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Frustrated Lewis Pairs | *Very Important Paper*

VIP A Highly Reactive Geminal P/B Frustrated Lewis Pair: Expanding the Scope to C–X (X = Cl, Br) Bond Activation

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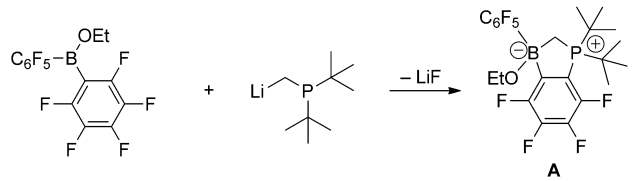
Abstract: The geminal frustrated Lewis pair tBu$_2$PCH$_2$B(Fxyl)$_2$ (**1**; Fxyl = 3,5-(CF$_3$)$_2$C$_6$H$_3$) is accessible in 65% yield from tBu$_2$PCH$_2$Li and (Fxyl)$_2$BF. According to NMR spectroscopy and X-ray crystallography, **1** is monomeric both in solution and in the solid state. The intramolecular P···B distance of 2.900(5) Å and the full planarity of the borane site exclude any significant P/B interaction. Compound **1** readily activates a broad variety of substrates including H_2, EtMe$_2$SiH, CO_2/CS_2, Ph$_2$CO, and H$_3$CCN. Terminal alkynes react with heterolysis of the C–H bond. Haloboranes give cyclic adducts with strong P–BX$_3$ and weak R$_3$B–X bonds. Unprecedented transformations leading to zwitterionic XP/BCX$_3$ adducts occur on treatment of **1** with CCl_4 or CBr_4 in Et$_2$O. In less polar solvents (C$_6$H$_6$, *n*-pentane), XP/BCX$_3$ adduct formation is accompanied by the generation of significant amounts of XP/BX adducts. FLP **1** catalyzes the hydrogenation of PhCH=NtBu and the hydrosilylation of Ph$_2$CO with EtMe$_2$SiH.

Introduction

Sterically demanding main group Lewis acids and bases that are unable to neutralize each other through adduct formation (frustrated Lewis pairs, FLPs) can still act synergistically on a third molecule and thereby exhibit reactivity commonly associated with transition metal complexes (e.g., H_2 activation).[1–7] To date, combinations of suitable organophosphines and organoboranes have been by far the most popular FLPs. Adjustment of their chemical behavior is possible through variation of the substituent patterns and/or the bridging unit between the reactive centers. A frequently employed substituent on boron is the C_6F_5 ring; the phosphine fragments often carry *tert*-butyl or mesityl groups. Multiple bimolecular (i.e., unbridged) FLPs do exist and are synthetically more conveniently accessible than their monomolecular (i.e., bridged) congeners.[1–7] However, the preorganization of Lewis acidic and basic sites that is achievable through the introduction of a linker can significantly aid in the fine-tuning of FLP reactivity, and thus makes the additional synthetic effort worthwhile. For example, Erker and co-workers studied a series of compounds R$_2$P(CH$_2$)$_n$B(C$_6$F$_5$)$_2$ (n = 2–4) and found the ethylene- and butylene-bridged species to be active FLPs (e.g., for H_2 cleavage), whereas the propylene derivative showed no indication of typical FLP activity.[8–14]

Methylene-bridged P/B pairs differ fundamentally from the abovementioned C$_2$-, C$_3$-, and C$_4$-linked compounds, because a one-atom spacer leads to less conformational flexibility of the molecular scaffold and thus to a well-defined P···B distance. Moreover, the degree of intramolecular P/B interaction should be small, because formation of a P–B σ bond would result in a strained three-membered ring and, in contrast to phosphinoboranes (C$_0$ species),[15,16] P=B π donation is not possible. Thus, in a geminal P/B FLP, the two reactive sites should be perfectly preoriented for small-molecule activation.

Our initial attempts at the synthesis of a first geminal P/B FLP relied on the nucleophilic substitution of EtOB(C$_6$F$_5$)$_2$ with tBu$_2$PCH$_2$Li.[17] However, the successful formation of the methylene bridge was accompanied by a cyclization reaction, during which the phosphorus atom displaced an *ortho*-fluorine atom of one of the C$_6$F$_5$ groups. The obtained zwitterionic five-membered heterocycle **A** is no longer an FLP (Scheme 1).[17–19] Shortly thereafter, Erker et al. used the hydroboration of (C$_6$F$_5$)$_2$PCH=CHMe and (C$_6$F$_5$)$_2$PC≡CMe with HB(C$_6$F$_5$)$_2$ to make (C$_6$F$_5$)$_2$PCH(Et)B(C$_6$F$_5$)$_2$ and (C$_6$F$_5$)$_2$PC(=C(H)Me)B(C$_6$F$_5$)$_2$, respec-



Scheme 1. Formation of the zwitterionic heterocycle **A** from EtOB(C$_6$F$_5$)$_2$ and tBu$_2$PCH$_2$Li.

