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 tBu₂PCH₂B(Fxyl)₂ (1; Fxyl = 3,5-(CF₃)₃C₆H₃) is accessible in 65% yield from tBu₂PCH₂Li and (Fxyl)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 H₂, EtMe₂SiH, CO₂/CS₂, Ph₂CO, and H₂CCN. Terminal alkenes react with heterolytic cleavage of the C–H bond. Haloboranes give cyclic adducts with strong P–BX₃ and weak R₂B–X bonds. Unprecedented transformations leading to zwitterionic XP/BCX₄ adducts occur on treatment with 1 with CCl₄ or CBr₄ in Et₂O. In less polar solvents (C₆H₆, n-pentane), XP/BCX₄ adduct formation is accompanied by the generation of significant amounts of XP/BX adducts. FLP 1 catalyzes the hydrogenation of PhCH=NRBu and the hydrosilylation of Ph₂CO with EtMe₂SiH.

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., H₂ activation). 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 C₆F₅ 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. 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 R₂P(CH₂)ₙB(C₆F₃₀)₂ (n = 2–4) and found the ethylene- and butylene-bridged species to be active FLPs (e.g., for H₂ cleavage), whereas the propylene derivative showed no indication of typical FLP activity.

Methylene-bridged P/B pairs differ fundamentally from the abovementioned C₅F₅, C₅F₇, and C₈F₉-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 bond would result in a strained three-membered ring and, in contrast to phosphinoboranes (C₅F₅ species), 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(C₅F₉)₂ with tBu₂PCH₂Li. 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 C₆F₅ groups. The obtained zwitterionic five-membered heterocycle A is no longer an FLP (Scheme 1). Shortly thereafter, Erker et al. used the hydroboration of (C₅F₉)₂PCH=CHMe and (C₅F₉)₂PC≡CMe with HB(C₅F₉)₂ to make (C₅F₉)₂PCH(Et)B(C₅F₉)₂ and (C₅F₉)₂PC(=C(H)Me)B(C₅F₉)₂, respectively.

Scheme 1. Formation of the zwitterionic heterocycle A from EtOB(C₅F₉)₂ and tBu₂PCH₂Li.

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tively.\[^{26,21}\] These geminal FLPs did not undergo the undesired cyclization reaction, likely because the nucleophilicities of the phosphorus atoms are tamed by their electron-withdrawing \(\text{CF}_3\) substituents. In an alternative approach, Slootweg, Lammertsma, and co-workers avoided cyclization by employing \(\text{ClBPh}_2\) instead of \(\text{EtOB(C}_3\text{F}_3)_2\), thereby synthesizing \(\text{tBu}_2\text{PCH}_3\text{BPh}_3\).\[^{22,23}\]

Even though the above \(\text{P–C–B}\) 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 \(\text{B(C}_3\text{F}_3)_2\) is comparable to that of \(\text{B(C}_3\text{F}_3)_2\),\[^{24}\] we first developed facile routes to the borane building blocks \(\text{XB(Fxyl)}_2\) (\(\text{X}\) = \(\text{H}, \text{Me}, \text{F}, \text{Cl}, \text{Br}\)) and now report the synthesis of \(\text{tBu}_2\text{PCH}_3\text{B(Fxyl)}_2\) (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 \(\text{CX}_4\) (\(\text{X}\) = \(\text{Cl}, \text{Br}\)) on the solvent employed, we isolated either the adduct \(\text{tBu}_2\text{P(X)}\text{CH}_3\text{B(CX}_3\text{)(Fxyl)}_2\) or its formal dihalocarbene-elimination product \(\text{tBu}_2\text{P(X)}\text{CH}_3\text{B}(\text{Fxyl})_2\).

