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Heterolytic Cleavage of Disulfides by Frustrated Lewis Pairs

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The addition of diphenyl disulfide (PhSSPh) to tBu$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ (**1**) affords the zwitterionic phosphonium borate [tBu$_2$P(SPh)(C$_6$F$_4$)B(SPh)(C$_6$F$_5$)$_2$] (**2**), while the addition of a base or donor solvent to **2** effected the liberation of disulfide and the formation of [tBu$_2$P(C$_6$F$_4$)B(donor)(C$_6$F$_5$)$_2$]. The reaction of **1** with S$_8$ gave tBu$_2$P(S)(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ (**3**). In a similar fashion, the frustrated Lewis pair of tBu$_3$P/B(C$_6$F$_5$)$_3$ reacts with RSSR to give [tBu$_3$P(SR)][(RS)B(C$_6$F$_5$)$_3$] (R = Ph (**4**), *p*-tolyl (**5**), *i*Pr (**6**)). In contrast, the corresponding reaction of BnSSBn yields a 1:1:1 mixture of tBu$_3$P=S, Bn$_2$S, and B(C$_6$F$_5$)$_3$. Species **4** reacts with *p*-tolylSS*p*-tolyl to give a mixture of **4**, **5**, PhSSPh, and *p*-tolylSS *p*-tolyl, while treatment of **5** with PhSSPh afforded a similar mixture. To probe this, a crossover experiment between [tBu$_3$P(SPh)][B(C$_6$F$_5$)$_4$] (**7**) and [NBu$_4$][(*p*-tolylS)B(C$_6$F$_5$)$_3$] (**9**) was performed. The former species was prepared by a reaction of **4** with [Ph$_3$C][B(C$_6$F$_5$)$_4$], while cation exchange of [(Et$_2$O)$_2$Li(*p*-tolylS)B(C$_6$F$_5$)$_3$] (**8**) with [NBu$_4$]Br gave **9**. The reaction of compounds **7** and **9** gave a statistical mixture of the cations [tBu$_3$P(SR)]$^+$ and anions [(RS)B(C$_6$F$_5$)$_3$]$^-$, R = Ph, S*p*-tolyl. The mechanism of this exchange process was probed and is proposed to be an equilibrium involving disulfide and the frustrated Lewis pair. Crystallographic data are reported for compounds **4**−**8**, and the natures of the P−S cations are examined via DFT calculations.

Introduction

The activation of E−E and E−H bonds (E = B, Si, S, Sn) and their transfer to unsaturated carbon molecules are important processes in organic synthesis.[1−4] Specifically, carbon−sulfur-bond-forming reactions are important for drug development, and many organosulfur compounds are biologically active.[5] The cleavage of S−H and S−S bonds is well-known and can be accomplished using transition metals[4,6] and main group nucleophiles and electrophiles.[7] Recently, several papers have described the Lewis acid catalyzed disulfidation of alkenes and alkynes employing BF_3,[8] $AlCl_3$,[9] $GaCl_3$,[10,11] $FeCl_3$,[9] and $ZnCl_2$[12] as catalysts. In each case, it is proposed that the Lewis acid initially interacts with a disulfide, generating a partial sulfenium cation which then reacts with the unsaturated carbon−carbon bond. Nucleophilic attack of the intermediate by the thiolate anion gives the desired dithiolated product. On the other hand, phosphines have been shown to promote the desulfurization of di- and trisulfides,[13] while the conversion of disulfides to thiols by phosphines in the presence of H_2O is widely known.[14−18] Additionally, a recent computation study has suggested that phosphines react with disulfides via an S_N2 mechanism, generating phosphonium cation−thiolate anion salts of the form [R_3PSR][SR],[19] which is thought to be involved in the phosphine-catalyzed metathesis of disulfides.[20] While

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these intermediates have not been isolated, thiophosphonium cations $[R_3PSR]^+$ are known to be stable species[21−23] and have been prepared by electrochemical reduction of disulfides[21] in the presence of phosphines or by the reduction of phosphine sulfides.[22]Related reports of sulfenium cations $[RS]^+$ are rare, with the elusive species only being observed in the gas phase[24] or via stabilization with one[25]or two[26] nitrogen donors.

In other work, we have recently described in a series of papers the activation of small molecules by frustrated Lewis pairs (FLPs).[27,28] These systems exploit the combination of unquenched Lewis acidity and basicity to react with H_2,[29−39] olefins,[40] dienes,[41] B−H bonds,[42] alkynes,[43] CO_2,[44] and N_2O.[45] In this report, we exploit FLPs to effect the heterolytic activation of disulfides and stabilize the resulting cleavage products as thiophosphonium thioborate zwitterions and salts.

Experimental Section

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glovebox. Solvents (pentane, hexanes, toluene, and methylene chloride) were purified employing a Grubbs' type column system manufactured by Innovative Technology and were stored over molecular sieves (4 Å). Molecular sieves (4 Å) were purchased from Aldrich Chemical Co. and dried at 140 °C under a vacuum for 24 h prior to use. Deuterated solvents were dried over Na/benzophenone (C_6D_6, C_7D_8, THF-d_8) or CaH_2 (CD_2Cl_2, C_6D_5Br) and vacuum-distilled prior to use. All common organic reagents were purified by conventional methods unless otherwise noted. ^1H, ^{13}C, ^{11}B, ^{19}F, and ^{31}P nuclear magnetic resonance (NMR) spectroscopy spectra were recorded on a Bruker Avance-300 spectrometer at 300 K unless otherwise noted. ^1H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B, and ^{19}F NMR experiments were referenced to 85% H_3PO_4, $BF_3(OEt_2)$, and $CFCl_3$, respectively. Chemical shifts are reported in parts per million and coupling constants in hertz as absolute vaules. DEPT and 2-D $^1H/^{13}C$ correlation experiments were completed for assignment of the carbon atoms. Combustion analyses were performed in-house employing a Perkin-Elmer CHN Analyzer. $B(C_6F_5)_3$ was generously donated by NOVA Chemicals Corporation. tBu$_3$P was purchased from Strem Chemicals and used as-received. tBu$_2$PH(C_6F_4)BH$(C_6F_5)_2$ and tBu$_2$P(C_6F_4)B$(C_6F_5)_2$ (**1**) were prepared as previously published.[46]

