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Polyfluorinated organic compounds of boron †

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Abstract. Data on polyfluorinated organic compounds of boron published in the last decade are generalized. Methods for the synthesis, NMR spectra, and the reactivities of organoboron compounds containing one or several polyfluorinated organic groups at the boron atom are considered. The bibliography includes 309 references.

I. Introduction

The chemistry of organoboron compounds was extensively developed in the last 50 years, and the results of these investigations have found use in organic and organometallic synthesis. Compounds containing one or several polyfluorinated organic groups at the boron atom occupy a special place. Qualitative changes in the properties of organic groups after the complete or almost complete replacement of hydrogens by fluorine atoms (for more details, see the monographs [1, 2]) combined with the diversity of chemical properties of organoboranes and organoborates result in the formation of compounds with unique characteristics, whose reactivity essentially differs from that of the corresponding hydrocarbon analogues. This has called for the development of special methods for the synthesis of perfluorinated organic derivatives of boron and significant modifications of standard procedures. First studies in this field were carried out in 1960 – 1970s, but extensive research started in the late 1980s. This was associated with the problems of the catalysis of the homogeneous olefin polymerization, the synthesis of salts with weakly nucleophilic (non-coordinating) anions, and the use of (polyfluoroorgano)boranes in the synthesis of organic derivatives of xenon and polyvalent halogens. Numerous studies have been performed, and their results were covered in a number of reviews. The development of the chemistry of trifluoromethyl boron derivatives up to 2007 was analyzed in the reviews [3, 4] and in the paper.[5] Selected problems of the synthesis and reactivity of perfluoroarylboranes and -borates were briefly described in the publications.[6 – 8] The high efficacy of tris(pentafluorophenyl)borane as the activator of metallocene and post-metallocene catalysts for the homogeneous olefin polymerization (for more details on post-metallocene catalysts, see Ref. 9) was considered in reviews on the reactivity of this borane and related perfluoroarylboranes [10 – 14] and complexes of $(C_6F_5)_3B$ with nitrogen-containing bases.[15] In a more detailed review,[16] methods for the synthesis and reactions of polyfluoroorgano(halo)boranes $(R_F)_nBHal_{3-n}$ and -borates $M[(R_F)_nBHal_{4-n}]$ (hereinafter, R_F is a poly- or perfluorinated alkyl, alkenyl, or aryl group, unless otherwise stated) were discussed. The possibilities of the use of borates $[(R_F)_nBF_{4-n}]^-$ ($R_F = CF_3$, perfluoroaryl; $n = 1-4$) as weakly coordinating anions were analyzed in the reviews.[17, 18] The application of $Ar_FB(OH)_2$ and $(Ar_F)_2BOH$ [$Ar_F = C_6F_5$, 3,4,5-$F_3C_6H_2$, 3,5-$F_2C_6H_3$, 3,5-$(CF_3)_2C_6H_3$] as acid catalysts in organic synthesis was described in the publications.[14, 19]

The above-mentioned publications concerned with special divisions of chemistry of fluorinated organic compounds of boron or their applications in other areas of chemistry and included primarily the results of studies reported before 2001. The present review considers methods for the synthesis and data on the reactivities of polyfluorinated organoboron compounds published in the last decade; earlier studies are cited, if necessary. The latter refers to

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the publications, which were not included in the previous reviews, or the results of investigations, which are important for the clarity and completeness of the presentation.

II. Synthesis of (polyfluoroorgano)borates

1. (Polyfluoroorgano)borates M[R_FBX_3]

(Polyfluoroorgano)borates M[R_FBX_3] containing the ligands X = OAlk or F (in this case, R_F is a polyfluorinated alkyl, alkenyl, alkynyl, or aryl group) and H ($R_F = C_6F_5$) were described in the literature.

Trialkoxyborates M[$R_FB(OAlk)_3$] are generally synthesized by the reactions of trialkoxyboranes with polyfluorinated organolithium or -magnesium compounds R_FM. However, unlike hydrocarbon analogues, these compounds are significantly less reactive, and their solutions in diethyl ether or diethyl ether–alkane mixtures are stable only at low temperatures. Reliable data on the generation of CF_3Li and CF_3MgHal are lacking. The thermal stability of polyfluoroorgano derivatives of lithium in solution increases in the series perfluoroalkyllithium (stable at temperatures below -80 °C) < perfluoroalkenyllithium ($CF_2{=}CFLi$ stable at temperatures below -60 °C) < perfluoroalkynyllithium ≈ perfluoroaryllithium (stable below -10 °C).[20–22] Hence, the choice of the method for the generation of (perfluoroorgano)lithium is an important problem. In organic synthesis, solutions of perfluoroalkyllithium $C_nF_{2n+1}Li$ ($n = 2–10$) in diethyl ether or a diethyl ether–hexane mixture prepared from $C_nF_{2n+1}I$ and organolithium reagents RLi (R = Me, Bu^n, Ph)[23–27] or, more rarely, lithium[28] are generally used. Solutions of pentafluoroethyllithium are most stable; the half-life time of this compound is ~8 h at -80 °C.[29] The metallation of C_2F_5I with metyllithium followed by the reaction of C_2F_5Li with $B(OMe)_3$ affords lithium pentafluoroethyltrimethoxyborate.[30] An increase in the chain length of $C_nF_{2n+1}I$ ($n > 2$) leads to a sharp decrease in the yields of lithium perfluoroalkyltrimethoxyborates due to the formation of the less reactive intermediate $Li[(C_nF_{2n+1})_2I]$ (for the synthesis and properties of perfluoroalkyllithium, see Refs 31–34).

