Potassium Trifluoro(organo)borates: New Perspectives in Organic Chemistry

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Potassium trifluoro(organo)borates, highly stable organoboron derivatives, have recently emerged as promising alternatives to other organoboron reagents. These salts have shown interesting reactivity, not only through the intermediate formation of difluoroboranes, but also in transmetallation reactions with transition metals. In numerous reactions they have proven to be more reactive than boronic acids or esters. The preparation and reactivity of these ate complexes is discussed.

Introduction

Organometallic reagents (R−M) are of increasing importance not only for organometallic chemists but also in organic chemistry and pharmaceutical synthesis, and for access to organic materials.[1] The usefulness of organomagnesium and organolithium compounds does not need to be demonstrated, but their high nucleophilicity and basicity sometimes preclude their use in many reactions involving sensitive functional groups. Thus, for decades, chemists have looked for less reactive organometallics that will tolerate a wider range of functionalities, such as Zn, Si, B, Sn for carbon−carbon bond formation, and these have been very useful in conjunction with transition metal catalysts.[2] Among all the described organometallic reagents, organoboranes and organostannanes have emerged as the reagents of choice in various transition metal catalyzed reactions. However, there are still drawbacks in their use: organostannanes and their by-products are generally toxic, and organoboranes, particularly alkyl- and alkynylboranes, have a lack of stability. This lack of stability of organoboranes is due to the vacant orbital on the boron atom, which can be attacked by oxygen or water, resulting in the decomposition of the reagent. One solution emerged in the 1960s with the use of potassium trifluoro(organo)borates, boron ate-complex derivatives.

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1. Potassium Trifluoro(organo)borates: Their Preparation

1.1. Historical Background

Trifluoro(organo)borate salts, or more generally compounds of formula $[R_nBF_{4-n}]^-$ ($n \leq 3$), for a long time

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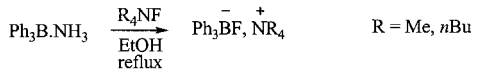
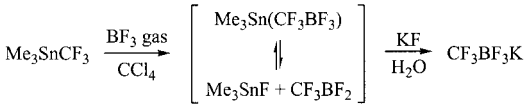
MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

remained laboratory curiosities. Until very recently, only a few compounds of this type had been prepared. To the best of our knowledge, the first report of the preparation of an trifluoro(organo)borate complex was published in 1940. The authors, Fowler and Krauss,[3] prepared tetramethylammonium and tetrabutylammonium triphenylfluoroborates by treatment of triphenylborane−ammonia complex with 1 equiv. of tetraalkylammonium fluoride, in unstated yield (Scheme 1).



Scheme 1. Preparation of tetraalkylammonium triphenylfluoroborates

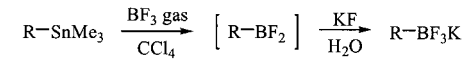
Twenty years later, some publications concerning the preparation of potassium trifluoro(organo)borates appeared in the literature. Their preparation was motivated by the formation of stable perfluoroalkylated boron derivatives. Effectively, trivalent boron compounds bearing a fluorine atom in their α or β positions are very unstable (migration of the fluorine atom from the carbon to the boron atom with formation of carbenes or alkenes), but this is not the case with boron ate complexes. The first of these compounds, potassium trifluoro(trifluoromethyl)borate,[4] was prepared by Chambers et al. from trimethyl(trifluoromethyl)stannane[5] (Scheme 2)



Scheme 2. First preparation of an trifluoro(organo)borate salt

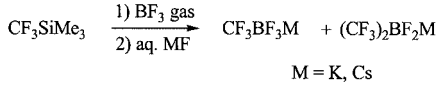
Treatment of trimethyl(trifluoromethyl)stannane (prepared from hexamethylditin and trifluoroiodomethane[6]) with boron trifluoride allowed the formation of trimethyltin trifluoro(trifluoromethyl)borate, in equilibrium with CF_3BF_2, which could further react with Me_3SnCF_3.[7,8] The compounds of the former equilibrium reacted with potassium fluoride in water to give potassium trifluoro(trifluoromethyl)borate in unstated yield. This compound was described as non-hygroscopic and thermally highly stable, not being decomposed below 300 °C. Other salts with different counter-ions were prepared, but showed inferior stability.[5]

Under the same conditions — treatment with gaseous BF_3, followed by the addition of potassium fluoride — other organostannanes were converted into potassium trifluoro(organo)borates. The behavior of the other organostannanes was quite different from that of CF_3SnMe_3, and only organodifluoroboranes were intermediately isolated: no salts of trimethyltin were observed (Scheme 3).



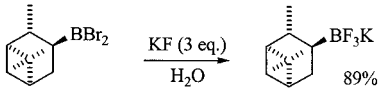
Scheme 3. Preparation of RBF_3K from organostannanes

By this procedure, potassium trifluoro(methyl)-,[9] -(vinyl)-,[9] -[2-(trifluoromethyl)phenyl]-,[10] and -(pentafluorophenyl)borate[11] were obtained. In the same way, by starting from CF_3SiMe_3, the products $CF_3BF_3^-$ and $(CF_3)_2BF_2^-$ were isolated as their potassium or cesium salts[4,7,8] (Scheme 4).



Scheme 4. Preparation of RBF_3K from organosilanes

Treatment of dihaloorganoboranes with excess KF also allowed the formation of trifluoroborate salts. By this procedure, potassium (1*S*)-isopinocampheyltrifluoroborate was obtained in 89% yield from the corresponding dibromoborane derivative[12] (Scheme 5).

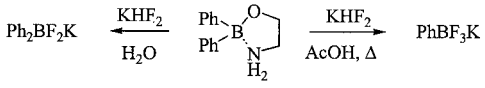


Scheme 5. Preparation of RBF_3K from dihaloboranes

All those first prepared salts were described as highly stable and non-hygroscopic. However, these approaches for the preparation of these salts were not satisfactory, since they implied the intermediate preparation of the highly reactive and unstable organodihaloboranes.

1.2. Use of Potassium Hydrogen Difluoride (KHF_2)

The development of potassium trifluoro(organo)borate chemistry in organic synthesis started with improvements in the preparation procedures. It was only in 1995 that a highly efficient method using potassium hydrogen difluoride (KHF_2) as a fluorinating agent for trivalent boron reagents was described.[13] The use of KHF_2 for the fluorination of boron compounds had been described earlier, however. In 1967, Thierig and Umland[14] reported the preparation of potassium difluorodiphenylborate in unstated yield on treatment of the ethanolamine complex of



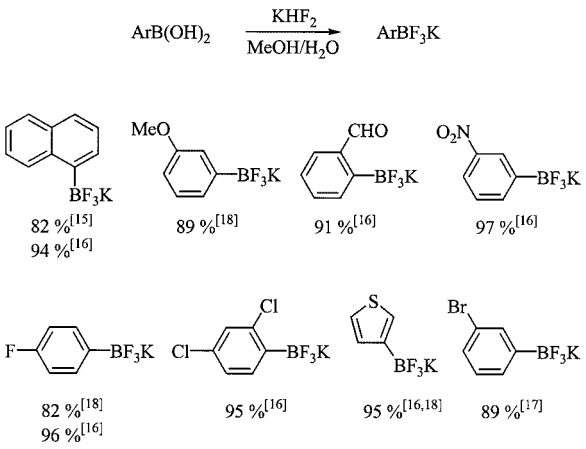
Scheme 6. First use of KHF_2 as fluorinating agent of boron

Ph_2BOH with aqueous KHF_2 (Scheme 6). The same reaction conducted in refluxing acetic acid allowed the formation of potassium trifluoro(phenyl)borate.

Formation of Potassium Aryltrifluoroborates

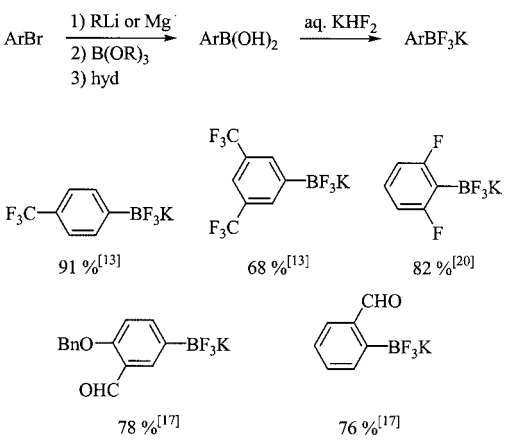
Some twenty years later, in 1995, Vedejs et al.[13] reported that arylboronic acids were efficiently converted into potassium aryltrifluoroborates on treatment with KHF_2 in aqueous methanol. Unlike dihaloboranes, KF was not able to displace the hydroxy ligands on trivalent boronic acids.