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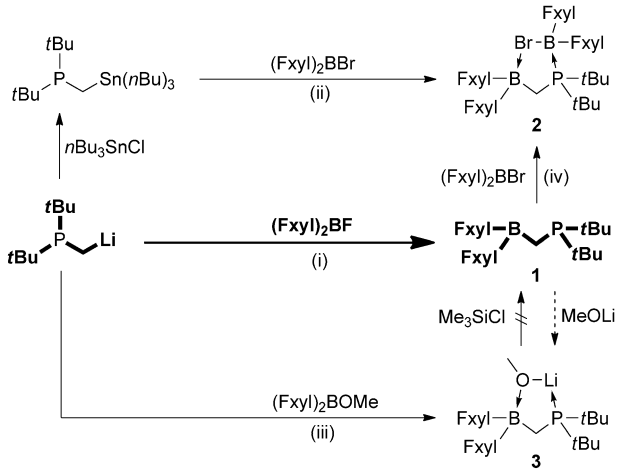
tively.[20,21] These geminal FLPs did not undergo the undesired cyclization reaction, likely because the nucleophilicities of the phosphorus atoms are tamed by their electron-withdrawing C_6F_5 substituents. In an alternative approach, Slootweg, Lammertsma, and co-workers avoided cyclization by employing $ClBPh_2$ instead of $EtOB(C_6F_5)_2$, thereby synthesizing $tBu_2PCH_2BPh_2$.[22,23]

Even though the above P–C–B Lewis pairs proved to be capable of activating a variety of small molecules, we still remained interested in the development of geminal FLPs featuring strongly Lewis acidic and strongly Lewis basic centers. Bearing in mind that the Gutmann acceptor number of B[3,5-$(CF_3)_2C_6H_3]_3$ ($B(Fxyl)_3$) is comparable to that of $B(C_6F_5)_3$,[24] we first developed facile routes to the borane building blocks $XB(Fxyl)_2$ (X = H, MeO, F, Cl, Br)[25] and now report the synthesis of $tBu_2PCH_2B(Fxyl)_2$ (**1**; Scheme 2). We further show that **1** is highly reactive toward a broad selection of substrates commonly employed in FLP chemistry. Moreover, unprecedented transformations were observed on treatment of **1** with CX_4 (X = Cl, Br). Depending on the solvent employed, we isolated either the adduct $tBu_2P(X)CH_2B(CX_3)(Fxyl)_2$ or its formal dihalocarbene-elimination product $tBu_2P(X)CH_2B(X)(Fxyl)_2$.



Scheme 2. Reactions performed with the aim to synthesize the geminal P/B FLP **1**. i) *n*-Heptane, 16 h, room temperature; ii) C_6D_6, 16 h, room temperature; iii) C_6H_6, 16 h, room temperature; iv) *n*-heptane/C_6H_6, 3 h, room temperature.

Results and Discussion

Synthesis of the geminal FLP $tBu_2PCH_2B(Fxyl)_2$ (1)

Using the protocol published by Slootweg, Lammertsma et al.[22] as a guideline, we first tried to prepare $tBu_2PCH_2B(Fxyl)_2$ (**1**) by treatment of tBu_2PCH_2Li[26,27] with $(Fxyl)_2BCl$.[25] Unfortunately, the reaction gave a complex mixture of inseparable products; the same result was obtained with $(Fxyl)_2BBr$ as starting material. We therefore switched from tBu_2PCH_2Li to the less nucleophilic $tBu_2PCH_2Sn(nBu)_3$ (Scheme 2). Even though the reaction with $(Fxyl)_2BBr$ was again not selective, we were able to isolate a few single crystals of **2**, the cyclic adduct between our target compound **1** and one equivalent of the borane reactant. We next tested the complementary approach, that is, the combination of tBu_2PCH_2Li with the less electrophilic borane $(Fxyl)_2BOMe$.[25] This reaction furnished **1** as the main product, albeit in the form of its LiOMe adduct **3** (Scheme 2). Addition of Me_3SiCl to a C_6D_6 solution of **3** led to decomposition rather than to the liberation of free **1**. $(Fxyl)_2BF$[25] is a similarly mild electrophile to $(Fxyl)_2BOMe$, but LiF has an exceptionally high lattice energy. Thus, the synthesis of the desired FLP **1** was finally achieved from tBu_2PCH_2Li and $(Fxyl)_2BF$ in 65% yield (Scheme 2).

The presence of a PCH_2B backbone in compound **1** is confirmed by a doublet at 2.08 ppm (2H; $^2J(H,P) = 3.1$ Hz) in the ^1H NMR spectrum with ^1H–^{13}C HMBC cross-peaks to the signals of the $C(CH_3)_3$ groups at P and the *B*-aryl *ipso*-carbon atoms. Moreover, the CH_2 ^{13}C resonance is significantly broadened due to the interaction of the C atom with the quadrupolar ^{11}B nucleus. The triorganoborane[28] and -phosphine[29] moieties give rise to resonances at $\delta(^{11}B) = 63$ ppm and $\delta(^{31}P) = 25.9$ ppm, in accord with an FLP nature of the compound. Correspondingly, the crystal lattice of **1** contains monomeric molecules with intramolecular P···B distances of 2.900(5) Å (Figure 1). For comparison, the calculated molecular structures of $tBu_2PCH_2B(C_6F_5)_2$ in its ring-opened and ring-closed forms show P···B distances of 2.89 and 2.04 Å, respectively.[22] The measured P1-C1-B1 angle of **1** is 114.9(3)°, and the sum of angles about the B center is 359.8°. Any significant σ interaction between P and B should lead to compression of the P1-C1-B1 angle from the ideal value of 107.5° and to pyramidalization of the B atom, which is not observed in the present case.

