2$] (Mes = C_6H_2Me-2,4,6). These reactions also occur consecutively to give the double THF ring-opened compounds [$Mes_2P(C_4H_8OB(C_6F_5)_3)_2$][$Li(THF)_4$] and [$t$-$Bu_2P(C_4H_8OB(C_6F_5)_3)_2Li$].

Ring-opening reactions of tetrahydrofuran (THF) mediated by Lewis acidic metal centers including complexes of U,[1,2] Sm,[3] Ti,[4] and Zr[5−7] have been described in the literature. In contrast, ring-opening reactions with main-group Lewis acids are less common. A boron center in a manganese carborane complex was shown to prompt THF ring opening in reactions with either PPh_3 or NEt_3.[8] Campbell and Gladfelter reported ring opening in reactions of an amine−alane adduct in THF,[9] while Kunnari et al. reported the ring opening of THF upon treatment of $TeBr_4$ with PPh_3 in THF.[10] More recently, Chivers and Schatte have reported that THF ring opening occurs in the reaction of a tellurium diimide dimer with $B(C_6F_5)_3$.[11] While often the isolation of these ring-opened products was unexpected, the now numerous examples suggest the possibility that such reactions could be used in a contrived manner. Our interest in phosphorus-based ligands prompted us to consider the reactions of THF and phosphorus-based nucleophiles in the presence of a Lewis acid. To that end, we have probed reactions of the Lewis acid−base adduct (THF)B(C_6F_5)$_3$ with sterically demanding phosphines and phosphides. Herein, we demonstrate that such reactions affect the facile and quantitative ring opening of THF, affording synthetic routes to zwitterionic phosphonium borates or the lithium salt of a phosphine borate. Alternatively, these reactions can be done in tandem to provide lithium salts of phosphonium diborate ligands.

In the selection of a suitable phosphorus-based nucleophile, we noted that the reaction of (THF)B(C_6F_5)$_3$ with Ph_2PH leads to the expected and known ligand-exchange product (Ph_2PH)B(C_6F_5)$_3$,[12] liberating THF. However, the analogous reaction employing the sterically demanding phosphine Mes_2PH (Mes = C_6H_2Me-2,4,6) does not proceed in this fashion. Rather, the reaction of $B(C_6F_5)_3$, THF, and Mes_2PH afforded a tan solid **1** in 79% yield after a 72-h reaction at 25 °C and appropriate workup.[13] The ^{11}B and ^{31}P NMR spectra revealed singlet resonances at −2.8 and −12.0 ppm, respectively. ^1H NMR data reveal methylene resonances at 3.48, 2.85, 1.62, and 1.23 ppm as well as resonances attributable to the mesityl groups. These spectroscopic data confirm the presence of the $B(C_6F_5)_3$ and $PMes_2$ fragments in **1** as well as a ring-opened THF molecule. Recrystallization afforded X-ray-quality crystals that provided confirmation of the formulation of **1** as the zwitterionic phosphonium borate [$Mes_2PHC_4H_8OB(C_6F_5)_3$] (Figure 1a and Scheme 1).[14] The ring-opened THF results in a O−B bond of 1.459(4) Å and a P−C bond of 1.804(3) Å. These parameters are typical, while the remaining metric parameters within the molecule are unexceptional. In a similar fashion, reaction of t-Bu_2PH with (THF)B(C_6F_5)$_3$ afforded the analogous zwitterionic ring-opened product [t-$Bu_2PHC_4H_8OB(C_6F_5)_3$] (**2**), as confirmed by both spectroscopic[13] and crystallographic data (Figure 1b and Scheme 1).[14]

The related anionic phosphine borate is readily formed via the reaction of a solution of (THF)B(C_6F_5)$_3$ with [$PMes_2$]-