Under these conditions, boroximes $(RBO)_3$ or boronic acid dimers $(BBO)_2$, which are usually present in isolated organoboronic acids, reacted equally well. Thus, by using commercially available arylboronic acids it was possible to obtain a large variety of aryltrifluoroborates[13,15–18] (Scheme 7).



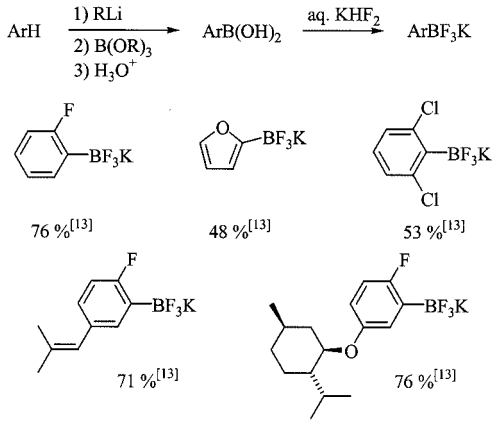
Scheme 7. Preparation of potassium aryltrifluoroborates from commercially available boronic acids

The use of purified organoboronic acids is not necessary, so the generation of potassium aryltrifluoroborates in situ, by use of classical methods for organoboron synthesis,[19] is straightforward. For example, lithium/halogen exchange or magnesium insertion, followed by boronation and hydrolysis allowed the isolation of the crude boronic acid, which on treatment with KHF_2 gave aryltrifluoroborates in high yields[13,17,20] (Scheme 8).



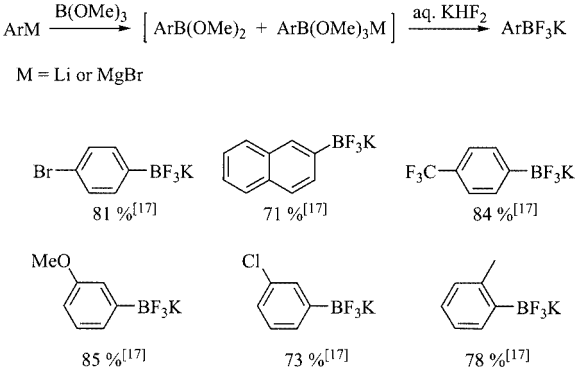
Scheme 8. Formation of potassium aryltrifluoroborates in situ

In these examples, the aldehyde moiety was protected with ethanediol, which was removed upon hydrolysis. In the same way, highly efficient *ortho*-lithiation/boronation procedures[21] may be used for the formation of potassium aryltrifluoroborates.[13] By this approach, functionalized aryltrifluoroborates were obtained in fair yields (Scheme 9).



Scheme 9. Orthometallation procedure in the preparation of potassium aryltrifluoroborates

In all cases, yields are comparable to or higher than those reported for the synthesis of the corresponding boronic acid derivatives. When not necessary, the hydrolysis step can be dispensed with before the treatment with KHF_2. Thus, we have shown that KHF_2 was able to displace alkoxo ligands on aryltrimethoxyborates generated in situ right after the boronation step[16,17] (Scheme 10).



Scheme 10. Formation of RBF_3K in situ

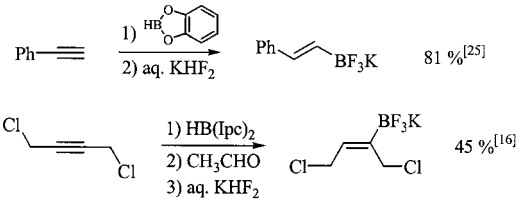
The isolation and purification of potassium aryltrifluoroborates are straightforward, as in many cases they precipitate upon formation and are easily filtered.[13] In our hands, we found that higher yields could generally be obtained by evaporation of the solvent after the addition of KHF_2 and extraction (or continuous extraction) of the resulting solid with an appropriate solvent, generally acetone.[16] This procedure proved to be quite general and has been efficiently used with success by others.[22]

Moreover, purification by reprecipitation or by recrystallization either from acetonitrile[9b,13,15,23] or from acetone/diethyl ether[16,22] has allowed the isolation of analytically pure compounds: inorganic salts such as KF, KHF_2, or KBF_4 are insoluble in acetonitrile or acetone, allowing their separation from the product. However, traces of KHF_2 have

been observed as a contaminant when acetonitrile was used as recrystallization solvent.[23]

Formation of Potassium Alken-1-yltrifluoroborate

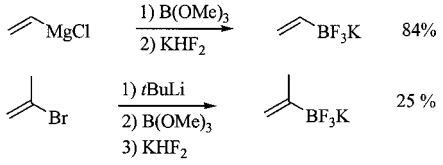
The generation of potassium trifluoro(organo)borates by the use of KHF_2 as a reagent is very general and has allowed the formation of various potassium alken-1-yltrifluoroborates. Several procedures common to other organoboron preparations have been used to access such compounds.[19] One of the most important consists of the hydroboration of the corresponding alk-1-yne, catalyzed if necessary by a transition metal[24] (Scheme 11).



Scheme 11. Formation of potassium alkenyltrifluoroborates by hydroboration

By this procedure, potassium trifluoro[(*E*)-2-phenylethenyl]borate and other alkenyl derivatives were obtained for the first time in high yield by a one-pot procedure[25] avoiding the isolation of the boronic acid. Moreover, catechol is readily removed during the purification procedure, because of the insolubility of RBF_3K in non-polar solvents. In another example, hydroboration of commercially available 1,4-dichlorobut-2-yne with diisopinocampheylborane, followed by oxidation with acetaldehyde[26] and treatment in situ with aqueous KHF_2, afforded the corresponding alkenyltrifluoroborate in fair yield.[16] From these examples, KHF_2 proved to be sufficiently reactive to cleave the boron−oxygen bounds in boronic esters.

As in the case of arylboron compounds, it is also possible to form alkenylboron reagents from lithium or magnesium organometallic derivatives. Simple potassium trifluoro(vinyl)borate was prepared on a large scale from vinylmagnesium chloride by treatment with trimethoxyborane fol-



Scheme 12. Potassium alkenyltrifluoroborates from organometallic derivatives

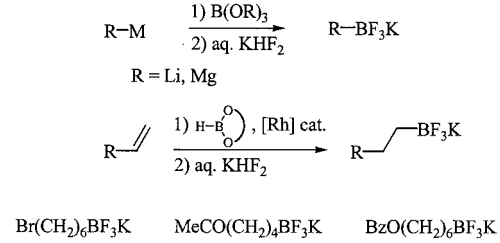
lowed by in situ addition of KHF_2 (Scheme 12).[16,27] In another example, potassium trifluoro(isopropenyl)borate was obtained from 2-bromopropene in a one-pot procedure involving lithium/bromine exchange, boronation with trimethyl borate, and subsequent treatment with KHF_2.[28]

Of course, potassium alkenyltrifluoroborates can be prepared from commercially available boronic acids or esters.[16,25] Purification and isolation of alkenyltrifluoroborate salts are conducted like those of their aromatic congeners.

Once again, all those alkenyltrifluoroborate salts proved to be highly stable for several years at room temperature, which is not the case for all trivalent alkenylboron compounds.[19] Vinylboronic acid, for example, is highly unstable and cannot be isolated,[29] its ester 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane is only slightly stable at −20 °C under nitrogen, whereas potassium trifluoro(vinyl)borate did not show any decomposition after several years.

Potassium Alkyltrifluoroborates

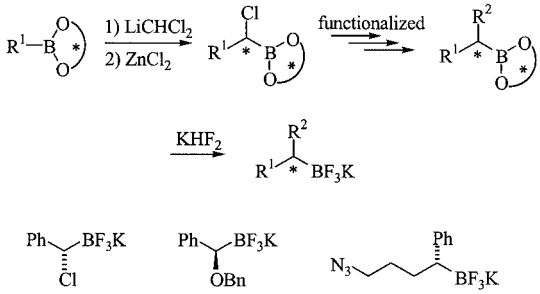
In the same way, potassium alkyltrifluoroborates were prepared by conventional procedures used for the preparation of trivalent organoboron compounds, the last step of the preparation being treatment in situ with potassium hydrogen difluoride[22] (Scheme 13).



