Frustrated Lewis Pairs

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Atom-Efficient Synthesis of Alkynylfluoroborates Using BF_3-Based Frustrated Lewis Pairs

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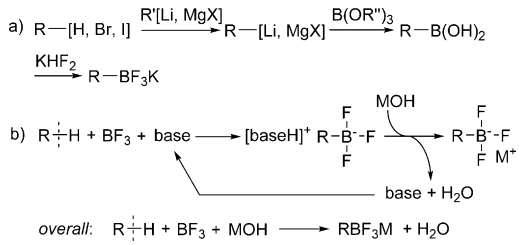
Dedicated to Professor Gerhard Erker on the occasion of his 70th birthday

Abstract: *A sterically demanding amine, 1,2,2,6,6-pentamethylpiperidine (PMP), forms a highly reactive Lewis acid–base pair with boron trifluoride. This pair reacts with terminal acetylenes to give the products of C(sp)–H borylation, previously unknown tri- and tetraalkynylboron compounds. Trialkynylfluoroborates can serve as surrogates of alkynyltrifluoroborates for C–C coupling reactions. Using aqueous NaOH, PMP can be recovered from its tetrafluoroborate salt, which is formed as a C–H borylation byproduct. Combining the discovered borylation reactivity with the PMP recovery provides a straightforward and atom-efficient approach to synthetically useful alkynylfluoroborates.*

Organotrifluoroborates, particularly alkynyl derivatives, are versatile reagents used in various organic transformations.[1] Traditional methods of alkynyltrifluoroborate preparation involve the deprotonation of terminal acetylenes by polar (Li, Mg, Na, K) organometallic reagents followed by multistep conversion (Scheme 1 a).[2] Recently, an alternative approach to alkynylborate generation by C–H borylation of terminal acetylenes was demonstrated, utilizing pairs of powerful Lewis acids and Lewis bases that are also known as frustrated Lewis pairs (FLPs).[3,4] The Lewis acid component of such pairs is typically represented by $B(C_6F_5)_3$ or other pentafluorophenylborane derivatives. However, simple boron halides are significantly less expensive and light-weight reagents with strongly Lewis acidic properties.[5,6] Using the principles of the FLP concept, we addressed a hypothetical access to organofluoroborates by using BF_3 as the Lewis acidic and a tertiary amine as the recyclable Lewis basic component (Scheme 1 b). The implementation of this approach may provide an atom-efficient and economic way to valuable reagents. Herein, we demonstrate that boron trifluoride complexes, along with 1,2,2,6,6-pentamethylpiperidine (PMP), can be used for the C(sp)–H borylation of terminal acetylenes.



Scheme 1. a) Conventional approach to organotrifluoroborates with organolithium or -magnesium derivatives. b) Hypothetical atom-efficient approach to organotrifluoroborates by C–H borylation with a BF_3/organic base FLP. M = alkali metal.

The balance between the steric properties and the Lewis acidity/basicity is crucial for establishing FLP reactivity.[7] Formation of the Lewis acid–base adduct does not necessarily destroy the FLP reactivity as previously shown.[8] In order to react, however, the adduct should first dissociate, producing reactive species ready for cooperative attack on various substrates. The energy required for dissociation increases the kinetic barrier and deteriorates the thermodynamics of the FLP+substrate reaction. Combinations of BF_3 complexes with amines, such as triethylamine and diisopropylethylamine, that produce amine–BF_3 adducts in situ have been used for N–H borylation, for instance, for the preparation of trifluoroborazines and BODIPY dyes.[9]