**Results and Discussion**

**Synthesis of the geminal FLP \(\text{tBu}_2\text{PCH}_3\text{B(Fxyl)}_2\) (1)**

Using the protocol published by Slootweg, Lammertsma et al.\[^{22}\] as a guideline, we first tried to prepare \(\text{tBu}_2\text{PCH}_3\text{B(Fxyl)}_2\) (1) by treatment of \(\text{tBu}_2\text{PCH}_3\text{Li}\) with \(\text{Fxyl}_2\text{BCl}\).\[^{26}\] Unfortunately, the reaction gave a complex mixture of inseparable products; the same result was obtained with \(\text{Fxyl}_2\text{Br}\) as starting material. We therefore switched from \(\text{tBu}_2\text{PCH}_3\text{Li}\) to the less nucleophilic \(\text{tBu}_2\text{PCH}_3\text{Sn(nBu)}_3\), (Scheme 2). Even though the reaction with \(\text{Fxyl}_2\text{Br}\) 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 \(\text{Bu}_2\text{PCH}_3\text{Li}\) with the less electrophilic borane \(\text{Fxyl}_2\text{BOMe}\).\[^{23}\] This reaction furnished 1 as the main product, albeit in the form of its LiOMe adduct 3 (Scheme 2). Addition of \(\text{Me}_2\text{SiCl}\) to a \(\text{C}_6\text{D}_6\) solution of 3 led to decomposition rather than to the liberation of free 1. \(\text{Fxyl}_2\text{B}^\text{Li}\) is a similarly mild electrophile to \(\text{Fxyl}_2\text{BOMe}\), but \(\text{LiF}\) has an exceptionally high lattice energy. Thus, the synthesis of the desired FLP 1 was finally achieved from \(\text{tBu}_2\text{PCH}_3\text{Li}\) and \(\text{Fxyl}_2\text{B}\) in 65% yield (Scheme 2).

The presence of a \(\text{PCH}_3\text{B}\) backbone in compound 1 is confirmed by a doublet at 2.08 ppm (2H; \(^2J(\text{H,P})=3.1\) Hz) in the \(^1\text{H}\) NMR spectrum with \(^1\text{H}-^\text{13}\text{C}\) HMBC cross-peaks to the signals of the \(\text{C}3\text{H}_3\) groups at P and the \(\text{B-aryl ipso-carbon atoms. Moreover, the CH}_3\) \(^\text{13}\text{C}\) resonance is significantly broadened due to the interaction of the C atom with the quadrupolar \(\text{Bcloxide}\). The triorganoborane\[^{26}\] and \(\text{phenylarene}\[^{26}\] moieties give rise to resonances at \(\delta(\text{B})=63\) ppm and \(\delta(\text{B})=25.9\) 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 \(\text{tBu}_2\text{PCH}_3\text{B(C}_3\text{F}_3)_2\), in its open-ring and 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 \(\alpha\) interaction between P and B should lead to compression of the P1–C1–B1 angle from the ideal value of 107.5° 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...
adduct 2 (85%) grew after equimolar solutions of 1 (in n-heptane) and (Fxy)2BBr (in C6H6) 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 BBr3 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 C6D6 furnished small amounts of 3 (NMR spectroscopic monitoring). The low conversion is probably due to solubility issues. The 11B NMR spectrum of 3 is characterized by a resonance at 1.5 ppm, typical of tetracoordinate boron species. In C6D6, the 31P{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 H3CCN to the sample. We therefore attribute the resonance fine structure in neat C6D6 to 31P–Li coupling (1J(P,Li) = 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, H2, reacted in the usual manner with activation of the H–H bond (1 atm, room temperature). Product 4 is characterized by a 11B NMR resonance at 60.1 ppm (1J(B,H) = 444 Hz) and an 31P NMR signal at −10.8 ppm (1J(B,P) = 88 Hz). The 1H NMR spectrum shows a doublet of triplets for the PH proton (4.08 ppm), due to coupling with the 31P nucleus and the CH2 bridge protons. The BH proton gives rise to the expected 1:1:1:1 quartet at 2.99 ppm. H2 addition is not reversible up to a temperature of 120 °C. Nevertheless, the imine PhCH=NtBu can be hydrogenated quantitatively in the presence of catalytic amounts of 4 already at 80 °C (pr(H2) < 1 atm, 20 mol% catalyst loading; see ref. [10] for related P/B FLP-mediated hydrogenation reactions).