Scheme 13. Preparation of potassium alkyltrifluoroborates

These literature procedures for the formation of organoboron derivative include addition of organometallic reagents (Li or Mg) to trimethyl borate[30] and hydroboration of alkenes either by dibromoborane−dimethyl sulfide complex[31] or by catecholborane or pinacolborane in the presence of rhodium catalysts.[24]

Optically active potassium alkyltrifluoroborates have been prepared by Matteson et al.,[23] by their α-haloboronic ester chemistry,[32] from pinanediol or 1,2-dicyclohexylethanediol (DICHED) boronic esters by treatment with



Scheme 14. Synthesis of optically active potassium alkyltrifluoroborates

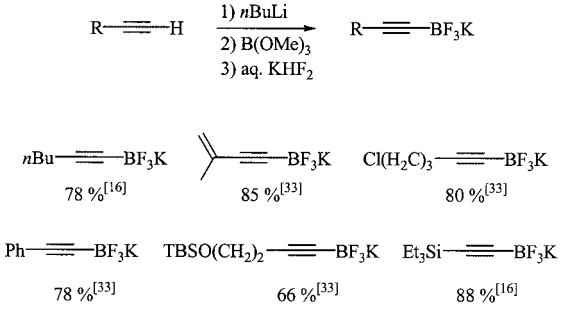
KHF_2 (Scheme 14). This procedure allowed quantitative and easy recovery of the chiral diol, which is not so easy by conventional cleavage of boronic esters.[23]

As we can see from those selected examples, the use of KHF_2 is compatible with various functional groups such as

Cl, Bn, N_3, ... It is important to note that in their work, the authors observed that formation of alkyltrifluoroborates from hindered alkylboronic esters (DICHED or pinanediol) is generally reversible and reaches equilibrium at 22 °C within 0.5−2 h, which explains the lower yields obtained from pinanediol esters.

Potassium Alkyn-1-yltrifluoroborates

An efficient route to potassium (alkyn-1-yl)trifluoroborates from readily available alk-1-ynes by the previously described methodology was also possible.[16] These salts were easily obtained by deprotonation of alk-1-ynes, boronation, and treatment with KHF_2 in situ (Scheme 15). This three-step, one-pot synthesis provides an efficient and versatile procedure for the preparation of various potassium (alkyn-1-yl)trifluoroborates.[16,33] Interestingly, a triethylsilyl group attached at the carbon atom and a TBS (*tert*-butyltrimethylsilyl) moiety attached at the oxygen atom were not removed, despite the use of a fluoride source.

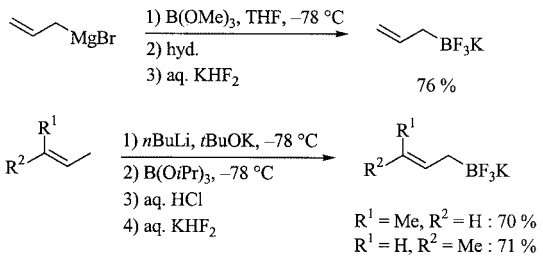


Scheme 15. Preparation of potassium alkyn-1-yltrifluoroborates

These compounds represent the first stable (toward oxygen and moisture) organoboron derivatives containing a C_{sp}−B bond, although the chemistry of alkynylborates has been well documented.[34] Unlike other alkynylboranes, which are not stable and are readily hydrolyzed in the presence of water or alcohol, these salts are indefinitely stable at room temperature.

Potassium Allyltrifluoroborates

The formation of potassium allyltrifluoroborates via the corresponding boronic acids was achieved in a manner analogous to that used for the synthesis of other trifluoro(organo)borate salts.[35,36] The requisite allylboronic acids were synthesized by the addition of allylmagnesium bromide or crotylpotassium to trialkyl borates (Scheme 16).

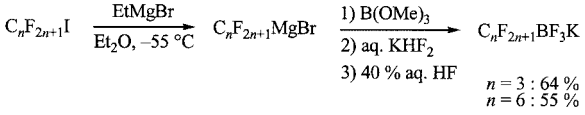


Scheme 16. Preparation of potassium allyltrifluoroborates

Subsequent conversion into trifluoroborate salts was achieved by treatment with aqueous KHF_2 in situ.[35,36] These salts, like the others, are crystalline, air- and water-stable solids.

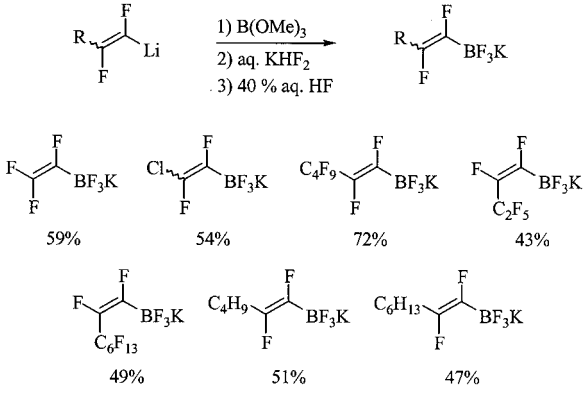
Potassium Trifluoro(perfluoroalkyl)- and -(polyfluoroalken-1-yl)borates

As already mentioned in the Introduction, one of the first potassium trifluoro(organo)borates was a perfluoroalkylated one, CF_3BF_3K,[5,6] which showed exceptional stability in comparison with other trivalent boron derivatives. With the exception of this compound, no other trifluoro(perfluoroorgano)borates had been described until very recently. The synthesis of such compounds was studied in several papers by Frohn et al.,[37−39] who first elaborated a convenient route to potassium trifluoro(perfluoroalkyl)borates from the easily available perfluoroalkyl iodides[37] (Scheme 17).



Scheme 17. Formation of potassium trifluoro(perfluoroalkyl)borates

The formation of the unstable perfluoroalkylmagnesium reagent was carried out at low temperature by magnesium/halogen exchange with ethylmagnesium bromide. Treatment with trimethoxyborane followed by KHF_2 gave incomplete formation of trifluoroborate salts but as mixtures with fluorinated boranes of formula $K[R_fBF_n(OMe)_{3-n}]$. The remaining OMe ligand could, however, be replaced by fluorine by treatment with aqueous HF.[37,38] The authors assumed[38] that the replacement of the OMe substituent by fluorine, a highly electron-withdrawing group, increases the Lewis acidity of the borane and hinders the elimination of the anion MeO^-. However, the protonation of the oxygen atom by acidification with aqueous HF facilitates the leaving of the OMe. In the same way, several trifluoro(polyfluoroalken-1-yl)borates were synthesized for the first time from the corresponding organolithium reagents[38,39] (Scheme 18).



Scheme 18. Preparation of potassium trifluoro(polyfluoroalken-1-yl)borates

As in the case of trifluoro(perfluoroalkyl)borates, final treatment with aqueous HF was generally necessary for complete conversion into trifluoroborate salts. All those salts are crystalline compounds showing exceptional stability toward air and water.

Stability and Properties of Potassium Trifluoro(organo)borates

With only very minor exceptions, all the prepared potassium trifluoro(organo)borates show high stability toward air and water, which is not the case for the vast majority of other organoboron compounds. For example, the very well known and widely used organoboronic acids show variable stability (vinyl-, alkyl-, and alkynylboronic acids are not very stable) and their purification is not straightforward. Moreover, isolated boronic acids generally contain large quantities of anhydrides or boroximes, which results in problems for determination of their stoichiometry. On the other hand, boronic esters show higher stability but are generally less reactive than the free boronic acids. Moreover, the diols used for their preparation are generally expensive and difficult to separate at the ends of the reactions. Finally, from an economic viewpoint, KHF_2 is half as expensive as catechol and 10 times cheaper than pinacol.

Potassium trifluoro(organo)borates are not hygroscopic and can be stored indefinitely at room temperature without any observed decomposition. They generally show high solubility in polar solvents such as methanol, acetonitrile, acetone, DMF, or DMSO, some are slightly soluble in toluene, THF, and water, but they are insoluble in nonpolar solvents such as dichloromethane, diethyl ether, and hydrocarbons. It is important to note that, unlike trivalent boron substituents, trifluoroborate is an electron-donating substituent.[20]

From a practical viewpoint, their preparation, by treatment with KHF_2, is straightforward and avoids the isolation of trivalent organoboron species. The use of KHF_2 as a fluorinating agent is compatible with most functional groups, and in particular, trialkylsilyl protecting groups are not removed despite the presence of fluorine anions.

The purities of the salts can easily be checked by ^{19}F or ^{11}B NMR (Table 1). The ^{11}B NMR spectra generally feature a reasonably well resolved 1:3:3:1 quadruplet, ranging from $\delta = -2.5$ to $+7$ ppm relative to BF_3, corresponding to the coupling of ^{11}B with three equivalent fluorine atoms. This gives an indication of the substitution at the boron atom. In ^{19}F NMR spectra, 1:1:1:1 quadruplets, ranging from $\delta = -160$ to -130 ppm relative to $CFCl_3$, are generally observed, as would be expected for the coupling of ^{19}F with ^{11}B of spin 3/2.