From both thermodynamic and kinetic perspectives, C–H bonds represent much more challenging targets for borylation. Therefore, we studied several commercially available tertiary amines of gradually increasing steric hindrance in combination with BF_3 to select the most reactive pairs. Boron trifluoride adducts with various Lewis bases were examined computationally by DFT methods[10] and experimentally by ^1H, ^{19}F, and ^{11}B NMR spectroscopy (see Table 1 and the Supporting information for experimental details). The dissociation Gibbs free energies of the BF_3 adducts that were computed for solutions in dichloromethane and benzene vary in the following order: $Et_3N \gg$ 2,6-dimethylpyridine $\approx$ $iPr_2NEt > Et_2O >$ PMP $> Me_2S >$ 2,6-di-*tert*-butylpyridine (see the ΔG_1 values in Table 1). The 2,6-di-*tert*-butylpyridine–BF_3 adduct could not be located computationally, and the amine did not show any interaction upon treatment with gaseous BF_3. In accordance with the calculations, the other amines produced the corresponding BF_3 adducts upon addition of boron trifluoride dimethyl sulfide complex (BFS). Boron trifluoride diethyl etherate ($BF_3{\cdot}Et_2O$, BFE) reacted similarly, except for with PMP, which remained intact.

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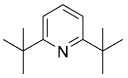
Table 1: Observed and calculated properties of tertiary amine/BF_3 pairs.

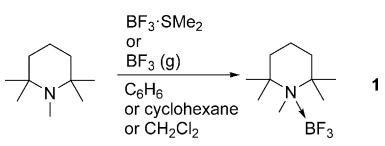
Tertiary amine	^{19}F NMR δ with BFE [ppm]	Reactivity with PhC≡CH	ΔG_1[a] [kcal mol^{-1}]	ΔG_2[a,b] [kcal mol^{-1}]
	−150.6	no	−16.7	1.4
	−142.5	yes,[c] traces	−7.8	−0.3
	−137.1	no	−8.0	8.0
	−153.7[d]	no	–[e]	7.2
	−153.7	yes[c]	−1.9	0
(PMP)				
Et_2O	−153.7	–	−4.2	–
Me_2S	−153.7	–	−0.7	–

[a] ΔG_1 and ΔG_2 refer to the computed Gibbs free energy changes of $LB + BF_3 \rightarrow LB–BF_3$ and $PMPH^+ + R_3N \rightarrow PMP + R_3NH^+$ (LB = Lewis base). The calculated values refer to solutions in CH_2Cl_2; for the corresponding energies in benzene, see the Supporting Information. [b] Basicity relative to PMP. [c] A resonance characteristic of tetra(phenylethynyl)borate was detected in the ^{11}B NMR spectrum at $\delta = -31.5$ ppm. [d] ^{19}F NMR chemical shift of BFE. [e] No dative B–N adduct found.

It is noteworthy that the extremely weak adduct BFS is a convenient alternative to gaseous BF_3.

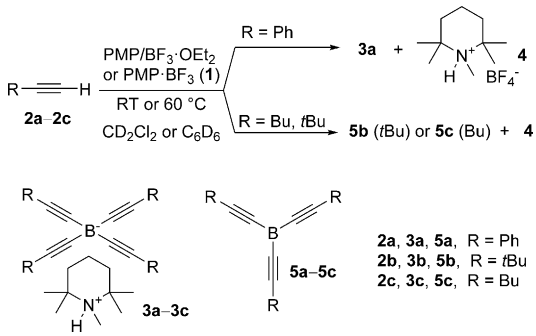
C–H borylation involves deprotonation of the substrate; therefore, the proton affinities of the amines were calculated and compared to that of PMP (see the ΔG_2 values in Table 1). Furthermore, the addition of a proton is not sensitive to steric factors, and Brønsted basicity can thus be used to refine the electronic contribution to the bonding between amines and hard Lewis acids. Combining the proton affinities and dissociation energies of the BF_3 adducts, we arranged the amine–BF_3 combinations according to their thermodynamic ability to activate X–H bonds, with PMP being the most reactive amine. Combinations of the same BF_3 source with 2,6-di-*tert*-butylpyridine or *i*Pr_2NEt appear to be less reactive than that with PMP by 3.5–9.5 kcal mol^{-1} owing to steric (*i*Pr_2NEt) and electronic (2,6-di-*tert*-butylpyridine) reasons.