As a first test of the reactivity of **1**, we attempted the targeted syntheses of **2** and **3**. Single crystals of the bromoborane

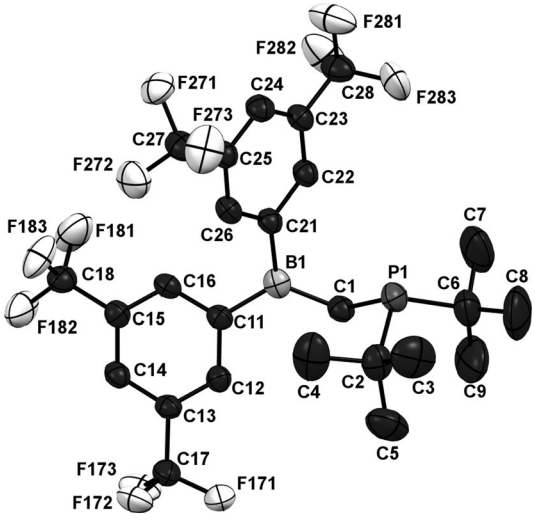


Figure 1. Molecular structure of **1** in the solid state; displacement ellipsoids are drawn at 50% probability. The disordered CF_3 groups are displayed in only one of two positions. H atoms are omitted for clarity. Selected bond lengths [Å], atom···atom distances [Å], and bond angles [°]: P1–C1 1.867(4), B1–C1 1.569(6); P1···B1 (intramolecular) 2.900(5), P1···B1 (intermolecular) 7.918(5); P1-C1-B1 114.9(3), C1-B1-C11 121.5(4), C1-B1-C21 119.5(4), C11-B1-C21 118.8(4).

adduct **2** (85%) grew after equimolar solutions of **1** (in *n*-heptane) and $(Fxyl)_2BBr$ (in C_6H_6) had been slowly combined at room temperature. The air-sensitive compound proved to be insoluble in common inert NMR solvents (for the NMR data of a corresponding BBr_3 adduct of **1**, see compound **12b** below). However, the constitution of **2** was unequivocally confirmed by X-ray crystallography (see the Supporting Information for more details).

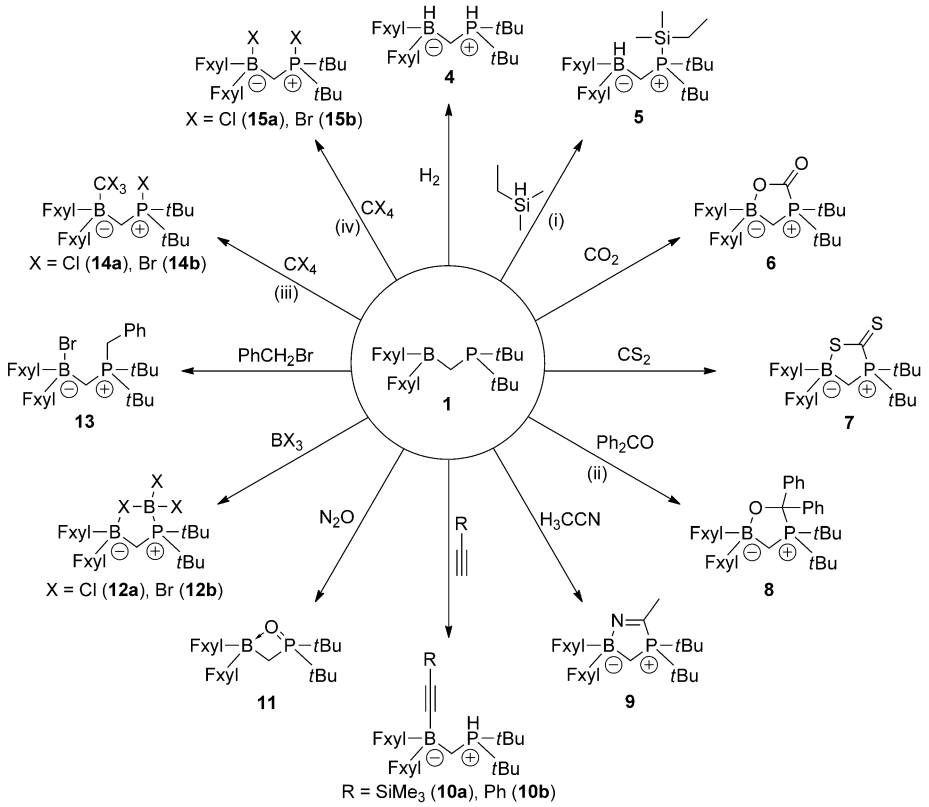
The addition of solid MeOLi to a solution of **1** in C_6D_6 furnished small amounts of **3** (NMR spectroscopic monitoring). The low conversion is probably due to solubility issues. The ^{11}B NMR spectrum of **3** is characterized by a resonance at 1.5 ppm, typical of tetracoordinate boron species.[28] In C_6D_6, the $^{31}P\{^1H\}$ NMR signal of **3** appears as a 1:1:1:1 quartet with a chemical shift of 22.3 ppm. The quartet collapses to a singlet on addition of THF or H_3CCN to the sample. We therefore attribute the resonance fine structure in neat C_6D_6 to $^{31}P–^7Li$ coupling ($^1J = 88$ Hz) and thus to contact ion pairs, which are separated in the presence of coordinating solvent molecules. A cyclic contact ion pair in which the Li^+ ion is chelated by the P atom and the BOMe moiety is also observed in the solid-state structure of **3** (see the Supporting Information for more details).