Synthesis of [tBu$_2$(PhS)P(C_6F_4)B(SPh)$(C_6F_5)_2$] (2). A 20 mL vial was charged with **1** (0.200 g, 0.31 mmol) and toluene (5 mL), forming an orange solution. To this solution was added PhSSPh (0.070 g, 0.32 mmol) in toluene (5 mL) dropwise at room temperature. An immediate color change from orange to faint yellow was observed. The reaction was stirred at room temperature for 1 h. All volatile materials were removed in vacuo to give an off-yellow solid. Yield: 205 mg (76%). ^1H NMR (C_6D_5Br): 7.86 (d, 2H, $^3J_{H-H}$ = 7 Hz, Ph), 7.78 (d, 2H, $^3J_{H-H}$ = 7 Hz, Ph), 7.54 (d, 2H, $^3J_{H-H}$ = 8 Hz, Ph), 7.43 (m, 2H, Ph), 7.21 (t, 2H, $^3J_{H-H}$ = 8 Hz, Ph), 1.34 (d, 18H, $^3J_{H-P}$ = 19 Hz, PtBu). $^{11}B\{^1H\}$ NMR (C_6D_5Br): −9.76. $^{13}C\{^1H\}$ NMR (C_6D_5Br) partial: 149.84 (dm, $^1J_{C-F}$ = 254 Hz, *C*F), 148.56 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 146.32 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 142.07 (s, PS*Ph*), 139.35 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 137.41 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 135.17 (s, PS*Ph*), 133.67 (s, BS*Ph*), 131.72 (s, PS*Ph*), 128.71 (d, $^2J_{C-P}$ = 120 Hz, quat, PS*Ph*), 127.91 (s, BS*Ph*), 124.64 (s, BS*Ph*), 45.16 (d, $^1J_{C-P}$ = 22 Hz, tBu), 28.58 (s, tBu). ^{19}F NMR (C_6D_5Br): δ −123.93 (br s, 3F, C_6F_4), −130.35 (br s, 1F, C_6F_4), −130.89 (m, 4F, $^3J_{F-F}$ = 20 Hz, *o*-C_6F_5), −161.04 (m, 2F, $^3J_{F-F}$ = 17 Hz, *p*-C_6F_5), −165.36 (m, 4F, $^3J_{F-F}$ = 20 Hz, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (C_6D_5Br): δ 76.2 (s). Anal. Calcd for $C_{38}H_{28}BF_{14}PS_2$: C, 53.29; H, 3.29. Found: C, 54.05; H, 3.85%.

Synthesis of tBu$_2$P(S)(C_6F_4)B$(C_6F_5)_2$ (3). Method A. A 20 mL vial was charged with **1** (0.132 g, 0.21 mmol), S_8 (0.007 g, 0.22 mmol), and toluene (10 mL), forming a yellow slurry. The reaction was stirred at room temperature for 12 h. The reaction mixture was filtered through Celite, and all volatile materials were removed in vacuo to give a sticky yellow solid. The product was slurried in hexanes and stirred for 30 min, and the solvent removed in vacuo to give an off-yellow powder. Yield: 120 mg (87%).

Method B. A Teflon cap-sealable J. Young NMR tube was charged with tBu$_2$PH(C_6F_4)BH$(C_6F_5)_2$, the precursor to **1** (0.029 g, 0.045 mmol), S_8 (0.010 mg, 0.31 mmol), and C_6D_5Br (0.75 mL), forming a slurry. The NMR tube was sealed and heated to 150 °C for 10 min. During this time, vigorous bubbling was observed (H_2 elimination), all solids dissolved, and the reaction became intense yellow in color. The reaction was cooled, and NMR confirmed 100% product formation and no coordination of the excess S_8 to boron.

^1H NMR (C_6D_5Br): 1.31 (d, 18H, $^1J_{H-P}$ = 17 Hz, PtBu. $^{11}B\{^1H\}$ NMR (C_6D_5Br): No signal observed. $^{13}C\{^1H\}$ NMR (C_6D_5Br) partial: 148.87 (dm, $^1J_{C-F}$ = 251 Hz, *C*F), 144.89 (dm, $^1J_{C-F}$ = 257 Hz, *C*F), 137.72 (dm, $^1J_{C-F}$ = 257 Hz, *C*F), 113.82 (quat) 33.62 (d, $^1J_{C-P}$ = 39 Hz, PtBu), 27.67 (s, C(CH_3)$_3$). ^{19}F NMR (C_6D_5Br): −119.44 (s, 1F, C_6F_4), −125.38 (s, 1F, C_6F_4), −126.74 (s, 1F, C_6F_4), 127.78 (s, 4F, *o*-C_6F_5), −130.01 (s, 1F, C_6F_4), −144.49 (s, 2F, *p*-C_6F_5), −160.46 (s, 4F, *m*-C_6F_5).

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$^{31}P\{^{1}H\}$ NMR (C_6D_5Br): 85.9 (s). Anal. Calcd for $C_{26}H_{18}BF_{14}PS$: C, 46.59; H, 2.71.

Synthesis of [*t*Bu$_3$P(SPh)][(PhS)B(C$_6$F$_5$)$_3$] (4), [*t*Bu$_3$P(S*p*-tolyl)][(*p*-tolylS)B(C$_6$F$_5$)$_3$] (5), and [tBu$_3$P(SiPr)][(iPrS)B(C$_6$F$_5$)$_3$] (6). These compounds were prepared in a similar fashion, and thus only one preparation is detailed. A solution of PhSSPh (106 mg, 0.4 mg) and $B(C_6F_5)_3$ (249 mg, 0.5 mmol) in toluene (10 mL) was cooled to −35 °C, and *t*Bu$_3$P (98 mg, 0.4 mmol) in toluene (1 mL) was added in one portion. A colorless immiscible oil formed immediately, and the toluene layer was decanted and the oil washed with toluene (2 × 10 mL). The oil was dried under reduced pressure and subsequently triturated with pentane until a white solid formed. This solid was washed with pentane (3 × 10 mL) and dried in vacuo (399 mg, 88%). ^{1}H NMR (CD_2Cl_2): 7.89 (m, 2H, $^{3}J_{H-H}$ = 8 Hz, Ph), 7.57 (m, 1H, $^{3}J_{H-H}$ = 8 Hz, Ph), 7.49 (m, 2H, $^{3}J_{H-H}$ = 8 Hz, Ph), 7.09 (m, 2H, $^{3}J_{H-H}$ = 8 Hz, Ph), 6.88 (m, 3H, $^{3}J_{H-H}$ = 8 Hz, Ph), 1.67 (d, 27H, $^{3}J_{H-P}$ = 16 Hz, P*t*Bu). $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2): −9.95 (s). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) partial: 148.56 (dm, $^{1}J_{C-F}$ = 245 Hz, *C*F), 142.72 (s, PS*Ph*), 138.96 (dm, $^{1}J_{C-F}$ = 240 Hz, *C*F), 138.48 (s, PS*Ph*), 137.11 (dm, $^{1}J_{C-F}$ = 245 Hz, *C*F), 133.43 (s, BS*Ph*), 131.30 (s, PS*Ph*), 128.94 (d, $^{2}J_{C-P}$ = 110 Hz, quat, PS*Ph*), 127.72 (s, BS*Ph*), 124.02 (s, BS*Ph*), 46.46 (d, $^{1}J_{C-P}$ = 15 Hz, *t*Bu), 30.96 (s, *t*Bu). ^{19}F NMR (CD_2Cl_2): −131.70 (d, 6F, $^{3}J_{F-F}$ = 23 Hz, *o*-C$_6$*F*$_5$), −163.65 (t, 3F, $^{3}J_{F-F}$ = 20 Hz, *p*-C$_6$*F*$_5$), −167.56 (m, 6F, $^{3}J_{F-F}$ = 20 Hz, *m*-C$_6$*F*$_5$). ^{31}P NMR (CD_2Cl_2): 85.7 (s). Anal. Calcd for $C_{42}H_{37}BF_{15}PS_2$ (932.648): C, 54.09; H, 4.00. Found: C, 54.19; H, 4.20.