Within these studies, we isolated the previously unknown PMP·BF_3 adduct **1**. Addition of BFS to or passing gaseous BF_3 through a PMP solution led to in situ formation of **1**, as evident by NMR spectroscopy. Evaporation of volatiles yielded **1** as a white crystalline solid (Scheme 2). Adduct **1** is stable under an inert atmosphere at ambient temperature, but heating a solution of **1** in dichloromethane-d_2 for 11 h at 80 °C leads to about 20 mol % degradation of the PMP. On the other hand, a PMP/BFE mixture showed very little decomposition (less than 1 mol % of the PMP ring degradation products) under similar conditions, which was attributed to the higher dissociation energy of BFE (see the Supporting information for details).



Scheme 2. Formation of the PMP·BF_3 adduct.

With such detailed insight into boron trifluoride adducts in hand, we examined the reactivity of various amine–BFE combinations with phenylacetylene in CD_2Cl_2 at room temperature. No changes were observed by NMR spectroscopy with triethylamine, 2,6-dimethylpyridine, and 2,6-di-*tert*-butylpyridine. Using diisopropylethylamine, a novel, very small resonance at −31.5 ppm was detected in the ^{11}B NMR spectrum after 15 h at room temperature. This resonance belongs to tetra(phenylethynyl)borate,[11] which had been formed as a result of phenylacetylene C–H borylation. The intensity of this resonance, however, did not increase upon further exposure. In contrast, addition of phenylacetylene to a PMP/BFE mixture led to instant appearance of an intense resonance corresponding to tetra(phenylethynyl)borate (**3a**) along with formation of pentamethylpiperidinium tetrafluoroborate (**4**; Scheme 3). The conversion of phenylacetylene into **3a** reached about 60 % within 30 min, but required hours (> 6 h) for completion. Using **1** instead of the BFE/PMP pair led to complete conversion into **3a** within five minutes. Running the same reaction in benzene enabled the isolation of **3a** in 90 % yield by hexane-promoted precipitation of **4**.

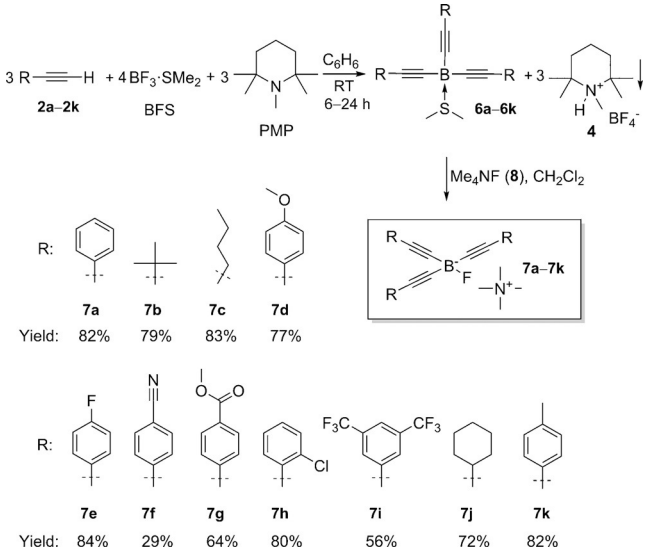


Scheme 3. C–H borylation of terminal acetylenes with **1** or the BFE/PMP pair.

Stirring *tert*-butylacetylene (**2b**) or *n*-butylacetylene (**2c**) with **1** in benzene at room temperature for 3.5 h or 15 min, respectively, enabled the isolation of trialkynylboranes **5b**[12] and **5c** in high yields (Scheme 3). Under similar conditions, the PMP/BFE pair gave the same products, but the reactions required prolonged heating for completion (20 h at 60 °C for **5b**). Owing to the instability of **5c**, its generation using the PMP/BFE pair at elevated temperatures led to significant decomposition. Interestingly, when benzene was replaced with dichloromethane, borylation of the alkylacetylenes by **1** or the PMP/BFE pair led to additional formation of tetraalkynylborates **3b** and **3c** as minor products (< 5 mol %). We also examined the borylation of other acetylenes by in situ NMR spectroscopy and concluded that the outcomes of the borylations by the PMP/BFE pair and by **1** are similar:

Alkylacetylenes mostly form ligand-free trialkynylboranes, whereas arylacetylenes produce tetraalkynylborates. It should be noted that tetra(arylethynyl)borates appear to be unstable in solution, as evident by the gradually growing intensity of the broad peaks in the aromatic area of the ^{1}H NMR spectra that were attributed to decomposition products.