Table 1. NMR properties of potassium trifluoro(organo)borates

RBF_3K	^{11}B NMR[a]	^{19}F NMR[b]	J_{B-F} [Hz]
Aryl/alkenyl	1.7 to 5.0	−143 to −132	43 to 60
Alkyl	5.4 to 6.3	−149 to −132	43 to 60
Alkynyl	−2.4 to −1.8	−133 to −132	37 to 40
Perfluoroalkyl	ca. −0.5	ca. −133	ca. 37
Perfluoroalkenyl	−0.2 to 0.7	−144 to −142	39 to 43

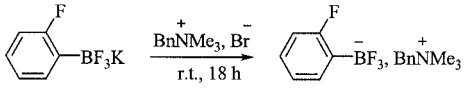
[a] In ppm relative to $BF_3{\cdot}Et_2O$. [b] In ppm relative to $CFCl_3$.

A recent study dealing with the stability of potassium trifluoro(organo)borates towards acids reveals some interesting features concerning the stability of these compounds toward hydrodeboration and gives an idea of the force of the carbon−boron bond.[40] In this work, several potassium trifluoro(organo)borates were treated with different acids of different strengths (CH_3CO_2H, CF_3CO_2H, and aqueous or anhydrous HF). From the results obtained, the following order of stability concerning the different organic substituents can be proposed: alkyl > aryl > alken-1-yl ≈ perfluoroalkyl > perfluoroaryl > perfluoroalken-1-yl. All the studied salts were stable for prolonged periods in acetic acid at room temperature.

Other Salts of Trifluoro(organo)borates

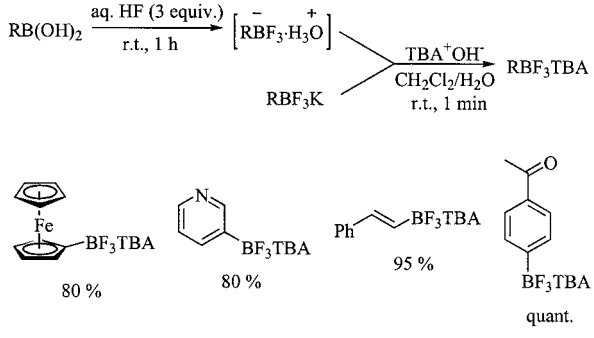
In their original publication, Chambers et al.[5] described other salts of (trifluoromethyl)trifluoroborates. The ammonium salt $[CF_3BF_3]NH_4$ appeared to be less stable than the potassium one, while the barium salts proved to be highly hygroscopic.

In order to increase the solubility of the fluoroborate salts in non-polar solvents, some groups have prepared and used tetraalkylammonium salts. The first example was reported by Vedejs et al.,[15] with the formation of benzyltrimethylammonium salts from their potassium counterparts on treatment with benzyltrimethylammonium bromide (Scheme 19).



Scheme 19. Counter-ion exchange in RBF_3K

This procedure was improved through the use of ammonium hydroxide in place of bromide.[41] Thus, counter-ion exchange of RBF_3K or $[RBF_3^-{\cdot}H_3O^+]$ was achieved by treatment of the salts with tetra-*n*-butylammonium (TBA) hydroxide (Scheme 20). All of the tetra-*n*-butylammonium



Scheme 20. Formation of tetraalkylammonium trifluoro(organo)-borates

compounds were found to be readily soluble in both polar and non-polar solvents[41] but no information concerning their stability compared to potassium salts was given.

2. Generation of RBF_2 in situ and Its Applications

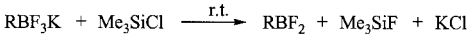
Very early on, potassium trifluoro(organo)borates were regarded as potential precursors of organodifluoroboranes as excellent Lewis acids. Thus, in the 1960s, the preparation of potassium trifluoro(vinyl)borate and trifluoro(methyl)borate and their use as precursors of the corresponding difluoroboranes were patented by Stafford et al.[9]

Scheme 21. High-temperature generation of RBF_2

(Scheme 21). These workers showed that heating of these salts at high temperature allowed the generation of difluoro(organo)boranes of high purity, which could be directly used for further applications (polymerization promoters, for example).

Potassium trifluoro(organo)borates were thus regarded as an "excellent means of storing and handling halo(organo)boranes, and of regenerating these compounds in a highly pure form".[9] Some 25 years later, it was reported that treatment of potassium trifluoro(organo)borates with $BF_3{\cdot}Et_2O$ allowed clean generation of the corresponding difluoroborane.[12] Only one example was described, however, and general methods for the generation of difluoro(organo)boranes were still needed.

Vedejs et al., in their original work[13] concerning the preparation and use of trifluoroborate salts, studied the generation of trivalent boranes from trifluoro(organo)borates. They first showed that the nature of the counter-ion of the trifluoroborate was governing their stabilities. Thus, in the presence of Mg^{2+} or Li^+ salts in water, trifluoro(organo)borates were rapidly decomposed into boronic acids, through the intermediate formation of RBF_2. A more efficient fluorophile was found in the electron-deficient trimethylsilyl chloride.[13] Thus, on treatment with 1 equiv. of trimethylsilyl chloride, potassium trifluoro(organo)borates decomposed cleanly in RBF_2, affording an efficient route to dihaloboranes (Scheme 22).

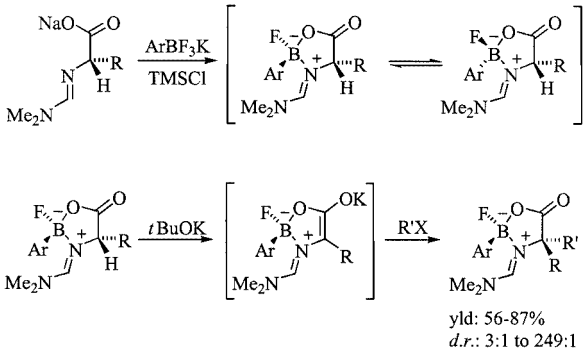


Scheme 22. Generation of difluoro(organo)boranes by use of chlorosilanes

It is believed that RBF_2 is released from a silicon-activated intermediate containing B−F−Si linkage by simple B−F heterolysis.[13] Other Lewis acids have been used for the generation of difluoro(organo)boranes in situ; these include BF_3,[20,35,36,42,43] AsF_5,[37] and $SiCl_4$,[23] but many other Lewis acids decompose trifluoro(organo)borates.[36] These RBF_2 species generated in situ have shown general application in organic synthesis.

2.1. $ArBF_3K$ in Crystallization-Induced Asymmetric Transformations

The first application of the aryldifluoroboranes generated in situ from potassium trifluoro(organo)borates was described by Vedejs et al.[13,15] These boranes were used as Lewis acids in crystallization-induced asymmetric transformations for the generation of α,α′-disubstituted amino acids. On treatment of crude amidinocarboxylates with aryltrifluoroborates in the presence of trimethylsilyl chloride in THF, two diastereoisomeric boron ate complexes were



Scheme 23. $ArBF_3K$ species as auxiliaries in amino acids synthesis

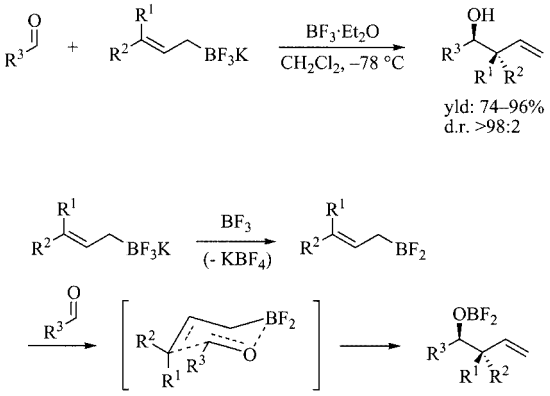
obtained (Scheme 23). Under appropriate conditions, it was possible to isolate only one boron epimer in theoretical quantitative yield because interconversion between the two epimers occur readily through the dissociation of the ate complex.

Thus, practically, the chiral information from the starting amino acid is stored at the boron atom. From the isolated major diastereoisomer, alkylation of the resulting enolate occurs with good diastereoselectivity at the face opposite the Ar substituent, allowing, after hydrolysis, the formation of amino acids containing quaternary carbon centers.[15] The two diastereoisomers resulting from the alkylation can be separated by chromatography, allowing the formation of amino acids with high enantiomeric excesses. Moreover, by variation of the nature of the trifluoro(organo)borate, it is therefore possible to increase the diastereoselectivity of the reaction and to facilitate the crystallization process.