Compound **5**. White crystalline solid (304 mg, 90%). ^{1}H NMR (C_6D_5Br): 7.49 (m, 4H, *m*-Ar), 7.11 (d, 2H, $^{3}J_{H-H}$ = 8 Hz, *o*-BS*Ar*), 6.88 (d, 2H, $^{3}J_{H-H}$ = 8 Hz, *o*-PS*Ar*), 2.25 (s, 3H, PSC$_6$H$_4$Me), 2.17 (s, 3H, BSC$_6$H$_4$Me), 1.28 (d, 27H, $^{3}J_{H-P}$ = 16 Hz, P*t*Bu). $^{11}B\{^{1}H\}$ NMR (C_6D_5Br): −9.13 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_5Br) partial: 148.8 (dm, $^{1}J_{C-F}$ = 240 Hz, *o*-C$_6$F$_5$), 143.8 (s), 139.5(s), 138.7 (dm, $^{1}J_{C-F}$ = 250 Hz, *p*-C$_6$F$_5$), 137.9 (s), 137.8 (s), 137.2 (dm, $^{1}J_{C-F}$ = 242 Hz, *m*-C$_6$F$_5$), 133.7 (s), 133.1 (s), 131.6 (s), 128.6 (s), 117.5 (d, J_{P-C} = 14 Hz), 45.4 (d, $^{1}J_{C-P}$ = 16 Hz, *t*Bu), 30.2 (s, *t*Bu), 21.5 (s, br, PSC$_6$H$_4$*Me*), 21.2 (s, BSC$_6$H$_4$*Me*). ^{19}F NMR (CD_2Cl_2): −131.68 (d, 6F, $^{3}J_{F-F}$ = 23 Hz, *o*-C$_6$*F*$_5$), −163.89 (t, 3F, $^{3}J_{F-F}$ = 21 Hz, *p*-C$_6$*F*$_5$), −167.76 (t, 6F, $^{3}J_{F-F}$ = 19 Hz, *m*-C$_6$*F*$_5$). ^{31}P NMR (C_6D_5Br): 84.9 (s). Anal. Calcd for $C_{44}H_{41}BF_{15}PS_2$ (960.702): C, 55.01; H, 4.30. Found: C, 54.82; H, 4.42. X-ray quality crystals were grown from the slow cooling of a saturated solution in PhCl.

Compound **6**. White crystalline solid (126 mg, 93%). ^{1}H NMR (CD_2Cl_2): 3.91 (m, 1H, PS*iPr*), 2.12 (sept, 1H, $^{3}J_{H-H}$ = 7 Hz, BS*i*Pr), 1.67 (m, 33H, P*t*Bu + PS*iPr*), 1.02 (d, 6H, BS*i*Pr). $^{11}B\{^{1}H\}$ NMR (C_6D_5Br): −11.04 (s). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) partial: 148.72 (dm, $^{1}J_{C-F}$ = 241 Hz, *o*-C$_6$F$_5$), 138.65 (dm, $^{1}J_{C-F}$ = 245 Hz, *p*-C$_6$F$_5$), 137.17 (dm, $^{1}J_{C-F}$ = 240 Hz, *m*-C$_6$F$_5$), 45.68 (d, $^{1}J_{C-P}$ = 18 Hz, PtBu), 42.02 (d, $^{2}J_{C-P}$ = 7 Hz, PS*iPr*), 33.44 (s, BS*iPr*), 30.69 (s, C(*C*H$_3$)$_3$), 27.25 (s, BS*iPr*), 27.14 (d, $^{3}J_{C-P}$ = 3 Hz, PS*iPr*). ^{19}F NMR (CD_2Cl_2): −131.13 (d, 6F, $^{3}J_{F-F}$ = 21 Hz, *o*-C$_6$F$_5$), −163.91 (t, 3F, $^{3}J_{F-F}$ = 21 Hz, *p*-C$_6$F$_5$), −167.76 (t, 6F, $^{3}J_{F-F}$ = 20 Hz, *m*-C$_6$F$_5$). ^{31}P NMR (C_6D_5Br): δ 88.0 (s). Anal. Calcd for $C_{36}H_{41}BF_{15}PS_2$ (864.614): C, 50.01; H, 4.78. Found: C, 49.77; H, 4.72. X-ray-quality crystals were grown from the slow cooling of a saturated solution in CH_2Cl_2.

Reaction of *t*Bu$_3$P, B(C$_6$F$_5$)$_3$ and BnSSBn. Dibenzyl disulfide (47 mg, 0.19 mmol) was added in one portion to a solution of *t*Bu$_3$P (one portion to a solution of *t*Bu$_3$P (50 mg, 0.19 mol) and $B(C_6F_5)_3$ (98 mg, 0.19 mmol) in toluene (3 mL) and the reaction mixture shaken until dissolution was complete. The solution remained colorless, and an immediate phase separation was observed. However, within 5 min of the initial mixing, the reaction mixture became monophasic. The solvent was removed under reduced pressure to afford a white solid that was spectroscopically identical to a 1:1:1 mixture of *t*Bu$_3$P=S, Bn$_2$S, and $B(C_6F_5)_3$.