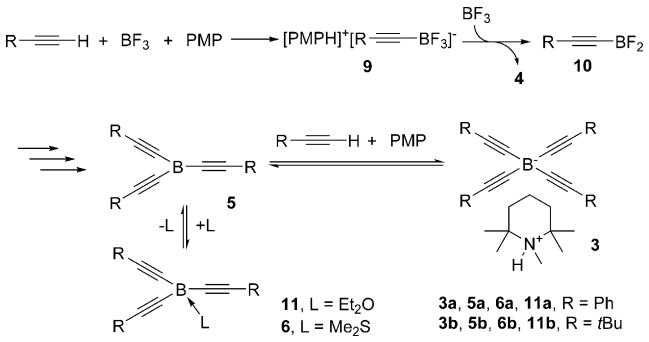
In addition to BFE, we explored the reactivity of PMP and acetylenes with BFS ($BF_3{\cdot}SMe_2$). Stirring terminal acetylenes **2a**–**2k** with the BFS/PMP pair in benzene at room temperature for 6–24 h resulted in the precipitation of **4** and the formation of the trialkynylborane–dimethyl sulfide adducts **6a**–**6k** (Scheme 4), which gave rise to characteristic broad



Scheme 4. C–H borylation of terminal acetylenes with the BFS/PMP pair. Formation of trialkynylborane adducts **6a**–**6k** and their conversion into trialkynylfluoroborates **7a**–**7k**.

resonances near −16 ppm in the ^{11}B NMR spectra. After removing **4** by filtration, some of the adducts, for example, the phenylacetylene derivative **6a**, were isolated in pure form by hexane-induced precipitation. The majority of the adducts were further converted without isolation into trialkynylfluoroborates **7a**–**7k** by treatment with a solution of tetramethylammonium fluoride (**8**)[13] in CH_2Cl_2. These new compounds were isolated as crystalline solids in good to high overall yields. We also prepared alkynylborate **7a** following this method but using the BFE/Me_2S mixture instead of BFS. Using a 1:1:1 ratio of the starting phenylacetylene, BFS, and PMP, **6a** was formed as an intermediate that was completely converted into tetraalkynylborate **3a** within 48 h at room temperature in dichloromethane. Similar but much slower conversion of **6a** into **3a** was observed in benzene (see the Supporting information for details).

Our attempts to detect intermediates of the C–H borylation by in situ NMR studies were unsuccessful; therefore, we concluded that the initial C–H borylation step of the acetylene leading to alkynyltrifluoroborate **9** might be the rate-determining step (Scheme 5). The mechanism of the further transformation of **9** into the ultimate tri- and



Scheme 5. Initial C–H borylation leads to tri- and tetraalkynylboron species via C–H insertion adducts **9**.

tetraalkynylboron species is presently unclear but it is a subject of ongoing studies. Organotrifluoroborates are known to loose fluoride upon treatment with BFE or gaseous BF_3[14] to give the corresponding organodifluoroboranes, such as alkynyl derivatives **10**. Stepwise dismutation of alkynyldifluoroboranes **10** into trialkynylboranes **5** and BF_3 is one of the possible mechanisms. This process, which proceeds via a four-centered transition state, was recently studied computationally.[15]

Summarizing these experimental data, several factors are noted that affect the product outcome during acetylene borylation: the nature of the starting acetylene (alkyl- or aryl-substituted), the presence of dimethyl sulfide, the ratio of the starting materials, and the solvent. To rationalize the observed reactivity, we examined the thermodynamics of some tri- and tetraalkynylboron species by DFT calculations (Table 2).