Reactions of 1 with selected substrates

For a thorough assessment of its chemical behavior, compound **1** was treated with 14 different reagents (Scheme 3).

The standard FLP substrate, H_2, reacted in the usual manner[2,3] with activation of the H–H bond (< 1 atm, room temperature). Product **4** is characterized by a ^{31}P NMR resonance at 60.1 ppm ($^1J(P,H) = 444$ Hz) and an ^{11}B NMR signal at −10.8 ppm ($^1J(B,H) = 88$ Hz). The ^1H NMR spectrum shows a doublet of triplets for the PH proton (4.08 ppm), due to coupling with the ^{31}P nucleus and the CH_2 bridge protons. The BH proton gives rise to the expected 1:1:1:1 quartet at 2.99 ppm. H_2 addition is not reversible up to a temperature of 120 °C. Nevertheless, the imine PhCH=N*t*Bu can be hydrogenated quantitatively in the presence of catalytic amounts of **4** already at 80 °C ($p(H_2) < 1$ atm, 20 mol% catalyst loading; see ref. [10] for related P/B FLP-mediated hydrogenation reactions).

Unlike H_2, $EtMe_2SiH$ adds to **1** in a reversible manner at room temperature in C_6D_{12} solution (the sterically more demanding Et_3SiH does not react at all). According to NMR spectroscopy, the association/dissociation equilibrium shifts toward quantitative formation of the Si–H activation product **5** only if excess $EtMe_2SiH$ is supplied (approximately 10 equiv). The NMR spectra of **5** are consistent with the presence of a hydridoborate ion ($\delta(^{11}B) = -13.2$ ppm; $^1J(B,H) = 82$ Hz) and a silylphosphonium ion ($\delta(^{29}Si) = 10.6$ ppm; $^1J(Si,P) = 40$ Hz). Further proof of the proposed molecular structure was gained by X-ray crystallography (see the Supporting Information for more details). In contrast to its behavior in solution, crystalline **5** does not tend to lose silane at room temperature, even under dynamic vacuum. Under hydrolytic conditions, the silane adduct **5** cleanly transforms into the H_2 adduct **4**.



Scheme 3. Reactions of **1** with selected substrates. i) Reversible at room temperature. ii) Dynamic association/dissociation equilibrium in solution. iii) Et_2O, room temperature. iv) C_6H_6 or *n*-pentane, room temperature.

The reaction between **1** and CO_2, another standard FLP substrate, takes a similar course to the reaction between tBu$_2$PCH$_2$BPh$_2$ and CO_2.[22] An almost-planar, five-membered, air- and moisture-stable heterocycle with an exocyclic C=O double bond is formed (**6**). The corresponding ^{13}C NMR signal appears at 168.3 ppm, in good agreement with the shift reported for the literature-known system mentioned above (167.8 ppm). An analogous structure to **6** is obtained from **1** and CS_2 (**7**). Compound **7** has a red-purple color, characteristic of phosphine–CS_2 adducts.[30–32] CS_2 activation by P/B Lewis pairs is far less common than CO_2 activation, and the only known examples are the addition of CS_2 to tBu$_2$PN≡Btmp (Htmp = 2,2,6,6-tetramethylpiperidine)[33] and Et$_2$PC(Ph)=C(nBu)B(nBu$_2$).[34]