Synthesis of [*t*Bu$_3$P(SPh)][B(C$_6$F$_5$)$_4$] (7). In one portion, $[Ph_3C][B(C_6F_5)_4]$ (112 mg, 0.12 mmol) was added to a solution of **4** (110 mg, 0.12 mmol) in dichloromethane (5 mL). The reaction mixture was shaken until it turned pale yellow. The solvent was removed under reduced pressure to afford pale yellow crystals, which were washed with pentane (5 mL) and dried further, affording 92 mg of product (79%). ^{1}H NMR (CD_2Cl_2): 7.86 (d, 2H, $^{3}J_{H-H}$ = 8 Hz, *o*-Ph), 7.62 (t, 1H, $^{3}J_{H-H}$ = 8 Hz, *p*-Ph), 7.51 (t, 2H, $^{3}J_{H-H}$ = 8 Hz, *m*-Ph), 1.68 (d, 27H, $^{3}J_{H-P}$ = 16 Hz, P*t*Bu). $^{11}B\{^{1}H\}$ NMR (CD_2Cl_2): −16.67 (s). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) partial: 148.15 (dm, $^{1}J_{C-F}$ = 243 Hz, *o*-C$_6$F$_5$), 138.16 (dm, $^{1}J_{C-F}$ = 245 Hz, *p*-C$_6$F$_5$), 137.80 (d, J_{P-C} = 3 Hz), 136.36 (dm, $^{1}J_{C-F}$ = 243 Hz, *m*-C$_6$F$_5$), 132.54 (d, J_{P-C} = 3 Hz), 130.72 (d, J_{P-C} = 2 Hz), 121.23 (d, J_{P-C} = 10 Hz, *ipso*-C$_6$H$_5$), 45.86 (d, $^{1}J_{C-P}$ = 16 Hz, *t*Bu), 30.38 (s, *t*Bu). ^{19}F NMR (CD_2Cl_2): −133.46 (s, br, 6F, *o*-C$_6$*F*$_5$), −164.15 (t, 3F, $^{3}J_{F-F}$ = 21 Hz, *p*-C$_6$*F*$_5$), −167.97 (t, 6F, $^{3}J_{F-F}$ = 19 Hz, *m*-C$_6$*F*$_5$). ^{31}P NMR (CD_2Cl_2): 86.0 (s). Anal. Calcd for $C_{42}H_{32}BF_{20}PS$ (990.536): C, 50.93; H, 3.26. Found: C, 50.80; H, 3.57. X-ray-quality crystals were grown from the slow cooling of a saturated solution in CH_2Cl_2. The crystalline product was suitable for X-ray diffraction.

Synthesis of [(Et$_2$O)$_2$Li(*p*-tolylS)B(C$_6$F$_5$)$_3$] (8). A solution of $B(C_6F_5)_3$ (180 mg, 0.35 mmol) in diethyl ether (5 mL) was cooled to −35 °C, and a slurry of $LiSC_6H_4Me$ (35 mg, 0.35 mmol, formed from the 1:1 reaction of MeC_6H_4SH and *n*BuLi) in diethyl ether (2 mL) was added in one portion. The reaction was warmed to room temperature, and the solution was concentrated to one-half its original volume, layered with pentane (4 mL), and cooled to −35 °C overnight to afford white crystals (187 mg, 79%). ^{1}H NMR (*d*$_8$-THF): 6.90 (d, 2H, $^{3}J_{H-H}$ = 8 Hz), 6.62 (d, 2H, $^{3}J_{H-H}$ = 8 Hz), 3.38 (q, 8H, $^{3}J_{H-H}$ = 7 Hz, OC*H*$_2$CH$_3$), 2.09 (s, 3H, BSC$_6$H$_4$Me), 1.11 (m, 8H, $^{3}J_{H-H}$ = 7 Hz, OCH$_2$C*H*$_3$). $^{11}B\{^{1}H\}$ NMR (*d*$_8$-THF): −11.73 (s). $^{13}C\{^{1}H\}$ NMR (*d*$_8$-THF), partial: 146.3 (dm, $^{1}J_{C-F}$ = 238 Hz, *o*-C$_6$F$_5$), 137.3 (s), 136.2 (dm, $^{1}J_{C-F}$ = 241 Hz, *p*-C$_6$F$_5$), 134.3 (dm, $^{1}J_{C-F}$ = 257 Hz, *m*-C$_6$F$_5$), 131.2 (s), 130.2 (s), 125.3 (s), 63.5 (s, O*C*H$_2$CH$_3$), 18.06 (s, BSC$_6$H$_4$*C*H$_3$), 12.82 (s, OCH$_2$*C*H$_3$). ^{19}F NMR (C_6D_5Br): −132.73 (d, 6F, $^{3}J_{F-F}$ = 24 Hz, *o*-C$_6$F$_5$), −167.34 (t, 3F, $^{3}J_{F-F}$ = 20 Hz, *p*-C$_6$F$_5$), −170.69 (t, 6F, $^{3}J_{F-F}$ = 19 Hz, *m*-C$_6$F$_5$). Anal. Calcd for $C_{33}H_{27}LiBF_{15}O_2S$ (790.371): C, 50.15; H, 3.44. Found: C, 48.04; H, 3.29. The crystalline product was suitable for X-ray diffraction.

Synthesis of [NBu$_4$][(*p*-tolylS)B(C$_6$F$_5$)$_3$] (9). To a solution of **8** (334 mg, 0.5 mmol) in diethyl ether (5 mL) was added tetrabutylammonium bromide (161 mg, 0.5 mmol) in one portion. The solvent was removed under reduced pressure and the white solid recrystallized from a 1:1 mixture of chlorobenzene and pentane to afford a white crystalline solid (156 mg, 36%). ^{1}H NMR (C_6D_5Br): 7.23 (d, 2H, $^{3}J_{H-H}$ = 8 Hz), 6.72 (d, 2H, $^{3}J_{H-H}$ = 8 Hz), 2.70 (m, 8H, NC*H*$_2$), 2.02 (s, 3H, BSC$_6$H$_4$Me), 1.21 (m, 8H, NCH$_2$C*H*$_2$), 1.11 (m, 8H, C*H*$_2$CH$_3$), 0.79 (t, 12H, $^{3}J_{H-H}$ = 8 Hz CH$_2$C*H*$_3$). $^{11}B\{^{1}H\}$ NMR (C_6D_5Br): −8.95 (s). $^{13}C\{^{1}H\}$ NMR (C_6D_5Br) partial: 148.3 (dm, $^{1}J_{C-F}$ = 244 Hz, *o*-C$_6$F$_5$), 138.5 (dm, $^{1}J_{C-F}$ = 230 Hz, *p*-C$_6$F$_5$), 136.9 (dm, $^{1}J_{C-F}$ = 255 Hz, *m*-C$_6$F$_5$), 133.7 (s), 133.6 (s), 128.3 (s), 58.4 (s, NC*H*$_2$), 23.3 (s, NCH$_2$C*H*$_2$), 20.7 (s, BSC$_6$H$_4$*C*H$_3$), 19.5 (s, *C*H$_2$CH$_3$), 13.5 (s, CH$_2$C*H*$_3$). ^{19}F NMR (C_6D_5Br): −130.17 (d, 6F, $^{3}J_{F-F}$ = 22 Hz, *o*-C$_6$*F*$_5$), −161.64 (t, 3F, $^{3}J_{F-F}$ = 21 Hz, *p*-C$_6$*F*$_5$), −165.80 (t, 6F, $^{3}J_{F-F}$ = 20 Hz, *m*-C$_6$*F*$_5$). Anal. Calcd for $C_{41}H_{43}BNF_{15}S$ (877.654): C, 56.11; H, 4.94; N, 1.60. Found: C, 56.04; H, 5.04; N, 1.59.