2.2. Diastereoselective Allylation of Aldehydes

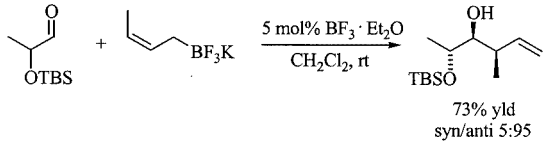
Aldehydes react with a variety of allylmetal compounds to give homoallylic alcohols,[44] and among these, trivalent

allyl- and crotylboron compounds are particularly useful because of the high yields and excellent levels of stereocontrol they provide.[45] A major disadvantage with such compounds, though, is their sensitivity to air and/or moisture, so they are generally prepared immediately prior to use. To circumvent this problem, Batey et al. developed the use of potassium allyl- and crotyltrifluoroborates in allylation reactions.[35,36] Allyldifluoroboranes were generated in situ by addition of a variety of Lewis acids and allowed to react with aldehydes at low temperatures (Scheme 24).



Scheme 24. Allylation of aldehydes with RBF_3K

Among the Lewis acids tested, $BF_3{\cdot}Et_2O$ was found to initiate the reaction most efficiently. Generally, high yields were achieved with a variety of aldehydes in very fast reactions. Crotylation with potassium (*Z*)- and (*E*)-crotyltrifluoroborates was found to work with excellent levels of stereocontrol, consistently with the addition of tricoordinate boron species through Zimmerman−Traxler-like transition states (Scheme 24). The reaction could also be conducted with catalytic $BF_3{\cdot}Et_2O$ (5 mol %) at room temperature without affecting the yields. This reaction has also been applied to the allylation of aldehydes bearing an α- or β-stereogenic center.[36] In particular, when the (*Z*)-crotyl reagent was used, very good *anti* selectivity was observed in the addition to α-OTBS-substituted (TBS = *tert*-butyldimethylsilyl) aldehydes (Scheme 25). Use of other allylboron derivatives or β-substituted aldehydes generally resulted in modest diastereoselectivity.

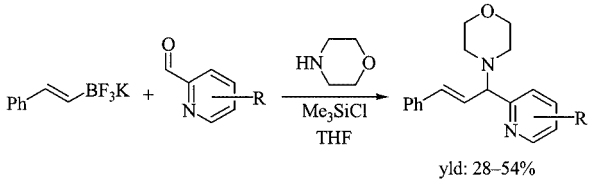


Scheme 25. Crotylation of α-substituted aldehydes

This reaction can also be conducted in aqueous biphasic medium[46] in the presence of a phase-transfer catalyst (PTC). Among the different PTCs tested, tetra-*n*-butylammonium iodide proved to be the most efficient, affording allylation products in high yields at room temperature in dichloromethane/water mixtures within 15 min. In the absence of PTC, the reaction was found to be rather sluggish. The presumed role of the PTC in this reaction is to transport the allyltrifluoroborate anion from the aqueous phase into the organic phase, with the reaction presumably occurring at the interface of the aqueous and organic phase.[46]

2.3. Addition of Trifluoro(organo)borates to Iminium Species Generated in situ

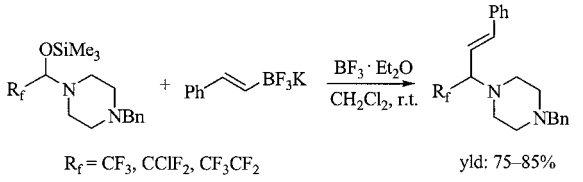
Thanks to their high Lewis acidity, difluoro(organo)boranes generated in situ have been shown to be very reactive in 1,2-additions to iminium derivatives. The first example described concerned the use of potassium trifluoro(organo)borates in the Boronic Mannich Reaction[47] (BMR, Scheme 26), a three-component reaction between aldehydes, amines, and organoboronic acids.[48] The authors were thus able to show that potassium trifluoro(styryl)borate could participate efficiently in BMRs[47]. The difluoroborane was generated in situ with the use of trimethylsilyl chloride as fluorophile.



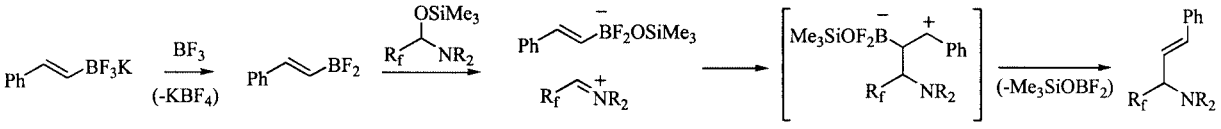
Scheme 26. Boronic Mannich reaction with potassium alken-1-yltrifluoroborates

Among the heterocyclic aldehydes tested, only aldehydes possessing a heteroatom α to the aldehyde group gave the BMR product. Under these standard conditions, the yields obtained on use of the corresponding boronic acid were always below 10%, demonstrating the higher electrophilicity of difluoro(organo)boranes in relation to other trivalent organoboron derivatives. Moreover, reaction times were generally shorter.

Potassium alken-1-yltrifluoroborates also proved to be good nucleophiles in reactions with trifluoroacetaldehyde hemiacetals.[43] In the presence of $BF_3{\cdot}Et_2O$ as Lewis acid, difluoro(styryl)borane derivatives generated in situ reacted with trifluoromethylated iminium ions with good yields in



Scheme 27. Vinylation of fluorinated iminium species with potassium alken-1-yltrifluoroborates



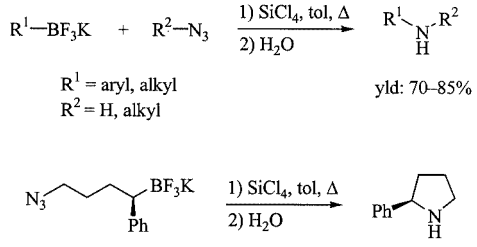
Scheme 28. Mechanism of the vinylation of iminium cations

dichloromethane at room temperature (Scheme 27). Under these conditions, alkenylsilanes failed to deliver α-fluoroalkylated amines.

With regard to the mechanisms of such reactions, some general considerations may be suggested. The RBF_2 species generated in situ acts as a Lewis acid to activate the hemiaminal, generating an iminium and a nucleophilic species.[43,49] The precise mechanism for the reaction between the iminium and organoboron species is still unclear, but should involve a nucleophilic attack of the electron-rich double bond onto the highly electrophilic iminium cation (Scheme 28). In the BMR reaction, chelation of the organoboron compound to the electrophilic substrate seems to be necessary for the reaction to proceed. These reactions, with use of difluoro(organo)boranes generated in situ, appear to be promising and call for further developments.

2.4. Trifluoro(organo)borates in Secondary Amine Synthesis

Very recently, alkyldifluoroboranes generated in situ from potassium alkyltrifluoroborates have been shown to react with organic azides to give secondary amines.[23] For the generation of difluoroborane, the authors found that the use of tetrachlorosilane allowed faster reactions than that of Me_3SiCl. Thus, reactions between trifluoroborates and slight excesses of azides were efficiently promoted by tetrachlorosilane to afford secondary amines in good yields (Scheme 29).

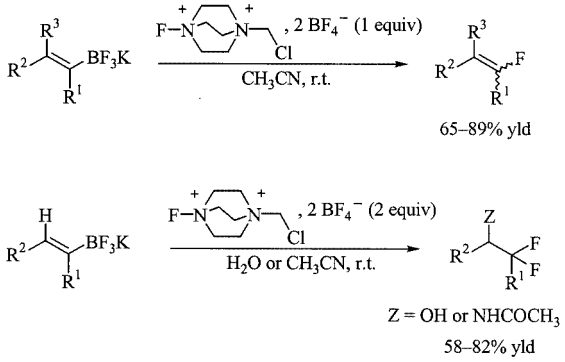


Scheme 29. Conversion of trifluoro(organo)borates into secondary amines

An example of the intramolecular reaction has also been reported, with the preparation of a chiral pyrrolidine.[23] This recently developed reaction is one of the most promising for the formation of secondary amines from organoboron compounds. Moreover, the use of reactive organodifluoroboranes generated in situ appeared to be superior to previously described reactions using highly reactive and unstable alkyldichloroboranes or trialkylboranes, in which only one of the three alkyl groups is transferred.[23]

3. Reactions between Potassium Trifluoro(organo)borate and Electrophiles

The first application of potassium trifluoro(organo)borates other than the generation of difluoro(organo)boranes in situ[13] concerns the use of trifluoroborate salts in electrophilic fluorination.[50] Petasis et al. used potassium alkenyltrifluoroborates to produce alkenyl fluoride in good yields through the use of Selectfluor™ as fluorinating agent[25] (Scheme 30).