Table 2: Calculated Gibbs free energies (kcal mol^{-1}) of the formation of tri- and tetraalkynylboron products in dichloromethane and benzene.[a]

R	Et_2O adducts **11a** and **11b**	Me_2S adducts **6a** and **6b**	Tetraalkynylborates **3a** and **3b**
Ph	−0.8 (0.8)	−3.9 (−2.8)	−13.8 (−7.9)[b]
*t*Bu	1.7 (3.4)	−1.9 (−0.9)	−0.1 (6.12)[c]

[a] The energies for the corresponding reactions in benzene are given in parentheses. [b] ΔG^{298} for PMP + **5a** + **2a** → **3a**. [c] ΔG^{298} for PMP + **5b** + **2b** → **3b**.

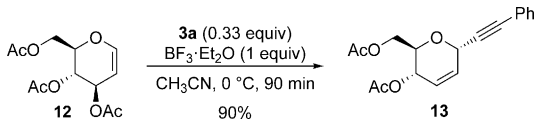
Using phenyl- and *tert*-butylacetylene as representative aryl- and alkylacetylenemodel substrates, we studied the reactivity of trialkynylboranes **5a** and **5b**. The results indicate that unlike BF_3, **5a** and **5b** bind dimethyl sulfide more strongly than diethyl ether, demonstrating the soft Lewis acidic character of trialkynylboranes. Although the addition of diethyl ether to phenyl-substituted borane **5a** in dichloromethane is slightly exergonic, the corresponding adduct **11a** was not observed experimentally probably owing to the energetically much more favorable formation of borate **3a**. In line with our observations, addition of Et_2O to **5b** appeared to be endergonic.[16]

The energies for acetylene C–H borylation by the trialkynylborane/PMP Lewis pair were calculated as well (Scheme 5 and Table 2). We found good consistency between

experiment and calculations. Dichloromethane, being a much more polar solvent than benzene, much better stabilizes the polar Lewis adducts and the ionic tetraalkynylborate salts **3a** and **3b**. Formation of **3a** was found to be more favorable than formation of adducts **6a** and **11a**, as also observed experimentally. In this regard, careful analysis of a sample of **4** that had precipitated during the preparation of adducts **6f** and **6g** revealed 10–12 mol% contamination with the corresponding tetraalkynylborates **3f** (*p*-C_6H_4CN) and **3g** (*p*-C_6H_4COOMe), which is likely a cause of the low target compound yields.

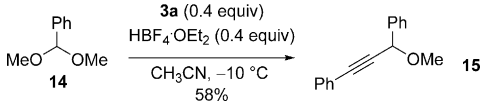
Our calculations clearly showed that aryl-substituted trialkynylborane **5a** is noticeably more Lewis acidic than alkyl-substituted **5b**. The addition of a hydride, a hard Lewis base with minimal steric requirements, can be used for rating the Lewis acidity of compounds.[5b,17] The energy of this process is also one of the key components of energy partition during H_2 activation by FLPs.[7] We found that borane **5a** is noticeably more acidic than **5b**, with respective hydride affinities of −49.0 and −40.1 kcal mol^{-1} in terms of the Gibbs free energy in benzene. These values are similar to that for monomeric BH_3 (−46.3 kcal mol^{-1}) but significantly lower than that of $B(C_6F_5)_3$ (−72.5 kcal mol^{-1}), a benchmark Lewis acidic component used for H_2 activation.[18]