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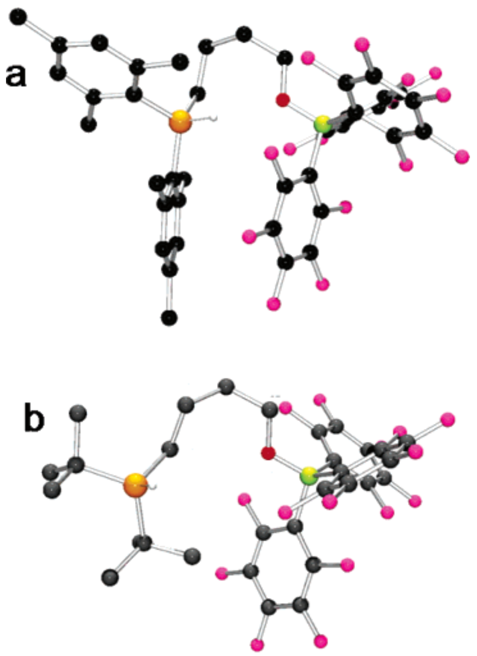
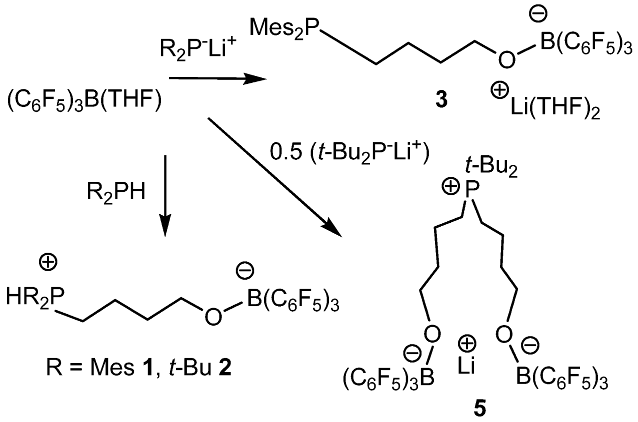


Figure 1. POV-ray depiction of (a) **1** and (b) **2**: carbon, black; phosphorus, orange; fluorine, pink; boron, yellow-green; oxygen, red; hydrogen, light gray.

Scheme 1. Ring-Opening Reactions of THF with Sterically Demanding Phosphines and Phosphides



Li. Subsequent workup yields a tan solid **3** in 80%.[13] Recrystallization afforded X-ray-quality crystals that provided confirmation of the formulation of **3** as $[Mes_2PC_4H_8OB(C_6F_5)_3Li(THF)_2]$ (Figure 2 and Scheme 1).[14] Again, as with **1** and **2**, THF ring opening has resulted in the formation of a four-coordinate boron center in **3**, with the formation of a B−alkoxide bond of 1.484(5) Å. However, the concurrently formed P−C bond affords a neutral and pendant diarylalkylphosphine moiety. Countering the anionic charge of the borate is a lithium cation. The lithium center is also pseudotetrahedral, being coordinated to two THF molecules, the alkoxide oxygen, and an o-fluorine atom from one of the arene groups on boron. The Li−O distances range between 1.891(10) and 1.967(10) Å, while the Li−F approach is 2.015(9) Å.

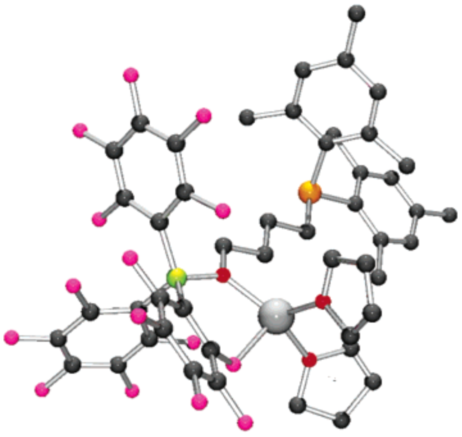


Figure 2. POV-ray depiction of **3**: carbon, black; phosphorus, orange; fluorine, pink; boron, yellow-green; oxygen, red; lithium, gray.