Reaction of 7 and 9. To an intimate mixture of **7** (8.8 mg, 0.01 mmol) and **9** (9.9 mg, 0.01 mmol) was added CD_2Cl_2 (ca. 1 mL). ^{1}H, ^{11}B, ^{19}F, and $^{31}P\{^{1}H\}$ NMR spectroscopy, 15 min post-mixing, showed no evidence of disulfide scrambling. However, 24 h later, a resonance attributable to $[t\text{Bu}_3\text{P}(\text{S}p\text{-tolyl})]^+$ was observed in the $^{31}P\{^{1}H\}$ spectrum at 84.9 ppm, and a triplet at −163.7 ppm corresponding to the *para*-fluorines in $[(PhS)B(C_6F_5)_3]^-$ was observed in the ^{19}F spectrum.

Table 1. Crystallographic Data

	4	**5**	**6**	**7**	**8**
formula	$C_{42}H_{10}BF_{15}PS_2$	$C_{44}H_{41}BF_{15}PS_2$	$C_{36}H_{41}BF_{15}PS_2$	$C_{36}H_{33}BF_{20}PS$	$C_{33}H_{27}BF_{15}LiO_2S$
fw	905.40	960.67	864.59	990.53	790.36
cryst syst	orthorhombic	triclinic	monoclinic	triclinic	triclinic
space group	*Pbca*	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	17.1871(8)	11.968(2)	14.9509(4)	10.9180(5)	10.6303(2)
b (Å)	20.1089(10)	13.989(3)	16.9921(4)	12.5771(5)	13.4360(4)
c (Å)	23.8650(10)	14.243(3)	15.2385(4)	15.3755(8)	13.9523(5)
α (deg)	90	70.79(3)	90	101.684(3)	89.076(2)
β (deg)	90	73.62(3)	98.3890(10)	91.286(3)	67.826(2)
γ (deg)	90	73.93(3)	90	98.070(2)	71.165(2)
V (Å^3)	8248.1(7)	2115.4(7)	3829.88(17)	2044.27(17)	1733.84(9)
Z	8	2	4	2	2
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
d (calcd) g cm^{-3}	1.458	1.508	1.499	1.492	1.514
Abs coeff, *μ*, mm^{-1}	0.266	0.263	0.281	0.236	0.205
data collected[a]	60605	27926	62433	474844	58806
R_{int}	0.0564	0.0748	0.0257	0.0495	0.0241
data used	5731	9621	13250	8389	11252
variables	604	568	496	586	478
R ($>2\sigma$)	0.0680	0.0540	0.0370	0.0506	0.0385
wR_2 ($>2\sigma$)	0.1767	0.1318	0.0982	0.1148	0.1012
GOF	1.105	1.048	1.015	1.013	1.037

[a] Data collected with Mo Kα radiation (λ = 0.71069 Å).

Table 2. Computation of Natural Bond Orders

basis set compd	*S*	HF/ca. 6-31+g(d) P/N/H	C(−S)	*S*	B3LYP/6-311++g(d,p) P/N/H	C(−S)
$[t\text{Bu}_3\text{P(SPh)}]^+$	0.02	1.51	−0.24	0.03	1.49	−0.21
$[\text{H}_3\text{N(SPh)}]^+$	0.56	−0.98	−0.35	0.47	−0.83	−0.30
PhSH	0.01	−0.23	0.13	−0.01	0.12	−0.19
PhSSPh	0.13		−0.26	0.11		−0.20

X-Ray Data Collection and Reduction. Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under a N_2 stream, thus maintaining a dry, O_2-free environment for each crystal. The data for crystals of **5** were collected on a Nonius Kappa-CCD diffractometer; for crystals of **4**, **6**, **7**, and **8**, data were collected on a Bruker Apex II diffractometer. The data were collected at 150(±2) K for all crystals. For crystals of **5**, data were processed with the DENZO-SMN package. For crystals of **4**, **6**, **7**, and **8**, the frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS). Table 1 provides crystallographic data for **4**−**8**.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[47] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $\omega (F_o - F_c)^2$, where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they were bonded, assuming a C−H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they were bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the Supporting Information.

Computational Methods. Optimizations were performed with the Gaussian (G98) suite.[48] The species given in Table 2 were fully optimized without constraints (save PhS−SPh, which was initially fixed to C_i symmetry and optimized to C_{2h} symmetry) at the HF level using a mixed basis set applying the 3-21G basis set to phenyl and *t*-butyl hydrogens, and the 6-31+g(d) basis set to all other atoms. Examination of the optimized structures by analytical frequency analysis at this level demonstrated them to be minima (no imaginary frequencies). The structures were then reoptimized at the B3LYP/6-311++g(d,p) level using the HF structures as starting points. Natural bond order (NBO) calculations[49,50] were performed using an upgraded version of the NBO subroutine in the G98 program, using structures and wave

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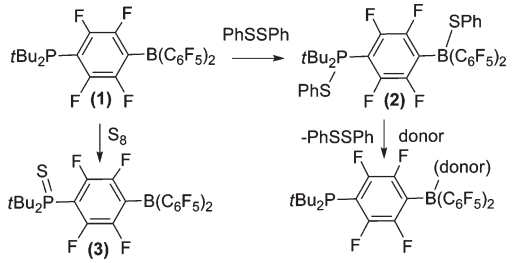
Scheme 1. Synthesis of **1** and **2**



functions from both model chemistries. The values differed little (Table 2). Optimized Cartesian coordinates for the compounds investigated are available as Supporting Information.