Alkynyldifluoroboranes **10** are unique reagents with ambivalent nucleophilic/Lewis acidic properties that can be generated in situ by treatment of potassium alkynyltrifluoroborates with BFE. Computational studies suggested that **10** can be in equilibrium with the corresponding trialkynylboranes **5** and BF_3.[15] With these considerations in mind, we investigated the reactivity of in situ generated trialkynylborane **5a** in the allylic substitution of tri-*O*-acetyl-D-glucal **12** mediated by the oxonium ion.[19] Glucal **12** was treated with **3a** and BFE in CH_3CN and produced alkynylglucal **13** in high yield with high stereoselectivity (Scheme 6). Moreover, the reaction demonstrated high atom efficiency: All three acetylene groups were transferred to **12** with sub-equimolar amounts of **3a**. Moreover, thymidine was selectively derivatized by using a similar C–C coupling reaction between a trialkynylfluoroborate and thymidine epoxide.[20]



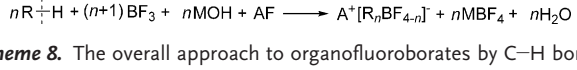
Scheme 6. Lewis acid promoted alkynylation of tri-*O*-acetyl-D-glucal with trialkynylfluoroborate **3a**.

A more general example of C–C coupling applications is presented by the alkynylation of acetals with alkynyltrifluoroborates by either Lewis (BFE)[14a] or Brønsted (HBF_4) acid activation.[21] The latter approach was found to be more powerful for the alkynylation of less reactive aromatic aldehyde derivatives. It was suggested that the Brønsted acid protonates the acetals, which then react directly with the alkynyltrifluoroborates. Similar to the reactivity of alkynyltrifluoroborates,[21] the **3a**/HBF_4 combination reacted with benzaldehyde dimethyl acetal **14**, which gave propargylic ether **15** in 58% yield, whereas only traces of **15** were generated when the reaction was run in the presence of BFE (Scheme 7). Interestingly, we found that either mono- or dialkynylation of **14** can be achieved depending on the amount of **3a** used (see the Supporting Information for details).



Scheme 7. Brønsted acid promoted alkynylation of benzaldehyde dimethyl acetal with trialkynylfluoroborate **4a**.

Finally, we achieved the recovery of PMP from tetrafluoroborate **4** in 83% yield by treatment with an aqueous NaOH solution followed by extraction and vacuum distillation.[22] The C–H borylation of alkynes presented herein is thus accomplished with the aid of BF_3 and alkali metal hydroxide as summarized in the overall equation in Scheme 8. The principal difference between the real transformation and the ideal one depicted in Scheme 1b is the additional formation of tetrafluoroborate as a result of a formal addition of F^- to BF_3. This process apparently improves the overall thermodynamics of the C–H borylation.



Scheme 8. The overall approach to organofluoroborates by C–H borylation with the BF_3/PMP pair accomplished in this work. A^+ = alkali metal or organic cation, M = alkali metal.

In conclusion, a simple aliphatic amine, 1,2,2,6,6-pentamethylpiperidine, and BF_3 form a highly reactive frustrated Lewis pair. No interaction was observed between PMP and $BF_3{\cdot}OEt_2$, whereas treatment of PMP with $BF_3{\cdot}SMe_2$ produced a previously unknown PMP·BF_3 adduct. Regardless of the BF_3 source, its combination with PMP enabled the C–H borylation of terminal acetylenes, giving tetra- or trialkynylboron compounds and pentamethylpiperidinium tetrafluoroborate. Using $BF_3{\cdot}SMe_2$ as the starting material, trialkynylborane–dimethyl sulfide adducts were generated. Upon treatment with tetramethylammonium fluoride, these compounds were converted into trialkynylfluoroborates, which can be used as alkynyltrifluoroborate surrogates, as demonstrated by C–C coupling reactions of the trialkynylfluoroborates with acetals and carbohydrates in the presence of Brønsted or Lewis acids. The recovery of PMP from its tetrafluoroborate salt together with the C–H borylation reactivity provides an atom-efficient approach to organofluoroborate compounds. FLPs based on boron trifluoride complexes and PMP are also promising reagents for the activation of other substrates, especially with regard to the recent reports on the C(sp^2)–H borylation reactivity of FLPs.[23] Such studies are currently in progress in our group.

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