Given the formation of **1**−**3**, it was proposed that the phosphine formed in **3** should be capable of initiating a second ring opening. Thus, the reaction of $(THF)B(C_6F_5)_3$ and Mes_2PLi was repeated with the adjusted stoichiometry of 2:1. Following a similar workup procedure, the product **4** was isolated in 80% yield.[13] While the ^{11}B NMR chemical shift of −2.99 ppm is similar to that seen in **3**, the ^{31}P NMR chemical shift of 30.9 ppm observed for **4** is markedly upfield of the corresponding resonance for **3**. This latter observation

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(13) All NMR data were recorded in C_6D_6 unless otherwise stated. J values are given in Hz. **1**: ^1H NMR δ 7.33 (dt, $^1J_{H-P} = 531$, $^3J_{H-H} = 7$, 1H), 6.40 (d, $^4J_{H-P} = 4$, 4H), 3.48 (m, 2H), 2.85 (m, 2H), 1.90 (s, 6H), 1.87 (s, 12H), 1.62 (m, 2H), 1.23 (m, 2H); ^{11}B NMR δ −2.8; $^{13}C\{^1H\}$ NMR δ 149.0 (dm, $^1J_{C-F} = 246$), 146.1 (s), 143.4 (d, $^2J_{C-P} = 11$), 139.3 (dm, $^1J_{C-F} = 252$), 137.5 (dm, $^1J_{C-F} = 257$), 132.2 (d, $^2J_{C-P} = 11$), 125.0 (s), 112.1 (d, $^1J_{C-P} = 80$), 65.6 (s), 30.9 (s), 24.9 (d, $^1J_{C-P} = 58$), 23.9 (s), 21.8 (d, $^3J_{C-P} = 8$), 21.1 (s); ^{19}F NMR δ −133.9 (d, $^3J_{F-F} = 23$), −162.2 (s), −165.9 (s); ^{31}P NMR δ −12.0. **2**: ^1H NMR (C_6D_6) δ 5.60 (dt, $^1J_{H-P} = 453$, $^3J_{H-H} = 4$, 1H), 3.24 (t, $^3J_{H-H} = 5$, 2H), 2.64 (m, 2H), 1.99 (m, 2H), 1.67 (m, 2H), 1.45 (d, $^3J_{H-P} = 16$, 18H); ^{11}B NMR δ −2.9; $^{13}C\{^1H\}$ NMR δ 149.2 (dm, $^1J_{C-F} = 230$), 139.3 (dm, $^1J_{C-F} = 244$), 137.4 (dm, $^1J_{C-F} = 237$), 125.7 (s), 64.4 (s), 33.6 (d, $^1J_{C-P} = 36$), 32.8 (d, $^3J_{C-P} = 11$), 27.1 (s), 26.9 (m), 15.0 (d, $^1J_{C-P} = 39$); ^{19}F NMR δ −133.9 (d, $^3J_{F-F} = 23$), −164.8 (t, $^3J_{F-F} = 11$), −168.0 (t, $^3J_{F-F} = 