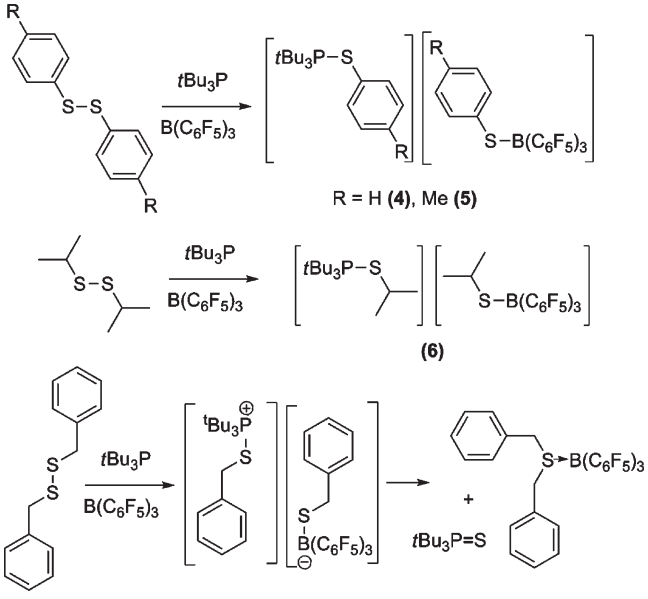
Results and Discussion

The addition of diphenyl disulfide (PhSSPh) to an orange toluene solution of the phosphino-borane tBu$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ (**1**) at room temperature resulted in an immediate loss of color. After stirring for 1 h at 25 °C and removal of the solvent, an off-yellow solid was recovered in 76% yield. The ^{31}P NMR spectrum revealed a singlet resonance at 76.2 ppm, which is about 51 ppm downfield from the parent phosphino-borane. The ^{1}H NMR spectrum showed resonances from 7.9 to 7.2 ppm and at 1.3 ppm attributable to Ph and tBu groups, respectively. The ^{11}B NMR chemical shift of −9.8 ppm is comparable to that of a related thioborate anion,[51] and the small gap between the meta and para ^{19}F NMR resonances ($\Delta_{m,p}$ = 4.4 ppm) is consistent with the formation of a four-coordiante anionic borate center.[52−57] On the basis of these data, the product (**2**) was formulated as the zwitterionic phosphonium borate [tBu$_2$P(SPh)(C$_6$F$_4$)B(SPh)(C$_6$F$_5$)$_2$] (Scheme 1).

While **2** was a stable and isolable species, the heating of trial reactions in the presence of a base such as PMe$_3$ or a donor solvent such as THF to temperatures in excess of 100 °C resulted in regeneration of the disulfide and the base coordinated phosphino−borane [tBu$_2$P(C$_6$F$_4$)B(donor)(C$_6$F$_5$)$_2$] as evidenced by NMR data. These observations suggest that the activation of the disulfide PhSSPh is reversible. This is directly analogous to the heterolytic loss of hydrogen from [(C$_6$H$_2$Me$_3$)$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$] upon thermolysis of [(C$_6$H$_2$Me$_3$)$_2$P(H)(C$_6$F$_4$)B(H)(C$_6$F$_5$)$_2$]. Nonetheless, the corresponding thermolysis of [tBu$_2$P(H)(C$_6$F$_4$)B(H)(C$_6$F$_5$)$_2$] does not yield **1**.

For comparative purposes, species **1** was oxidized with elemental sulfur in toluene at room temperature, affording the phosphine−sulfide tBu$_2$P(S)(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ (**3**) as an off-yellow solid (Scheme 1). The ^{31}P NMR chemical shift of **3** is observed at 85.9 ppm. The ^{19}F NMR spectra of **3** exhibit slightly broadened ortho, meta, and para fluorine resonances for two equivalent C$_6$F$_5$ rings. Additionally, the meta−para

Scheme 2. Reactions of Disulfides with FLPs



fluorine resonance gap of 16 ppm is similar to that found for **1** and B(C$_6$F$_5$)$_3$ ($\Delta_{m,p}$ = 18)[58] consistent with the presence of a three-coordiante boron center. This phosphine−sulfide (**3**) showed no sign of aggregation via phosphine−sulfide coordination to boron at 25 °C consistent with the known ability of such soft donors to form only weak adducts with Lewis acids.[59] However, upon cooling to −50 °C, the meta, para fluorine chemical shift difference changes from 16 to 8 ppm, suggesting the presence of weak aggregation at low temperatures.

In a similar fashion, the FLP tBu$_3$P/B(C$_6$F$_5$)$_3$ readily activates PhSSPh at 25 °C in toluene to give [tBu$_3$P(SPh)][(PhS)B(C$_6$F$_5$)$_3$] (**4**) as a white solid in 84% yield (Scheme 2). The NMR data show a characteristic ^{11}B chemical shift at −10.0 ppm. The ^{31}P resonance for the cation appears at 85.7 ppm, downfield from the parent phosphine resonance (57.8 ppm) and yet clearly distinct from the known shift of tBu$_3$PS (90 ppm).[60] The formulation of **4** was also confirmed crystallographically. The structural data for the pseudotetrahedral thio−borate anion showed a B−S distance of 1.966(4) Å, while the B−S−C angle was found to be 103.90(19)°. This angle positions the phenyl ring at an approximately 28.6° angle to one of the fluoro−arene rings on B, suggesting that electron-rich, electron-poor $\pi-\pi$ stacking[61] dictates the solid-state orientation of this thiolate fragment. The corresponding cation of **4** exhibited a disorder of the t-butyl groups. Nonetheless, the P−S bond distance was determined to be 2.0929(15) Å.

In corresponding reactions, FLP tBu$_3$P/B(C$_6$F$_5$)$_3$ readily activates the disulfides RSSR (R = p-tolyl, iPr) to give [tBu$_3$P(Sp-tolyl)][(p-tolylS)B(C$_6$F$_5$)$_3$] (**5**) and [tBu$_3$P(SiPr)][(iPrS)B(C$_6$F$_5$)$_3$] (**6**) in yields of 90 and 93%, respectively (Scheme 2). These products were also characterized crystallographically (Figure 1). The B−S distances in the anions of

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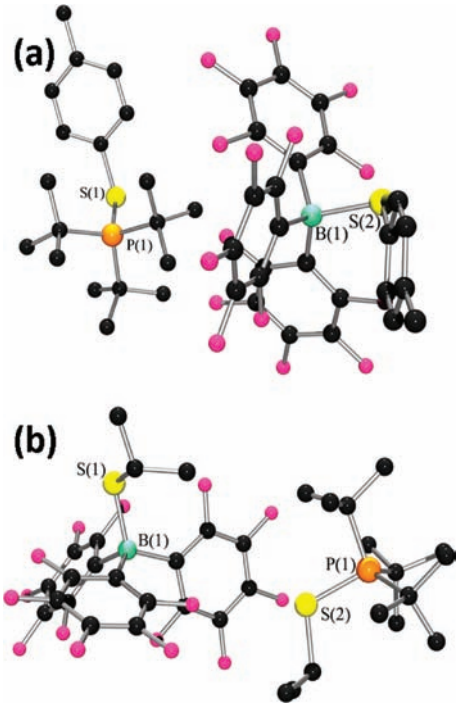


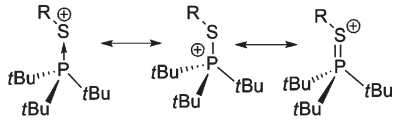
Figure 1. POV-ray depictions of (a) **5** and (b) **6**. Hydrogen atoms are omitted for clarity.