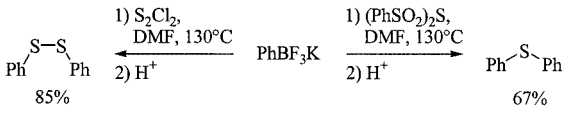
Scheme 30. Fluorination of potassium alkenyltrifluoroborates

Reaction conditions (acetonitrile, room temperature) proved to be very mild. Under these conditions the reaction was quite slow when the corresponding alkenylboronic acids were used and the product was contaminated with variable amounts of the fluorine-free alkene. With regard to the mechanism, the reaction presumably involves an addition/elimination pathway via a carbocation intermediate.[25] The formation of a mixture of isomers and a faster reaction with trifluoro(organo)borates than with boronic acids are consistent with this mechanism.

In the presence of a second equivalent of Selectfluor™, the alkenyl fluoride undergoes further reaction to produce a putative carbocationic intermediate, which is quenched by the solvent.[25] This reaction only worked with compounds affording benzylic carbocations (R^2 = Ar).

Another example of reactions between trifluoro(organo)borates and electrophiles concerns their sulfuration. Thus, Gingras et al.[51] showed that potassium trifluoro(phenyl)borate reacted with different sulfurating agents to afford sulfides or disulfides. As an example, treatment of $PhBF_3K$ with bis(phenylsulfonyl) sulfide in DMF at 130 °C afforded, after acidic treatment, diphenyl sulfide in 67% yield (Scheme 31). On the other hand, treatment with sulfur monochloride (S_2Cl_2) under identical conditions allowed

the formation of diphenyl disulfide in 85% yield (Scheme 31).



Scheme 31. Sulfuration of potassium trifluoro(phenyl)borate

Among the organoborate salts tested, the most reactive proved to be potassium trifluoro(organo)borates. The reaction is believed to operate in a carbanion-like manner and suggests an ionic mechanism.[51]

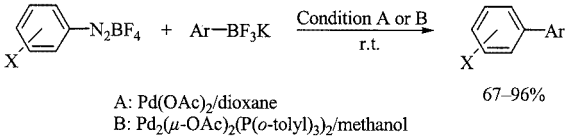
4. Potassium Trifluoro(organo)borate in Transition Metal Catalyzed Reactions

We were able to show very early that potassium trifluoro(organo)borates participated in transition metal catalyzed reactions,[52] or in other words, that transmetallation of trifluoro(organo)borate to transition metals was feasible. At present, potassium trifluoro(organo)borates have been used in two distinct processes: palladium-catalyzed reactions with aryl halides or pseudohalides (Miyaura−Suzuki-type reactions[53]) and 1,4- and 1,2-additions to α,β-unsaturated substrates or aldehydes (Miyaura−Hayashi-type reactions[54]).

4.1. Palladium-Catalyzed Cross-Coupling Reactions

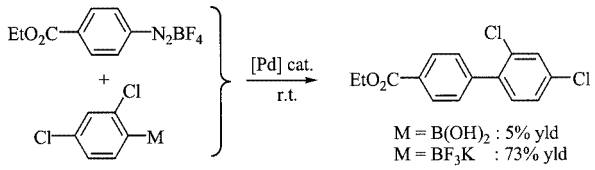
Cross-Coupling with Arenediazonium Salts

In 1997, we were the first to show that potassium trifluoro(organo)borates were suitable substrates in palladium-catalyzed reactions.[52] As coupling partners, the highly stable and non-explosive arenediazonium tetrafluoroborates[55] were chosen, because of their availability from inexpensive aromatic amines.[56] We showed that, in the presence of catalytic amounts of palladium and in the absence of any base, cross-coupling reactions between arenediazonium species and potassium aryltrifluoroborates occurred at room temperature and with high yields[16,27,52] (Scheme 32).



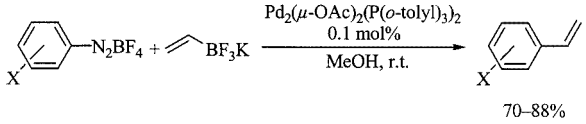
Scheme 32. Cross-coupling of arenediazonium species with aryltrifluoroborates

Optimization of the reaction revealed that two sets of catalyst/solvent systems were efficient: $Pd(OAc)_2$ in 1,4-dioxane, and the palladacycle $Pd_2(\mu\text{-}OAc)_2[P(o\text{-tolyl})_3]_2$[57] in methanol. Under such conditions, high yields of biaryls were obtained at room temperature within 1−4 h. The reactivity of aryltrifluoroborates in this coupling was far superior to that of the corresponding boronic acids,[55] giving higher yields of biaryls,[16,52] particularly when hindered substrates were involved. Coupling between, for example, 4-(ethoxycarbonyl)benzenediazonium tetrafluoroborate and (2,4-dichlorophenyl)boronic acid afforded only traces of biaryl[55] [$Pd(OAc)_2$, dioxane], whereas the use of the corresponding trifluoroborate gave the coupling product in 73% yield[16,52] {$Pd_2(\mu\text{-}OAc)_2[P(o\text{-tolyl})_3]_2$, MeOH} (Scheme 33).



Scheme 33. Comparison of reactivities of RBF_3K and $RB(OH)_2$

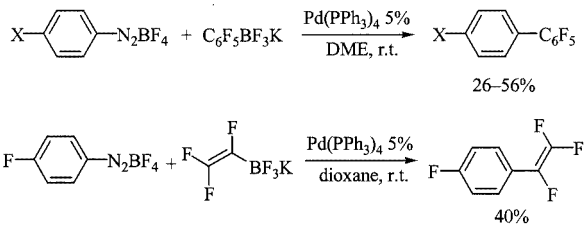
These optimized conditions could also be applied for the introduction of an alken-1-yl substituent onto diazonium salts through the use of potassium alkenyltrifluoroborates.[16,27] More particularly, potassium trifluoro(vinyl)borate proved to be a highly efficient vinylating agent for diazonium salts. Indeed, palladium-catalyzed cross-coupling reactions between arenediazonium tetrafluoroborates and potassium trifluoro(vinyl)borate afforded styrene derivatives in good yields at room temperature[27] (Scheme 34).



Scheme 34. Vinylation of arenediazonium tetrafluoroborates

The reactions were generally very fast (less than a few minutes), even with low catalyst loading at room temperature (TOF > 3000). Other alken-1-yltrifluoroborates also participated in this coupling.

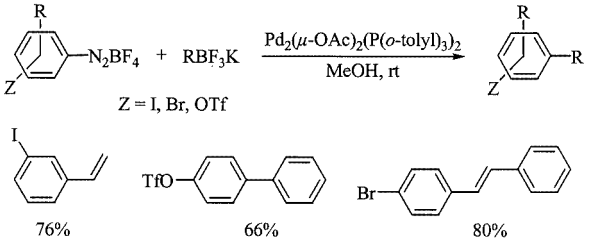
Extension of this coupling to potassium trifluoro(polyfluorophenyl)borates has recently been described.[58] Reaction conditions were optimized for that particular type of substrate, as under our described conditions[16,52] only traces of the expected cross-coupling product were obtained because of the decomposition of the catalyst. The authors showed that moderate yields of biaryls could be obtained by use of $Pd(PPh_3)_4$ as catalyst in DME at room temperature[58] (Scheme 35).



Scheme 35. Cross-coupling with polyfluorinated trifluoro(organo)-borates

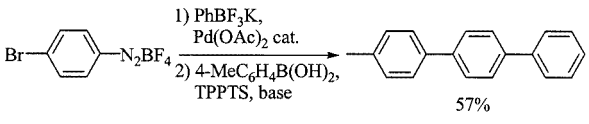
These lower yields of biaryls in comparison with those obtained with non-fluorinated aryltrifluoroborates may be attributed to the lower reactivity of $C_6F_5BF_3K$ and to its sensitivity to hydrodeboration. In another example,[58] the authors showed that (trifluoroethenyl)trifluoroborate, the fluorous analogue of trifluoro(vinyl)borate, could also couple with diazonium salts, although in lower yields. This example represents the first coupling of a perfluoroalken-1-yl organometallic reagent catalyzed by a transition metal.

One interesting feature of this cross-coupling reaction is its high chemoselectivity towards diazonium in the presence of triflate, bromo, or iodo substituents.[16,27,52] Indeed, it was possible to couple the diazonium group selectively with potassium trifluoro(organo)borates in the presence of triflate, bromo, and − in many cases − iodo substituents (Scheme 36).