20$); ^{31}P NMR δ 50.9. **3**: ^1H NMR (CD_2Cl_2) δ 6.75 (s, 4H), 3.72 (s, 8H), 3.22 (m, 2H), 2.33 (m, 2H), 2.20 (s, 18H), 1.85 (s, 8H), 1.49 (m, 2H), 1.14 (m, 2H,); ^{11}B NMR (CD_2Cl_2) δ −3.1; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 148.4 (dm, $^1J_{C-F} = 240$), 142.2 (d, $^2J_{C-P} = 13$), 139.7 (dm, $^1J_{C-F} = 240$), 138.1 (s), 137.3 (dm, $^1J_{C-F} = 240$), 130.4 (s), 122.5, 117.9, 68.9 (s), 65.6 (s), 33.4 (d, $^2J_{C-P} = 14$), 28.2 (d, $^1J_{C-P} = 14$), 25.9 (s), 23.9 (s), 23.2 (d, $^3J_{C-P} = 13.6$), 21.0 (s); ^{19}F NMR (CD_2Cl_2) δ −137.6 (d, $^3J_{F-F} = 20$), 161.0 (t, $^3J_{F-F} = 20$), −165.6 (t, $^3J_{F-F} = 20$); ^{31}P NMR (CD_2Cl_2) δ −21.4. **4**: ^1H NMR (CD_2Cl_2) δ 6.99 (d, $^4J_{H-P} = 4$), 3.69 (s, 16H), 3.15 (m, 4H), 2.75 (m, 4H), 2.32 (s, 6H), 2.17 (s, 12H), 1.85 (s, 16H), 1.48 (m, 4H), 1.36 (m, 4H); ^{11}B NMR (CD_2Cl_2) δ −3.0; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 148.4 (dm, $^1J_{C-F} = 240$), 145.8 (s), 142.2 (d, $^2J_{C-P} = 10$), 139.3 (dm, $^1J_{C-F} = 240$), 137.3 (dm, $^1J_{C-F} = 240$), 133.5 (d, $^3J_{C-P} = 10$), 123.4, 117.1 (d, $^1J_{C-P} = 88$), 68.7 (s), 64.8 (s), 32.3 (d, $^2J_{C-P} = 13$), 27.2 (d, $^1J_{C-P} = 45$), 25.9 (s), 23.5 (d, $^3J_{C-P} = 14$), 21.2 (s), 21.0 (s); ^{19}F NMR (CD_2Cl_2) δ −136.1 (s), −161.8 (s), −166.0 (m); ^{31}P NMR (CD_2Cl_2) δ 30.9. **5**: ^1H NMR (THF-d_8) δ 3.22 (t, $^3J_{H-H} = 5$, 4H), 2.51 (m, 4H), 1.92 (m, 4H), 1.65 (m, 2H), 1.35 (d, $^3J_{H-P} = 14$, 18H); ^{11}B NMR δ −2.9; $^{13}C\{^1H\}$ NMR δ 149.2 (dm, $^1J_{C-F} = 246$), 139.2 (dm, $^1J_{C-F} = 244$), 137.5 (dm, $^1J_{C-F} = 245$), 126.2, 64.5 (s), 35.3 (d, $^1J_{C-P} = 38$), 33.4 (d, $^3J_{C-P} = 12$), 27.5 (s), 26.6 (m), 17.8 (d, $^1J_{C-P} = 40$); ^{19}F NMR δ −133.9 (d, $^3J_{F-F} = 23$), −165.2 (t, $^3J_{F-F} = 11$), −168.2 (t, $^3J_{F-F} = 20$); ^{31}P NMR δ 45.3.