Whereas aldehydes have already been reported to react with P/B FLPs,[12,35,36] the Ph_2CO adduct **8** is a rare example of an activated ketone. In a related case, Ph_2CO undergoes a [2+2] cycloaddition with the phosphinoborane tBu$_2$PBFlu (HBFlu = 9-borafluorene). The primary product then undergoes heterolytic cleavage of the P–B bond to furnish tBu$_2$PCPh$_2$OBFlu.[16] The room-temperature ^{1}H NMR spectrum of **8** shows poorly resolved phenyl resonances. Steric repulsion between the Ph and tBu substituents likely restricts intramolecular motion and/or causes an association/dissociation equilibrium between FLP **1**, the ketone, and **8**. To clarify this point, we also recorded NMR spectra of **8** at elevated temperatures. The ^{31}P NMR signal (84.4 ppm) became severely broadened at 50 °C and completely vanished at 80 °C; similarly, the ^{11}B NMR resonance of **8** (4.9 ppm) was no longer detectable in the high-temperature spectrum. Both signals reappeared when the sample was cooled back to room temperature. Moreover, the colorless solution of **8** adopts the yellow color of free **1** on heating, but becomes colorless again on cooling. Adduct formation of the FLP with Ph_2CO is thus a reversible dynamic process. Accordingly, compound **8** is hydrolyzed much more readily than compound **6**. As a major hydrolysis product, we identified tBu$_2$P(H)CH$_2$B[OB(Fxyl)$_2$](Fxyl)$_2$ by X-ray crystallography and NMR spectroscopy (see the Supporting Information for more details). This species is formally derived from (Fxyl)$_2$BOH by O–H addition to **1**.

Geminal FLP **1** efficiently catalyzes the hydrosilylation of Ph_2CO with EtMe$_2$SiH (12 mol% catalyst loading, room temperature, 30 min, C_6D_6).[37] Note that **1** not only interacts with Ph_2CO, but also with EtMe$_2$SiH (cf. **5**), the other reagent of the hydrosilylation sequence.

FLP **1** not only traps compounds containing a C=O bond, but also adds to the C≡N bond of H_3CCN to give the five-membered cyclic compound **9**. The only comparable example of a P/B-mediated H_3CCN activation was described by Nöth and co-workers, who again used the species tBu$_2$PN≡Btmp. At room temperature, they observed kinetically controlled formation of the imine fragment PC(CH$_3$)=NB. On thermal treatment, the imine tautomerized to the thermodynamically preferred enamine PC(=CH$_2$)N(H)B.[33] In the case of **9**, we found a proton resonance at 1.88 ppm (d, ^3J(H,P) = 4.9 Hz) with an integral of 3H, assignable to a CH_3 group. The corresponding ^{13}C NMR signal was observed at 26.5 ppm (d, ^2J(C,P) = 47 Hz). The molecular structure of **9** in the solid state shows an endocyclic C–N distance of 1.258(10) Å and an exocyclic C–C distance of 1.505(10) Å, which are typical values of C=N bonds[38] and C(sp^2)–C(sp^3) single bonds,[39] respectively. We therefore conclude that **9** is the imine rather than the enamine tautomer. In contrast to the adduct of Nöth et al., **9** is thermally stable up to 120 °C.

Reactions of P/B FLPs with terminal alkynes are governed by the basicity of the phosphine: FLPs containing less basic phosphines tend to add to the C≡C bond, whereas the use of strongly basic phosphines (e.g., tBu$_3$P) results in deprotonation of the alkyne to give phosphonium alkynylborate salts.[40] Accordingly, **1** cleaves the terminal C–H bonds of Me$_3$SiCCH and PhCCH with generation of **10a** and **10b**, respectively. Phosphine protonation is evidenced by doublets of multiplets at about 53 ppm in the ^{31}P NMR spectra with ^1J(P,H) coupling constants of 450 Hz. The corresponding ^{1}H resonances appear at about 5 ppm as doublets of triplets (^1J(H,P) = 450 Hz, ^3J(H,H) = 4.5 Hz). ^{11}B NMR signals are observed at −14.5 ppm. As a further characteristic, the BC≡C signals are broadened beyond detection in the ^{13}C{^{1}H} NMR spectrum. A ^{1}H–^{13}C HMBC experiment, however, revealed chemical shifts of 131.9 ppm (**10a**) and 109.8 ppm (**10b**). The proposed molecular structures of **10a** and **10b** were further corroborated by X-ray crystallography (see the Supporting Information).

Stephan and co-workers trapped N_2O with a bimolecular P/B FLP to obtain tBu$_3$PN=NOB(C$_6$F$_5$)$_3$.[41] Although kinetically stable, the compound loses N_2 with formation of the phosphine oxide adduct tBu$_3$P=OB(C$_6$F$_5$)$_3$ on photolysis or heating to 135 °C. In contrast, the intramolecular phosphine oxide adduct **11** was already generated when an n-pentane solution of **1** was stored under N_2O at 4 °C in the dark. The ^{11}B NMR resonance of **11** appears at 7.5 ppm and thus in the typical shift range of tetracoordinate boron nuclei.[28] Compared to the ^{31}P{^{1}H} NMR resonance of **1** (25.9 ppm), the signal of **11** is shifted to lower field (113.1 ppm). In the solid state, **11** has a P=O bond length of 1.576(2) Å and a B–O bond length of 1.612(3) Å. Both these bonds are significantly longer than those of the related intramolecular adduct tBu$_2$P(μ-O)(μ-C$_6$H$_4$)B(C$_6$F$_5$)$_2$ featuring a five-membered heterocycle (P=O 1.546(2), B–O 1.550(2) Å).[42]