Unlike H2, EtMe2SiH adds to 1 in a reversible manner at room temperature in C6D6 solution (the sterically more demanding Et3SiH 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 EtMe2SiH is supplied (approximately 10 equiv). The NMR spectra of 5 are consistent with the presence of a hydridoborate ion (δ(11B) = −13.2 ppm; 1J(B,H) = 82 Hz) and a silylphosphonium ion (δ(29Si) = 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 H2 adduct 4.

Scheme 3. Reactions of 1 with selected substrates. i) Reversible at room temperature. ii) Dynamic association/dissociation equilibrium in solution. iii) Et3O, room temperature. iv) C6H6 or n-pentane, room temperature.
The reaction between 1 and CO, another standard FLP substrate, takes a similar course to the reaction between \( \text{rBu}_{2}\text{PCH}_{2}\text{BPh}_{3} \) and CO.\(^{22}\) 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\(_{2}\). 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 activation, and the only known examples are the addition of CS\(_{2}\) to \( \text{rBu}_{2}\text{PNEt}_{2} \) (Htmp = 2,2,6,6-tetramethylpiperidine)\(^{33}\) and Et\(_{3}\)PC(Ph) = C(nBu)B(nBu)\(_{3}\).\(^{34}\)

Whereas aldehydes have already been reported to react with P/B FLPs,\(^{32,35,36}\) the Ph\(_{2}\)CO adduct 8 is a rare example of an activated ketone. In a related case, Ph\(_{2}\)CO undergoes a [2+2] cycloaddition with the phosphinoborane \( \text{rBu}_{2}\text{PBFlu} \) (HFlu = 9-borafluorene). The primary product then undergoes heterolytic cleavage of the P–B bond to furnish Ph\(_{2}\)PCPh\(_{2}\)OBFlu.\(^{36}\) The room-temperature \(^1\)H NMR spectrum of 8 shows poorly resolved phenyl resonances. Steric repulsion between the Ph and B 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 \(^3\)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 (4.99 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\(_{2}\)CO is thus a reversible dynamic process. Accordingly, compound 8 is hydrolyzed much more readily than compound 6. As a major hydrolysis product, we identified \( \text{rBu}_{2}\text{P}(\text{H})\text{CH}_{2}\text{B}(\text{Fluyl})\_2\) (Fluyl) by X-ray crystallography and NMR spectroscopy (see the Supporting Information for details). This species is formed from (Fluyl)BOH by O–H addition to 1.