(14) X-ray data. **1**: space group $P2_1/c$, $a = 16.3017(14)$ Å, $b = 15.3950(13)$ Å, $c = 19.5528(17)$ Å, $\beta = 103.1340(10)°$, $V = 4778.7(7)$ Å^3, $R = 0.0577$, $R_w = 0.1364$, GOF = 0.978. **2**: space group $C2/c$, $a = 15.488(3)$ Å, $b = 21.574(3)$ Å, $c = 19.979(3)$ Å, $\beta = 111.543(3)°$, $V = 6209.7(18)$ Å^3, $R = 0.0423$, $R_w = 0.1102$, GOF = 1.011. **3**: space group $P2_1/c$, $a = 21.187(5)$ Å, $b = 12.700(3)$ Å, $c = 21.530(5)$ Å, $\beta = 109.807(3)°$, $V = 5451(2)$ Å^3, $R = 0.0691$, $R_w = 0.1697$, GOF = 0.988. **5**: space group $P2_1/n$, $a = 12.841(9)$ Å, $b = 15.686(11)$ Å, $c = 29.97(2)$ Å, $\beta = 94.046(12)°$, $V = 6022(7)$ Å^3, $R = 0.1266$, $R_w = 0.3381$, GOF = 0.990.

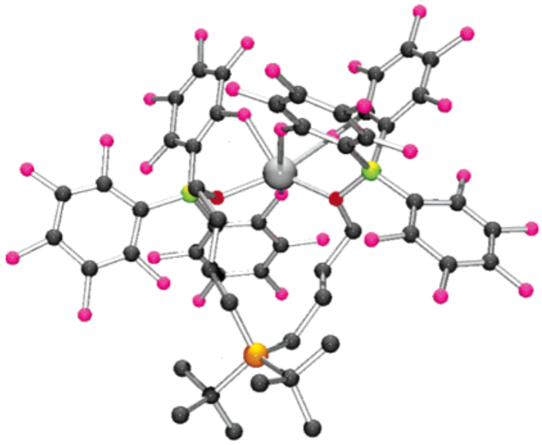

Figure 3. POV-ray depiction of **5**: carbon, black; phosphorus, orange; fluorine, pink; boron, yellow-green; oxygen, red; lithium, gray.

suggests the formation of a phosphonium center. The ^{19}F NMR spectra give resonances at −136.1, −161.8, and −166.0 ppm, typical of the anionic $OB(C_6F_5)_3$ fragment. The ^{1}H NMR data for **4** are consistent with the ring opening of THF because methylene resonances are observed at 3.15, 2.75, 1.48, and 1.36 ppm, although the integration is consistent with a 1:1 ratio of mesityl/methylene chain fragments. In addition, resonances at 3.69 and 1.85 ppm were attributed to THF coordinated to lithium. On the basis of these data, **4** was formualated as $[(C_6H_2Me\text{-}2,4,6)_2P(C_4H_8OB(C_6F_5)_3)_2][Li(THF)_4]$. Unfortunately, attempts to obtain X-ray-quality crystals of **4** were unsuccessful, and thus this formulation was not confirmed crystallographically.

Following a similar procedure, the analogous reaction of a 2:1 ratio of $(THF)B(C_6F_5)_3$ and $t\text{-}Bu_2PLi$ was performed. The resulting white solid **5** was isolated in 89% yield.[13] The NMR data for **5** were similar to those reported for **4**, with a ^{11}B NMR signal at −2.90 ppm and a ^{31}P NMR resonance at 45.3 ppm consistent with the presence of both borate and phosphonium fragments. In a similar fashion, the ^{1}H NMR data were consistent with THF ring opening, affording two methylene chains on phosphorus. In contrast to **4**, compound **5** does not contain THF. The resulting formulation for **5** based on these data is $[t\text{-}Bu_2P(C_4H_8OB(C_6F_5)_3)_2]Li$. Crystals of $[t\text{-}Bu_2P(C_4H_8OB(C_6F_5)_3)_2]Li\cdot 0.5C_6H_6$ were grown from a THF/benzene/pentane solution at 25 °C (Figure 3 and Scheme 1).

Although the crystal quality of **5** is not the best, the data do confirm the formulation and establish the connectivity.[14] Two butoxide chains link the cationic phosphonium center to two anionic borate fragments. The lithium counterion is coordinated to the two oxygen atoms and interacts with four fluorine atoms on the boron-bound aryl rings. This results in a distorted octahedral coordination sphere for the lithium atom. The Li−O distances average 2.052(19) Å, while the Li−F interactions range from 2.02(2) to 2.240(19) Å.

It should be noted that in the absence of $B(C_6F_5)_3$ the reaction of THF with $[Et_2P]Li$ was reported in 1959 to give an uncharacterized product upon standing in a THF solution for prolonged periods.[15] Subsequently, in 1968, the ring opening of THF by $[Me_2P]Li$ in refluxing THF was reported.[16] In related chemistry, PX_3 and THF in the presence of HgX_2 has been shown to give moderate yields of ring-opened phosphorus acid esters.[17] However, the formation of **1**−**5** demonstrates that sterically demanding nucleophilic phosphines and phosphides effect the ring opening of THF in $(THF)B(C_6F_5)_3$. This stands in contrast to the related reactions of sterically less demanding phosphines such as Cy_2PH or Ph_2PH, which form the simple adducts $(R_2PH)B(C_6F_5)_3$.[12] Steric demand is thought to disfavor ligand-exchange reactions and thus prompt ring-opening reactions. The quantitative nature of these reactions affords the opportunity to examine the chemistry of phosphonium borate zwitterions and the coordination chemistry of new anionic phosphine and anionic phosphonium−dialkoxide ligands. This work and the versatility of the reactions of Lewis acid adducts and sterically demanding nucleophiles in ligand synthesis are under investigation. The results of these studies will be reported in due course.

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

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