The serendipitous finding of the (Fxyl)$_2$BBr adduct **2** drew our attention to the possibility of trapping BCl_3 and BBr_3, too. Previously Uhl and co-workers prepared cyclic adducts between BX_3 (X = F, Cl, Br, I) and the P/Al FLP Mes$_2$PC[=C(H)Ph]-AltBu$_2$.[23a] Interestingly, the products with X = F and Cl proved to be thermally stable and could be stored at room temperature, whereas the adducts with X = Br and I decomposed above 0 °C.[23a] In the case of FLP **1**, both the BCl_3 adduct **12a** and the BBr_3 adduct **12b** are isolable under ambient conditions. We did not observe any signs of substituent scrambling between the two B atoms of **12a** or **12b**. BX_3 binding results in downfield shifts of the ^{31}P NMR resonances from 25.9 ppm in free **1** to 39.4 and 38.6 ppm in **12a** and **12b**, respectively (broadened 1:1:1:1 quartets). In turn, the FLP ^{11}B NMR signals experience an upfield shift from 63 ppm (**1**) to 35 ppm (**12a**) or 34 ppm (**12b**), attributable to a certain degree of intramo-

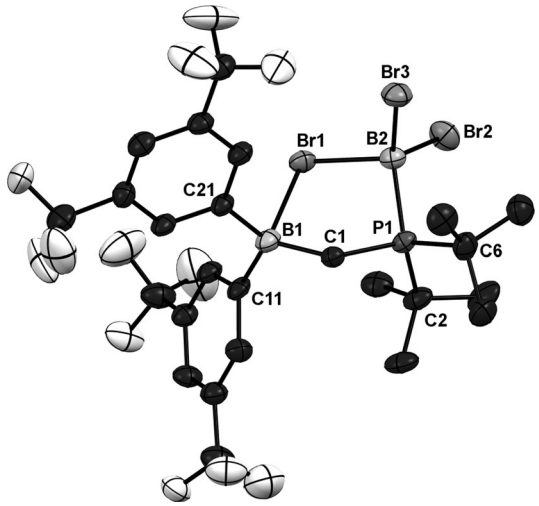


Figure 2. Molecular structure of **12b** in the solid state; displacement ellipsoids are drawn at 50% probability. The disordered CF_3 groups are displayed in only one of two positions. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–B2 2.000(6), B1–Br1 2.408(7), B2–Br1 2.093(6), B2–Br2 1.980(6), B2–Br3 1.990(6); C1-B1-C11 118.8(4), C1-B1-C21 114.5(5), C11-B1-C21 116.7(5), Br1-B2-Br2 109.3(3), Br1-B2-Br3 106.3(3), Br2-B2-Br3 110.4(3).

lecular X–B coordination. Likely due to magnetic anisotropy effects,[28] the ^{11}B NMR chemical shifts of the trihalogenated boron atoms differ by as much as 17.4 ppm between **12a** (7.2 ppm, $^1J(B,P) = 150$ Hz) and **12b** (−10.2 ppm, $^1J(B,P) = 140$ Hz). Adducts **12a** and **12b** both crystallize from *n*-alkanes in the monoclinic space group $P2_1/c$ (see Figure 2 for a plot of the molecular structure of **12b**). The P–BX_3 bond lengths of **12a** and **12b** are identical (2.002(2) Å versus 2.000(6) Å). In each molecule, the B1–X distance is remarkably longer than the B2–X distance (**12a**: B1–Cl1 2.361(3), B2–Cl1 1.925(2) Å; **12b**: B1–Br1 2.408(7), B2–Br1 2.093(6) Å). By the same token, the B1 atoms are much less pyramidalized than the corresponding trihalogenated B2 atoms [sums of angles around boron: **12a**: 352° (B1), 328° (B2); **12b**: 350° (B1), 326° (B2)]. We therefore conclude that **12a** and **12b** are essentially phosphine adducts of BCl_3 and BBr_3 with additional weak interactions between the FLP B centers and the bridging halogen atoms.

Combinations of Lewis acids and bases (usually $AlCl_3$ with amines) are known to facilitate the electrophilic borylation of arenes by boron halides. These reactions can be performed with a broad variety of aromatic compounds and most often involve borenium salts, such as $[Cl_2B(amine)]^+[AlCl_4]^-$, as the actual borylating agents.[43–50] On thermal treatment, the BX_3 adducts **12a** and **12b** could conceivably undergo B–X heterolysis with formation of borenium species $t\mathrm{Bu}_2\mathrm{P}(\mathrm{BX}_2^+)\text{-}\mathrm{CH}_2(\mathrm{X}^-)\mathrm{B}(\mathrm{Fxyl})_2$. We therefore examined the reactivity of **12b** toward electron-rich *o*-xylene in C_6D_6. According to NMR spectroscopy, no conversion occurred at 60 °C (4 h) or 100 °C (1 h). Maintaining a temperature of 100 °C for 16 h led to quantitative decomposition of the FLP scaffold, while *o*-xylene remained inert. We attribute this result to one of the following factors: 1) Phosphine-supported borenium cations[51,52] may be less active borylating agents than their amine-supported congeners. 2) Due to the high fluorophilicity of borenium electrophiles, the presence of CF_3 groups in the FLP could effect unwanted side reactions. Indeed, the thermolized sample gave rise to a prominent broad ^{11}B NMR signal at 24 ppm, which lies in a similar range to the ^{11}B resonances of $FBBr_2$ (30 ppm) and F_2BBr (20 ppm).[28] 3) As discussed above, the interaction between the $(Fxyl)_2B$ moiety and the BBr_3 bromine atom in **12b** may be too weak to induce B–Br bond heterolysis.