Scheme 36. Chemoselectivity of coupling with arenediazonium salts

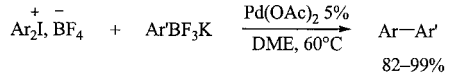
This higher reactivity of the diazonium substituent allowed the formation of products that could be further functionalized by iterative cross-coupling. Thus, two-step, one-pot coupling with the same palladium catalyst was achieved. As an example, chemoselective coupling of the diazonium functionality with potassium trifluoro(phenyl)borate in the presence of palladium acetate, followed by the addition of TPPTS ligand, base, and boronic acids, allowed a second coupling with the bromo substituent to give a teraryl[17] (Scheme 37). From these results it clearly appeared that the diazonium group was far more reactive, and that the order of reactivity of the different electrophiles could be classified as: $N_2^+ > I > Br, OTf$.



Scheme 37. Iterative cross-coupling reactions

Cross-Coupling with Hypervalent Iodonium Compounds

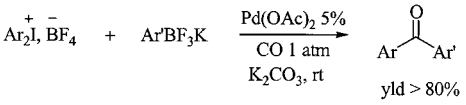
Hypervalent iodonium salts can be used efficiently as partners in palladium-catalyzed cross-coupling reactions with potassium trifluoro(organo)borates. Chen et al.[59] showed that, in the presence of 5 mol % of palladium acetate in DME at 60 °C, coupling between diaryliodonium tetrafluoroborates and potassium aryltrifluoroborates afforded high yields of biaryls (Scheme 38).



Scheme 38. Cross-coupling with aryliodonium salts

As in the case of diazonium salts, addition of a base for the cross-coupling was unnecessary, and (hydroxy)iodo(tosyloxy)arenes [ArI(OH)OTs] also participated as coupling partners in this reaction.[59] This coupling was neither sensitive to the nature of the solvent, nor to the palladium catalyst precursor employed, all the tested solvents and catalysts affording yields of over 80% in all the optimization studies.

Diaryliodonium salts can also serve as substrates for carbonylative cross-coupling reactions with potassium aryltrifluoroborates (Scheme 39).[60] Optimization of the reaction revealed that the presence of a base was necessary in the palladium carbonylative process in order to suppress the direct formation of biaryl compounds.

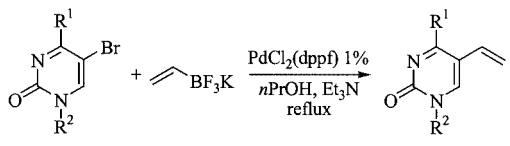


Scheme 39. Carbonylative cross-coupling reactions

In this reaction, the tetrafluoroborate counter-ion proved to be superior to chloride or tosylate anions, while (hydroxy)iodo(tosyloxy)arenes were not suitable, as they afforded only direct cross-coupling products.

Cross-Coupling with Aryl Halides and Triflates

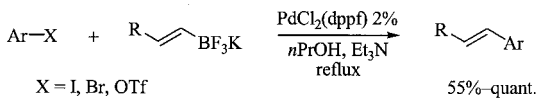
We have just shown that efficient cross-coupling reactions with arenediazonium or aryliodonium species can be accomplished at low temperature and in the absence of any added base. Unfortunately, cross coupling between potassium trifluoro(organo)borates and aryl halides or triflates required the addition of a base for the reaction to proceed. In its absence, no cross-coupling products were obtained.[16,61] Thus, under basic conditions, aryl-, alken-1-yl-, alkyl-, and alkyn-1-yltrifluoroborates have been shown to participate efficiently in palladium-catalyzed cross-coupling reactions. In 2000, a European patent described the introduction of a vinyl substituent onto pyrimidine derivatives through the use of potassium trifluoro(vinyl)borate[62] (Scheme 40).



Scheme 40. Vinylation of bromopyrimidine

Several conditions were tested in order to optimize the reaction. Among the catalysts tested, $PdCl_2(dppf)$ showed the highest activity. With regard to the solvent, high-boiling

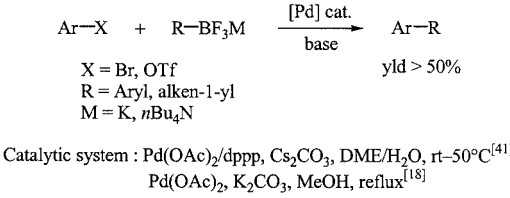
alcoholic solvents such as propanol or butanol gave the higher conversions and purities. The influence of the base was less pronounced, but aliphatic amines (iPr$_2$NEt, tBuNH$_2$, or Et$_3$N) were the most effective bases. These conditions proved to be quite general for the introduction of alkenyl moieties onto aryl iodides, bromides, and triflates. Indeed, under such conditions [PdCl$_2$(dppf), propanol, and Et$_3$N or tBuNH$_2$], an efficient route to alken-1-yl-substituted aromatic compounds was described (Scheme 41).[28,63]



Scheme 41. Cross-coupling between alkenyltrifluoroborates and aryl halides

High yields were achieved with aryl iodides and with non-electron-rich aryl bromides and triflates, but no reaction occurred with aryl chloride. It is important to note that, as in the case of palladium-catalyzed cross-coupling of alken-1-ylboronic acids,[53] the reaction is stereospecific, as coupling of (*Z*)-styryltrifluoroborate afforded only cross-coupling adducts with (*Z*) stereochemistry.[63] These conditions are very useful since they utilize inexpensive solvents and reagents.

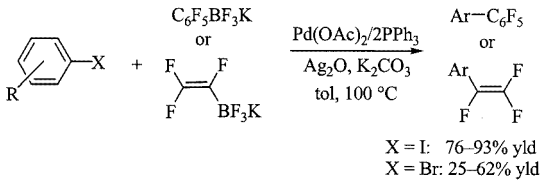
Another system has been developed for the cross coupling of sp^2 trifluoro(organo)borates and aryl halides. Batey et al.[41] showed that aryl bromides and triflates were alkylated in the presence of Cs_2CO_3 as a base by the use of palladium acetate complexed with dppb ligand as catalyst (Scheme 42).



Scheme 42. Coupling of aryl- and alken-1-yltrifluoroborates

Under these conditions, higher yields (25−50%) were generally achieved by the use of tetrabutylammonium rather than potassium salts, but the reactivity of the latter was restored by the use of tetrabutylammonium iodide as a phase-transfer agent.[41] For the coupling of potassium aryltrifluoroborates, more efficient conditions have recently been described by Molander et al.,[18] who used palladium acetate as catalyst and potassium carbonate as a base. Aerobic couplings are possible under these conditions, and the reaction is faster than when chelated palladium catalysts are used.[41] Interestingly, similar reactivity was observed for the use of either tetrabutylammonium or potassium salts.[18]

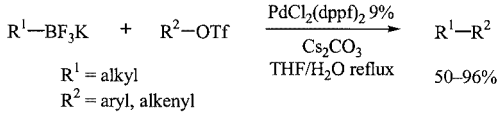
Cross-coupling reactions between trifluoro(pentafluorophenyl)borate or trifluoro(trifluoroethenyl)borate and aryl iodides or bromides was recently described.[64] Previously investigated conditions were inefficient with such perfluorinated reagents, the coupling only occurring in the presence of Ag_2O (Scheme 43).



Scheme 43. Cross-coupling with polyfluorinated trifluoro(organo)borates

The presence of K_2CO_3 is not essential when using Ag_2O, but it seems to prevent hydrodeboronation of the trifluoroborate salt.[64] This, together with the use of arenediazonium salts as coupling partners, constitutes the first example of the introduction of perfluorous chains through palladium-catalyzed cross-coupling reactions.

Introduction of an alkyl substituent through a palladium-catalyzed cross-coupling reaction is not generally a straightforward reaction because of the undesirable β-elimination side reaction. Trivalent alkylboron derivatives have been shown to be good candidates in these reactions,[53] but still suffer from sensitivity toward air and moisture. On the other hand, the highly stable potassium alkyltrifluoroborates have been shown to transmetallate to palladium complexes efficiently. Indeed, Molander et al.[22] have shown that quite efficient palladium-catalyzed reactions between potassium alkyltrifluoroborates and aryl- and alkenyltrifluoroborates can be achieved. Optimization of the reaction established that the use of 9−10 mol % of PdCl$_2$(dppf) with 3 equiv. of Cs_2CO_3 as a base in a THF/water mixture heated at reflux afforded cross-coupling product in good yields (Scheme 44).