Geminal FLP 1 efficiently catalyzes the hydrosilylation of Ph\(_{3}\)CO with EtMe\(_2\)SiH (12 mol% catalyst loading, room temperature, 30 min; \( C_{\text{D}} \_\text{Ph} \)).\(^{37}\) Note that 1 not only interacts with Ph\(_{3}\)CO, 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\(_3\)CCN to give the five-membered cyclic compound 9. The only comparable example of a P/B-mediated H\(_3\)CCN activation was described by Nöth and co-workers, who again used the species \( \text{rBu}_{2}\text{PNEt}_{2} \) (Htmp). At room temperature, they observed kinetically controlled formation of the imine fragment PC(\( \text{CH}_{2}\)_2) = NB. On thermal treatment, the imine tautomerized to the thermodynamically preferred enamine PC(\( \text{CH}_{2}\))NH\(_3\). In the case of 9, we found a proton resonance at 1.88 ppm (d, \( ^3\)J(H,P) = 4.9 Hz) with an integral of 3 H, assignable to a CH\(_2\) group. The corresponding \(^{13}\)C NMR signal was observed at 26.5 ppm (d, \( ^3\)J(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 and C(sp\(^2\))–C(sp\(^2\)) 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≡N bond, whereas the use of strongly basic phosphines (e.g., \( \text{rBu}_{2}\text{P} \)) results in deprotonation of the alkyne to give phosphonium alkynylborate salts.\(^{40}\) Accordingly, 1cleaves the terminal C–H bonds of Me\(_3\)SiCCCH and PhCCCH with generation of 10a and 10b, respectively. Phosphine protonation is evidenced by doublets of multiplets at about 53 ppm in the \(^3\)P NMR spectra with \( ^1\)J(PH) coupling constants of 450 Hz. The corresponding \(^1\)H resonances appear at about 5 ppm as doublets of triplets (\( ^3\)J(PH) = 450 Hz, \( ^3\)J(H,P) = 25 Hz). \(^{11}\)B NMR signals are observed at ~14.5 ppm. As a further characteristic, the B≡C signals are broadened beyond detection in the \(^1\)C(N) NMR spectrum. A \(^1\)H–\(^1\)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\(_2\)O with a bimolecular P/B FLP to obtain \( \text{rBu}_{2}\text{PNEt}_{2} = \text{NOB}_{(C_F)} \).\(^{41}\) Although kinetically stable, the compound loses \( \text{N}_2 \) with formation of the phosphoxide adduct \( \text{rBu}_{2}\text{P} = \text{OB}_{(C_F)} \) on photolysis or heating to 135°C. In contrast, the intramolecular phosphoxide oxide adduct 11 was already generated when an n-pentane solution of 1 was stored under N\(_2\)O 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.\(^{42}\) Compared to the \(^3\)P(N) 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 \( \text{rBu}_{2}\text{P} = \text{O} = \text{O}_{(C_F)} \) featuring a five-membered heterocycle (P–O 1.546(2), B–O 1.550(2) Å).\(^{42}\)

The serendipitous finding of the (Fluyl)BBr adduct 2 drew our attention to the possibility of trapping BCl\(_3\) and BBr\(_3\). Previously Uhl and co-workers prepared cyclic adducts between BX\(_3\) (X = F, Cl, Br, I) and the P/Al FLP Mes\(_3\)PC(=N(H)Ph) – AlTBu\(_{2}\)). 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, 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 \(^3\)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 Cl′ groups are displayed in only one of two positions. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 2.002(2), C1–B1 2.000(6), C1–B1 1.990(6), C1–B2 1.980(6), B2–Br1 2.093(6), B2–Br2 2.090(6), C1–B1–C11 118.8(4), C1–B1–C21 114.5(5), C11–B1–C21 116.7(5), Br1–Br2–Br3 109.3(3), Br1–B2–Br3 106.3(3), Br2–B2–Br3 110.4(3).

Leukar X–B coordination. Likely due to magnetic anisotropy effects, the 11B 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 P21/c (see Figure 2 for a plot of the molecular structure of 12b). The P–BX3 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 3.261(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 BC1 and BBr with additional weak interactions between the FLB centers and the bridging halogen atoms.

Combinations of Lewis acids and bases (usually AlCl3 with amines) are known to facilitate the electrophilic borylation of arynes by boron halides. These reactions can be performed with a broad variety of aromatic compounds and most often involve borenium salts, such as [ClB(Bamino)][AlCl4]−, as the actual borylating agents. On thermal treatment, the BX3 adducts 12a and 12b could conceivably undergo B–X heterolysis with formation of borenium species [Bu4N][BX3−]· CH3JX·J(BF3) · Br. We therefore examined the reactivity of 12b toward electron-rich o-xylene in C6D6. 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 may be less active borylating agents than their amine-supported congeners. 2) Due to the high fluorophilicity of borenium electrophiles, the presence of ClF3 groups in the FLP could effect unwanted side reactions. Indeed, the thermolized sample gave rise to a prominent broad 11B NMR signal at 24 ppm, which lies in a similar range to the 11B resonances of FBr2 (30 ppm) and F3BBr (20 ppm).3 As discussed above, the interaction between the (FXY)2 moiety and the BBr3 bromine atom in 12b may be too weak to induce B–Br bond heterolysis.