FLP **1** was unable to heterolytically cleave the B–X bond of BX_3 and form a phosphine-coordinated borenium/haloborate ion pair. Yet, **1** readily splits the C–Br bond of $PhCH_2Br$ to afford the benzylphosphonium bromoborate zwitterion **13**. The ^{11}B NMR signal of compound **13** (−0.9 ppm) appears at considerably higher field relative to the corresponding resonance of **12b** (34 ppm). Accordingly, the B–Br bond length of **13** (2.16(2) Å) is shorter by 0.25 Å than the B1···Br1 distance in **12b**.

Compared to the latter conversion, which took the expected course, the outcome of the reaction between **1** and CBr_4 is less predictable. Given the considerable stability of the $[CBr_3]^-$ ion,[53,54] abstraction of Br^+ from CBr_4 by the phosphine site (cf. the Corey–Fuchs reaction[55]) and immediate trapping of $[CBr_3]^-$ by the boron center offers a conceivable alternative to the tribromomethylation of the phosphorus atom. Therefore, we finally investigated the behavior of **1** toward CBr_4 and also included CCl_4 in our study (cf. the Appel reaction[56]). Addition of CX_4 (X = Cl, Br) to **1** in Et_2O indeed provided the C–X-activated species **14a** and **14b**, featuring halophosphonium ions in combination with trihalomethanide-coordinated boron atoms. Single crystals were grown at 4 °C (**14a**) or room temperature (**14b**). Both compounds are remarkably stable at room temperature in the solid state and in ethereal solutions; even in undried THF, they are not hydrolyzed. Moreover, they do not undergo rearrangement reactions, such as the Matteson homologation.[57] NMR spectra were recorded in $[D_8]$THF. The ^{31}P chemical shifts of **14a** (129.0 ppm) and **14b** (122.3 ppm) are similar, although the molecules contain different halogen substituents. The ^{11}B NMR resonances appear in the typical region of tetracoordinate boron nuclei, that is, −4.8 ppm (**14a**) and −4.1 ppm (**14b**). The CX_3 carbon atoms attached to boron are not detectable in the 1D $^{13}C\{^1H\}$ NMR spectrum, likely due to quadrupolar broadening. Their chemical shifts were therefore determined from cross-peaks with the CH_2 proton signals in ^1H–^{13}C HMBC NMR spectra. We found values of 113.7 (**14a**) and 76.2 ppm (**14b**), which are intermediate between those of $LiCX_3$ [146 ppm (Cl); 101 ppm (Br)] on the one hand and HCX_3 [80 ppm (Cl); 14 ppm (Br)] on the other.[54] These NMR features nicely reflect the fact that the covalent character of the B–C bonds lies between those of Li–C and H–C bonds.

Compounds **14a** and **14b** are isostructural in the solid state. Thus, only the molecular structure of **14b** is discussed here (Figure 3; see the Supporting Information for more details of that of **14a**). Contrary to all other open-chain adducts of **1**, **14b** adopts a B1–C1 *s-trans* conformation (P1-C1-B1-C10 178.3(3)°). The P1–Br1 bond length is 2.174(1) Å, and the B1–C10 (1.688(6) Å) and B1–C1 bonds (1.692(6) Å) have essentially

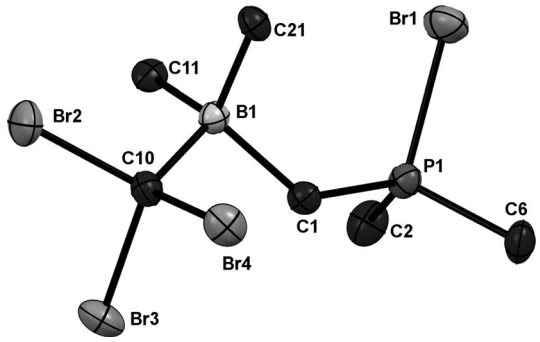


Figure 3. Molecular structure of **14b** in the solid state; displacement ellipsoids are drawn at 50% probability. H atoms are omitted for clarity, the Fxyl and *t*Bu groups are represented by the C atoms attached to the reactive centers. Selected bond lengths [Å], bond angles [°], and torsion angle [°]: P1–Br1 2.174(1), B1–C1 1.692(6), B1–C10 1.688(6); P1-C1-B1 130.0(3), C1-B1-C10 101.8(3); P1-C1-B1-C10 178.3(3).