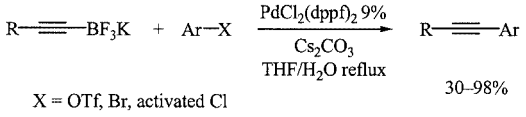


Scheme 44. Cross-coupling with potassium alkyltrifluoroborates

The presence of water in the reaction was found to be essential, and alkylboronic acids and esters also participated in the cross-coupling under these conditions. Aryl bromide proved to be more reactive than triflates, as the coupling of (4-bromophenyl)trifluoroborate only afforded products bearing triflate substituents.[22] Thus, in this system, the reactivity of the electrophiles decreases in the order I > Br > OTf >> Cl. Finally, secondary alkylborates were found to be reluctant in this coupling, the major pathway affording β-elimination and dehydroboration products.

Coupling reactions between terminal alkynes and organohalides, known as the Sonogashira reaction,[65] have proven to be a powerful method for the preparation of substituted alkynes. Nevertheless, in cases in which the Sonogashira reaction fails to deliver products, alternative approaches with alkynylmetal reagents, including zinc, tin,

and boron, have been developed. Indeed, Molander et al.[33] have shown that the crystalline potassium alkyn-1-yltrifluoroborates participated in palladium-catalyzed cross-coupling reactions with aryl halides and triflates. Under the conditions described for the coupling of alkyltrifluoroborates — that is, $PdCl_2(dppf)$ as catalyst and Cs_2CO_3 as a base — moderate to good yields of substituted alkynes were obtained (Scheme 45).

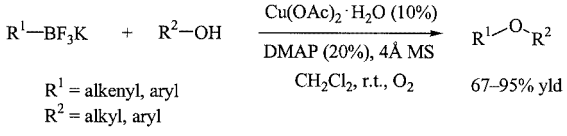


Scheme 45. Cross-coupling with potassium alkynyltrifluoroborates

Once again, the presence of water was found to have a beneficial effect through increasing the reaction kinetics. Nevertheless, cross-coupling with aryl triflates was best conducted under anhydrous conditions to prevent their hydrolysis. With regard to the catalyst loading, it could be reduced to 0.005 mol % in the case of triflate derivatives, while with aryl bromide, a decrease in the catalyst loading resulted in a proportional decrease in the yield. Under these conditions, activated heterocyclic aryl chlorides were alkynylated in good yields. This time, the order of reactivity was found to be OTf > Br > I, which is different from that observed for the cross coupling of alkyltrifluoroborates.[22]

4.2. Copper-Catalyzed Ether Synthesis

Transition metal catalyzed formation of carbon−heteroatom bonds has emerged rapidly as a powerful tool in organic synthesis.[66] It was shown simultaneously by Chan and Evans that cross-coupling between arylboronic acids and phenols was efficiently mediated by copper salts.[67] In this reaction, stoichiometric amounts of base and $Cu(OAc)_2$ were necessary in order to achieve high yields of biaryl ethers. Very recently, Batey et al. have described a procedure for copper(II)-catalyzed etherification with potassium trifluoro(organo)borates as coupling partners.[68] Indeed, treatment of 2 equiv. of potassium aryl- or alken-1-yl-trifluoroborate with 1 equiv. of aliphatic alcohol in the presence of 10 mol % $Cu(OAc)_2 \cdot H_2O$, 20 mol % DMAP, and 4-Å molecular sieves in CH_2Cl_2 at room temperature under O_2 furnishes good yields of ethers (Scheme 46).



Scheme 46

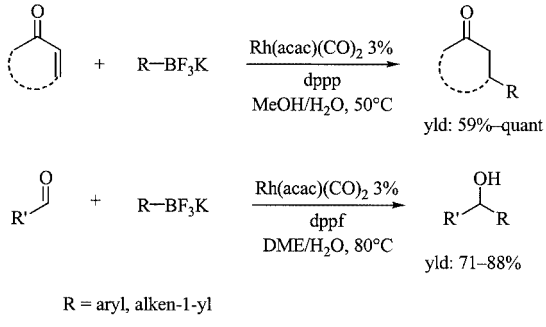
The presence of 4-Å molecular sieves was required, as only traces of ether were observed in their absence. Moreover, the reaction seems to be sensitive to steric effects around the hydroxy group, and lower yields were obtained with secondary alcohols. Under these conditions, boronic acids also undergo cross-coupling reaction, although yields were lower than with potassium trifluoro(organo)borates.

4.3. Rhodium-Catalyzed 1,4- and 1,2-Addition

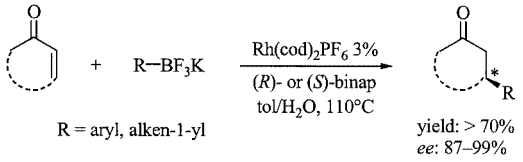
The 1,2- and 1,4-additions of organometallic reagents to unsaturated compounds are some of the most versatile reactions in organic synthesis.[69] In that context, it has recently been shown that trivalent organoboronic acids can efficiently add to unsaturated substrates in the presence of catalytic amounts of rhodium catalysts.[54,70] In the presence of chelating chiral phosphane ligands, asymmetric versions have also been developed. Very early on, Batey et al.[71] showed that potassium trifluoro(organo)borates also participated in rhodium-catalyzed 1,2- and 1,4-additions to aldehydes and enones (Scheme 47).

Indeed, good yields of 1,4- and 1,2-addition adducts were obtained in the presence of catalytic amounts of $Rh(acac)(CO)_2$ and a bidentate ligand (dppp or dppf). Moreover, it is important to note that, under otherwise identical conditions, the reaction proceeded more rapidly when trifluoro(organo)borates were used than with the corresponding boronic acids.[71] This greater reactivity of trifluoro(organo)borates in this rhodium-catalyzed reaction presumably reflects the more facile transmetallation to form the active Rh−R species. Another significant improvement from the use of potassium trifluoro(organo)borates instead of organoboronic acids is that higher yields were generally obtained, and also that certain boronic acids sometimes proved to be unreactive. The addition of water in this reaction has an accelerating effect on the kinetics.

More recently, we showed that asymmetric versions of the 1,4-addition of potassium trifluoro(organo)borates were feasible.[72] Optimization of the conditions revealed that high yields and enantiomeric excesses could be achieved by the use of cationic $Rh(cod)_2PF_6$ chelated with an atropisomeric binap ligand in a toluene/water mixture as solvent, the reaction being conducted above 100 °C (Scheme 48).

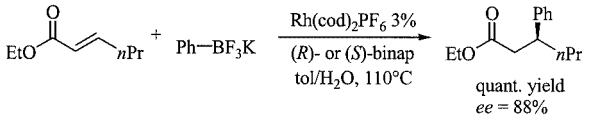


Scheme 47. Rh-catalyzed 1,4- and 1,2-addition of RBF_3K



Scheme 48. Asymmetric Rh-catalyzed 1,4-addition of RBF_3K

Among the rhodium complexes tested, only cationic precursors allowed quantitative conversion and high *ee* values. The solvent has a major influence on the enantioselectivities, with higher *ee* values being obtained in aprotic and nonpolar solvents (toluene, heptane). The presence of water is also crucial for this reaction; in its absence, the reaction was very slow and the asymmetric induction poor. On the other hand, an excess of water slows the reaction down and in pure water no asymmetric induction was observed. Indeed, for practical purposes, one should therefore use an excess of water over boron reagent (typically a 10:1 mixture of toluene/water). Under these conditions, organoboronic acids reacted more slowly, although similar yields and enantiomeric excesses were obtained,[72] once again showing the higher reactivity of potassium trifluoro(organo)borates. Moreover, this reaction generally required smaller quantities of the organometallic reagent than the use of Miyaura−Hayashi conditions with organoboronic acid derivatives.[70] Under these conditions, α,β-unsaturated esters also proved to be suitable Michael acceptors for rhodium-catalyzed 1,4-additions with trifluoro(organo)borates[73] (Scheme 49). In such rhodium catalyzed 1,4- and 1,2-additions, potassium trifluoro(organo)borates compared favorably with and even surpassed the use of boronic acids because of their higher reactivity and their exceptional stabilities.



Scheme 49. 1,4-Additions to α,β-unsaturated esters

Conclusion

Discovered in the 1960s, potassium trifluoro(organo)borates are emerging as promising alternatives to the use of the known organoboronic acids. Thanks to the filling of the vacant orbital of the trivalent boron atom, these ate complexes show exceptional stabilities towards oxygen and moisture, in relation to all other described organoboron compounds. Moreover, in comparison with boronic acids, they have shown higher reactivity, not only in the intermediate formation of difluoroborane but also in transmetallation reactions with transition metals.

Moreover, potassium trifluoro(organo)borates are easily prepared in high yields by use of classical procedures for the preparation of boronic acid derivatives followed by final treatment in situ with potassium hydrogen difluoride. Their isolation and purification procedures are straightforward, particularly in relation to those used for organoboronic acids or esters.

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