FLP and 1 form a phosphine-coordinated borenium/haloborate ion pair. Yet, 1 readily splits the C–Br bond of PhCH2Br to afford the benzylphosphonium bromoborate zwitterion 13. The 11B 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 CBr5 is less predictable. Given the considerable stability of the [CBr5]− ion and immediate trapping of [CBr5]− by the boron center offers a conceivable alternative to the tribromomethylation of the phosphorus atom. Therefore, we finally investigated the behavior of 1 toward CBr5 and also included CCl5 in our study (cf. the Appel reaction). Addition of C5X5 (X = Cl, Br) to 1 in Et2O indeed provided the C–X-activated species 14a and 14b, featuring halophosphonium ions in combination with trihalomethane-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 homolysis. NMR spectra were recorded in [D8]THF. The 31P chemical shifts of 14a (129.0 ppm) and 14b (122.3 ppm) are similar, although the molecules contain different halogen substituents. The 11B NMR resonances appear in the typical region of tetra-coordinate boron nuclei, that is, −4.8 ppm (14a) and −4.1 ppm (14b). The C5X5 carbon atoms attached to boron are not detectable in the 13C(1H) NMR spectrum, likely due to quadrupolar broadening. Their chemical shifts were therefore determined from cross-peaks with the CH3 proton signals in 1H–13C HMBC NMR spectra. We found values of 113.7 (14a) and 76.2 ppm (14b), which are intermediate between those of LiC5H4 [146 ppm (Cl); 101 ppm (Br)] on the one hand and HXC5 [80 ppm (Cl); 14 ppm (Br)] on the other. 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 (1.686(6) Å) and B1–C1 bonds (1.692(6) Å) have essentially...
the same lengths. The CB₃ fragment is fully pyramidalized with Br–C10–Br bond angles ranging between 104.8(2) and 105.6(2)°.

The addition of CX₄ to 1 in Et₂O gives 14a or 14b as the sole products. Yet, less polar solvents, such as C₆H₆ and n-pentane, effect a different result: alongside each CX₄ adduct, a second species is generated in an approximately equimolar quantity. These compounds were identified as the formal X₂ 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 Br₂ failed). Compounds 15a and 15b are likely formed because dihalocarbene extrusion from [CX₄]⁺ 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–¹³C HMBC cross-peaks observed between the CH₃ proton signals and the CX₄ 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 Cl₂ and Br₂ 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).

Finally, we note that 15b was also obtained (albeit in low yields) from the reaction between 1 and HCB₉ in n-pentane, whereas 1 did not activate H₂CBr₃, HCCI₉, or H₂CCl₉ (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 CₓFₓ boranes readily undergo o-F substitution by the phosphate to form zwitterionic five-membered rings containing tetracoordinate B and P atoms.

Recently, the (Fxyl)₂B (Fxyl = 3,5-(CF₃)₂C₆H₄) building block became available as an alternative to the (CₓFₓ)₂B moiety. This granted us access to the geminal FLP rBu₂PCH₂BFxyl 2 (which features a strong Lewis base and a strong Lewis acid. Compound 2 does not show any indications of P=½ 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 Hₓ, Et₅MeSiH, COₓ/CO, PhₓCO, and HₓCCN. Most importantly, 1 activates certain alkyl halides, such as CClₓ nBu and HCB₉ through heterolysis of the C–X bonds. In this way, unprecedented XₓC borates were isolated and structurally characterized. We are currently investigating the suitability of such XₓC borates for the introduction of XₓC substituents into organic molecules through Suzuki-type C–C coupling reactions.

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