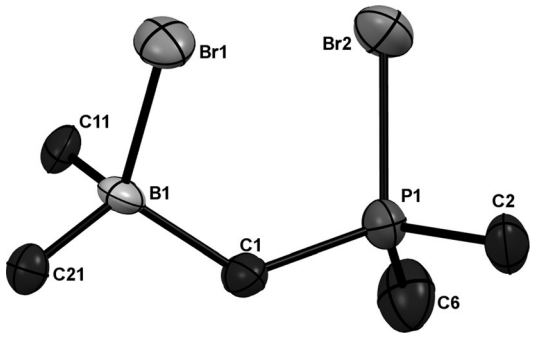


Figure 4. Molecular structure of **15b** in the solid state; displacement ellipsoids are drawn at 50% probability. H atoms are omitted for clarity, the Fxyl and *t*Bu groups are represented by the C atoms attached to the reactive centers. Selected bond lengths [Å], atom···atom distance [Å], and bond angle [°]: P1–Br2 2.167(2), B1–Br1 2.135(8); Br1···Br2 3.581(1); P1-C1-B1 127.7(6).

the same lengths. The CBr_3 fragment is fully pyramidalized with Br–C10–Br bond angles ranging between 104.8(2) and 105.6(2)°.

The addition of CX_4 to **1** in Et_2O gives **14a** or **14b** as the sole products. Yet, less polar solvents, such as C_6H_6 and *n*-pentane, effect a different result: alongside each CX_4 adduct, a second species is generated in an approximately equimolar quantity. These compounds were identified as the formal X_2 adducts **15a** (X = Cl) and **15b** (X = Br) by NMR spectroscopy and X-ray crystallography (we note in this context that attempts to synthesize **15b** directly from **1** and Br_2 failed). Compounds **15a** and **15b** are likely formed because dihalocarbene extrusion from $[CX_3]^-$ successfully competes with boron coordination of the anion under these conditions.

The differences in the 1D NMR spectra of **15a/15b** compared to **14a/14b** are surprisingly small and therefore not very diagnostic. More information regarding the chemical constitution of **15a** and **15b** can be gained from the 2D NMR spectra: the ^1H–^{13}C HMBC cross-peaks observed between the CH_2 proton signals and the CX_3 carbon resonances in the cases of **14a** and **14b** are absent in the spectra of **15a** and **15b**. Definite proof for the postulated structures of **15a** and **15b** stems from X-ray crystallography, which clearly identified the two compounds as formal Cl_2 and Br_2 adducts. As in the cases of **14a** and **14b**, the molecular structures of **15a** and **15b** are rather similar, and we therefore restrict ourselves to the discussion of that of **15b** (Figure 4; see the Supporting Information for more details of that of **15a**). As expected, the P1–Br2 bond length of **15b** (2.167(2) Å) is virtually the same as that of **14b** (2.174(1) Å). In turn, the B1–Br1 bond length (2.135(8) Å) agrees with that of **13** (2.16(2) Å). Br1 and Br2 approach each other rather closely, such that the Br1···Br2 distance (3.581(1) Å) becomes shorter than the sum of the van der Waals radii of two Br atoms (3.8 Å).[38]

Finally, we note that **15b** was also obtained (albeit in low yields) from the reaction between **1** and $HCBr_3$ in *n*-pentane, whereas **1** did not activate H_2CBr_2, $HCCl_3$, or H_2CCl_2 (in *n*-pentane or in the respective neat halomethane).

Conclusion

The length of the bridging unit in a monomolecular FLP greatly influences the chemical behavior. The bridge governs the conformational flexibility of the FLP scaffold, the ring size of transition states during small-molecule activation, and the charge separation and dipole moment in the activation products. Thus, geminal FLPs should be particularly reactive, but only a few examples have been reported until now. Especially the combination of highly Lewis acidic boranes and highly basic phosphines in methylene-bridged P/B FLPs is synthetically challenging: commonly used C_6F_5 boranes readily undergo *o*-F substitution by the phosphine to form zwitterionic five-membered rings containing tetracoordinate B and P atoms.

Recently, the $(Fxyl)_2B$ (Fxyl = 3,5-$(CF_3)_2C_6H_3$) building block became available as an alternative to the $(C_6F_5)_2B$ moiety. This granted us access to the geminal FLP $tBu_2PCH_2B(Fxyl)_2$ (**1**), which features a strong Lewis base and a strong Lewis acid. Compound **1** does not show any indications of P···B interaction in solution or in the solid state and can therefore be regarded as a genuine FLP. We have shown that **1** readily reacts with all standard FLP substrates, including H_2, $EtMe_2SiH$, CO_2/CS_2, Ph_2CO, and H_3CCN. Most importantly, **1** activates certain alkyl halides, such as CCl_4, CBr_4, and $HCBr_3$, through heterolysis of the C–X bonds. In this way, unprecedented X_3C borates were isolated and structurally characterized. We are currently investigating the suitability of such X_3C borates for the introduction of X_3C substituents into organic molecules through Suzuki-type C–C coupling reactions.

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Keywords: boron · carbon–halogen activation · frustrated Lewis pairs · phosphorus · trihalomethanides

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