5 and **6** were found to be 1.991(3) and 1.9536(13) Å, respectively, consistent with the stronger electron-donating nature of the alkylthiolate fragment in **6**. The corresponding P−S distances in the cations of **5** and **6** were found to be 2.0916(13) and 2.0694(4) Å, respectively. The longer P−S bond length in **5** also reflects the poor electron-donating character of the aryl substituent.

In efforts to garner further mechanistic data on the formation of the salts, independent combinations of tBu$_3$P and PhSSPh and B(C$_6$F$_5$)$_3$ and PhSSPh were examined. In the former case, no interaction was observed from −80 to +25 °C, and no desulfurization of the disulfide was observed in a CD_2Cl_2 solution after a week from mixing, while in the latter case, only a weak donor−acceptor interaction was observed below −30 °C. Thus, the activation of the disulfide required both phosphine and borane. Indeed, the addition of PhSSPh to **1** in C_6D_5Br at −30 °C resulted in the rapid formation of **2**, and no intermediate was detected. In addition, it is noteworthy that an analogous combination of R$_3$P (2,4,6-C$_6$H$_2$Me$_3$, 2-C$_6$H$_4$Me) and B(C$_6$F$_5$)$_3$ with PhSSPh or (C$_6$H$_2$Me$_3$)$_2$P(C$_6$F$_4$)B(C$_6$F$_5$)$_2$ and PhSSPh resulted in no reaction. This latter observation suggests that the disulfide activation requires a more nucleophilic phosphine as a constituent of the FLP. In a similar sense, the electronic nature of the FLP has been shown to limit the reaction with H_2.[27−30,38] Nonetheless, the combinations of R$_3$P (2,4,6-C$_6$H$_2$Me$_3$, 2-C$_6$H$_4$Me) and B(C$_6$F$_5$)$_3$ do react with H_2.

The combination of tBu$_3$P and B(C$_6$F$_5$)$_3$ with the disulfide BnSSBn also results in a rapid reaction. However, in contrast to the reactions above affording the salts **4**−**6**, this reaction does result in the formation of a clathrate but immediately converts to a monophasic solution. Spectroscopic examination of the reaction mixture showed that the products were a 1:1:1 mixture of tBu$_3$P═S, Bn$_2$S, and B(C$_6$F$_5$)$_3$. This was confirmed by a comparison to an authentic mixture prepared independently. This reaction is thought to proceed via the transient formation of the salt [tBu$_3$P(SBn)][(BnS)B(C$_6$F$_5$)$_3$] (efforts to observe this intermediate spectroscopically were futile), with a subsequent benzyl group transfer from the cation to the S of the anion, yielding tBu$_3$P═S and Bn$_2$S·B(C$_6$F$_5$)$_3$ (Scheme 2). In contrast, thermolysis of **4** or **6** at 150 °C does not result in the formation of tBu$_3$P═S, rather, only a mixture of uncharacterized decomposition products. The contrasting reactivity of BnSSBn suggests that the P−S bond in the transient cation is significantly stronger than that in the cation of **4**, possibly due to the stability of the benzyl cation,[62] consistent with the trends in the P−S bond distances observed in **4**−**6**. In addition, in the case of BnSSBn, diminished steric demands can permit the facile approach of the transient cation to effect alkyl group transfer. Consistent with the impact of steric effects, the combination of tBu$_3$P and B(C$_6$F$_5$)$_3$ with tBuSStBu resulted in no reaction at room temperature and multiple unidentified products at high temperatures.

Scheme 3. Resonance Forms of Thiophosphonium Cation, [tBu$_3$P(SPh)]$^+$



One can formally describe these species as phosphine-stabilized sulfenium cations, consistent with the heterolytic cleavage of the S−S bond. Alternatively, once formed, the cations could be described simply as a thiolate-susbstituted phosphonium salt, or for that matter as an alkylated phosphine−sulfide (Scheme 3). In order to assess the best description, calculations were employed to probe the NBO in the cations in **4**. For comparative purposes, [tBu$_3$P(SPh)]$^+$, [H$_3$N(SPh)]$^+$, PhSH, and PhSSPh were examined at the Hartree−Fock and DFT B3LYP levels (Table 2). The NBO charges suggest that virtually all of the positive charge in [tBu$_3$P(SPh)]$^+$ reside on the P atom. This reflects the greater electronegativity of S versus P and the fact that in the cation P is hypervalent four-coordinate while S is normal two-coordinate. Support for this view comes from the data for [H$_3$N(SPh)]$^+$ where the sulfur holds most of the positive charge because the bound N is more electronegative and has less of an ability to disperse the charge. In general, the S atom in SPh fragments holds little charge, as shown by the data for the neutral species PhSH and PhSSPh. These data support the description of the cation in **4** as a thiolate-susbstituted phosphonium salt.

Crossover Experiments. The treatment of **4** with *p*-tolylSS*p*-tolyl was monitored by NMR spectroscopy, revealing the form formation of a mixture of **4**, **5**, PhSSPh, and *p*-tolylSS*p*-tolyl. Conversely, the treatment of **5** with PhSSPh afforded a similar mixture. These data suggest the possibility that the formation of the salts **4** and **5** is reversible, although this equilibrium goes undetected.

To confirm this hypothesis, a crossover experiment was envisioned in which specifically labeled cations and anions were combined. To this end, the species [tBu$_3$P(SPh)][B(C$_6$F$_5$)$_4$] (**7**) was prepared via the reaction of **4** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] (Scheme 4). Compound **7** was

(62) Olah, G. A.; Schleyer, P. v. R. *Carbonium Ions*; Interscience Publishers: New York, 1968.

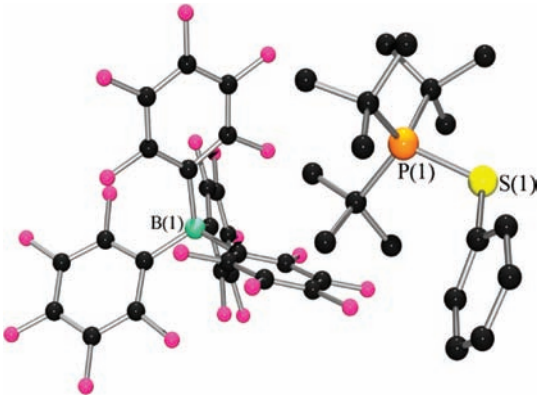
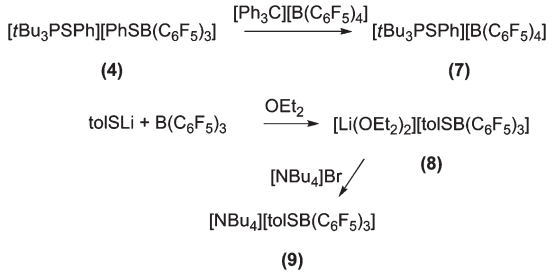


Figure 2. POV-ray depiction of **7**. Hydrogen atoms are omitted for clarity.

Scheme 4. Synthesis of **7**–**9**



isolated in 79% yield as pale yellow crystals. NMR data were consistent with the formulation, and X-ray data confirmed the nature of the salt **7** (Figure 2). The metric parameters in the anion of **7** were unexceptional, while the cation in **7** was not disordered as it was in **4**. The P–S distance was found to be 2.0820(10) Å. Treatment of **7** with excess *p*-tolylSS*p*-tolyl resulted in no spectroscopically observable $[t\mathrm{Bu_3P(S}p\text{-tolyl)}]^+$, indicating that the thiophosphonium cation alone does not exchange a sulfenium cation with disulfides.

The crossover experiment required a thiolate-labeled anion salt. It was accessed in a two-step synthesis. Initially, the reaction of $B(C_6F_5)_3$ with $LiSC_6H_4Me$ in diethyl ether afforded the species $[(Et_2O)_2Li(p\text{-tolylS})B(C_6F_5)_3]$ (**8**) as white crystals in 79% isolated yield (Scheme 4). ^{1}H NMR data confirmed the presence of 2 equiv of diethyl ether while the ^{19}F NMR resonances at −132.73, −167.34, and −170.69 ppm and the ^{11}B signal at −11.73 confirmed quaternization of B. The X-ray structure of **8** (Figure 3) contains an interesting six-membered Li–S–B–C–C–F ring, where the thiolate group, which is coordinated to a B–S distance of 2.0042(12) Å, bridges to Li with a Li–S distance of 2.459(2) Å and a B–S–Li angle of 113.38(6)°. The coordination sphere of Li is comprised of S, two coordinated diethyl ether molecules, and a Li–F interaction to one of the ortho-F atoms on $B(C_6F_5)_3$. The Li···F distance was found to be 2.043(2) Å. In a cation exchange reaction of **8** with $[NBu_4]Br$ (Scheme 4), the corresponding salt $[NBu_4][(p\text{-tolylS})B(C_6F_5)_3]$ (**9**) was isolated as a white crystalline solid in 36% yield. The treatment of **9** with excess PhSSPh resulted in no spectroscopically observable $[(p\text{-tolylS})B(C_6F_5)_3]^-$, indicating that the thioborate anion alone does not exchange a thiolate anion with disulfides.

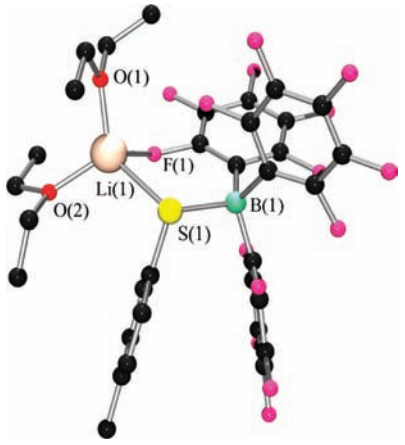
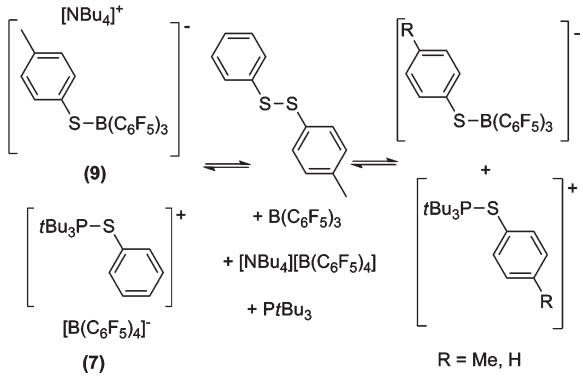


Figure 3. POV-ray depiction of **8**. Hydrogen atoms are omitted for clarity.

Scheme 5. Proposed Mechanism of RS Group Exchange in Reaction of **7** and **9**



The combination of compounds **7** and **9** was monitored by NMR spectroscopy; 24 h after mixing, integration of the signals showed a statistical mixture of the cations $[t\mathrm{Bu_3P(SR)}]^+$ and anions $[(RS)B(C_6F_5)_3]^-$ (R = Ph, S*p*-tolyl). Particular evidence of this scrambling process was the observation of a ^{31}P resonance at 84.9 ppm attributable to $[t\mathrm{Bu_3P(S}p\text{-tolyl)}]^+$, and a triplet in the ^{19}F spectrum at −163.7 ppm corresponded to the para-fluorines in $[(PhS)B(C_6F_5)_3]^-$. The mechanism of this scrambling of a formally thiolate and sulfenium fragment was considered. Two possible mechanisms can be envisioned given that neither the cation nor the anion react independently with disulfides. Alkylation of the thioborate by the cation could generate transient phosphine–sulfide and thioether–borane species. The reverse of this reaction would result in scrambling of the arene substituents. However, independent combination of $t\mathrm{Bu_3PS}$ and Ph_2S-$(B(C_6F_5)_3$ showed no evidence of alkylation to give **4**, suggesting that this mechanism is unlikely. A more likely mechanism involves a small, apparently not discernible (by NMR spectroscopy) equilibrium in which disulfides and the FLP are in equilibrium with the salt products of heterolytic disulfide activation (Scheme 5). An analogous mechanism has been proposed for the heterolytic activation of H_2 by FLPs.[63,64] The reformation of disulfide

(63) Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *Angew. Chem., Int. Ed.* **2008**, *47*, 2435–2438.
(64) Rokob, T. A. S.; Hamza, A.; Stirling, A. S.; Pápai, I. *J. Am. Chem. Soc.* **2009**, *131*, 2029–2036.

suggests that, despite the apparent localization of charge on P in the thiophosphonium cations $[t\mathrm{Bu}_3\mathrm{P(SPh)}]^+$, this cation reacts as a source of sulfenium cations to allow the regeneration of disulfide by reaction with the thioborate anion.

Summary. In conclusion, we have shown that FLPs react with disulfide to effect the heterolytic cleavage of the S−S bond affording formally sulfenium cations stabilized by phosphine and the corresponding thio-borate anion. This reactivity appears to be limited to sterically demanding yet basic FLP systems and sterically demanding or electron-poor disulfides. Such limitations are analogous to that previously described for H_2 activation by FLPs. The activation of disulfides is reversible, as evidenced by exchange and crossover experiments. Efforts are underway to exploit this heterolytic cleavage for subsequent thiolation chemistry. Reports of this reactivity will follow in due course.

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Supporting Information Available: Crystallographic data in CIF format; table of optimized (B3LYP/6-311++G(d,p)) Cartesian coordinates of various thiolate species. This material is available free of charge via the Internet at http://pubs.acs.org.