The alternative approach to the synthesis of lithium perfluoroalkyltrialkoxyborates involves the generation of pentafluoroethyllithium from pentafluoroethane and Bu^nLi followed by the alkylation of trialkoxyboranes with this compound. This method was used for the synthesis of the salts $Li[C_2F_5B(OAlk)_3]$ (Alk = Me, Et) in high yields;[35] however, in the presence of C_3F_7H instead of C_2F_5H, the yield of the salt ($Li[C_3F_7B(OMe)_3]$) decreases to 20%.[36] A substantial increase in the yield of borates $Li[C_nF_{2n+1}B(OMe)_3]$ was achieved by the metallation of $C_nF_{2n+1}H$ with *tert*-butyllithium in a diethyl ether–pentane mixture at temperatures below -110 °C followed by the reaction of $C_nF_{2n+1}Li$ with trimethoxyborane.[36]

$$C_nF_{2n+1}H \xrightarrow[2)\ B(OMe)_3]{1)\ Bu^tLi,\ Et_2O-C_5H_{12},\ -110\ ^\circ C} Li[C_nF_{2n+1}B(OMe)_3],$$

n = 3 (92%), 4 (94%), 6 (96%).

An interesting approach to the synthesis of the salts $K[C_nF_{2n+1}B(OAlk)_3]$ ($n = 1, 2$) was described in the study.[35] In this approach, the nucleophile is generated by the reaction of perfluoroalkyltrimethylsilane with potassium or tetramethylammonium fluoride. Methoxy- and ethoxyborates are produced in very good yields, whereas the reactions of sterically hindered boranes $B(OPr^i)_3$, $B(OBu^t)_3$, and $B(OPh)_3$ do not occur. This method is efficient for the synthesis of trifluoromethyl- and pentafluoroethyltrialkoxyborates,[35,37] whereas potassium heptafluoropropyltrimethoxyborate is produced in low yield.[36]

$$C_nF_{2n+1}SiMe_3 + B(OAlk)_3 + KF \xrightarrow{DME} K[C_nF_{2n+1}B(OAlk)_3] + Me_3SiF,$$

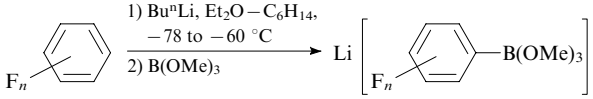
n = 1: Alk = Me (98%), Et (95%); n = 2: Alk = Me (98%), Et (96%); n = 3, Alk = Me (20%); DME is dimethoxyethane.

As opposed to perfluoroalkyllithium, the nucleophilicity of polyfluoroalkenyllithium is quite high for the addition to trialkoxyborane (for the synthesis and properties of perfluoroalkenyllithium, see Refs 21–24). Hence, the choice of the precursor is determined by its availability. For example, the derivatives (*E*)-RCF=CFH can be readily synthesized from perfluoroalkenes $RCF{=}CF_2$ by the reaction with PBu^n_3 followed by the hydrolysis of the resulting phosphorane (Burton method[21,23,24,38]). The universal method for the generation of polyfluoroalkenyllithium for the subsequent addition to $B(OAlk)_3$ involves the addition of a solution of Bu^nLi in hexane to a solution of (*E*)-RCF=CFH in diethyl ether at a temperature from -78 to -60 °C (Refs 30 and 39–41) or a solution of *tert*-butyllithium in pentane to a solution of alkenes $RCX{=}CF_2$ (R = R_F, H, Cl; X = H, Cl) in THF at -110 °C.[42] The alternative and inexpensive method for the synthesis of $CF_2{=}CFLi$ is based on the reaction of CF_3CFH_2 with 2 equiv. of Bu^nLi in a diethyl ether–hexane mixture at -78 °C, which was discovered by two UK research groups.[43,44] It should be noted that the reaction of $CF_3CF_2CFH_2$ with Bu^tLi in diethyl ether (-78 °C) affords $CF_3CF{=}CFLi$ ($Z:E = 75:25$),[45] whereas the reactions of alkanes $CF_3(CF_2)_nCF_2CFH_2$ with Bu^nLi (diethyl ether–hexane, -78 °C, $n = 5$)[46] or Pr^i_2NLi (THF–hexane, -78 °C; n = 0, 1, 3–5, 9)[47] give (*Z*)-$CF_3(CF_2)_nCF{=}CFLi$ ($Z:E = 95:5$) as the major product. The resulting solution is treated with a small excess of $B(OMe)_3$ and concentrated followed by the precipitation of the salt with pentane.

$$RCF{=}CFH \xrightarrow[2)\ B(OMe)_3]{1)\ Bu^nLi,\ Et_2O-C_6H_{14},\ -78\ to\ -60\ ^\circ C} Li[RCF{=}CFB(OMe)_3],$$

R = F (90%), (*Z*)-CF_3 (74%), (*E*)-CF_3 (81%).

This method was used also for the synthesis and isolation of lithium polyfluorophenyltrimethoxyborates.[30,48,49]



n = 3–5 (46%–99%).

(Polyfluoroorgano)trialkoxyborates react with potassium or tetrabutylammonium bifluoride to form the corresponding (polyfluoroorgano)trifluoroborates.[40,41,49]

$$Li[R_FB(OMe)_3] + KHF_2 \xrightarrow{HF\ (aqueous)} K[R_FBF_3] + LiF + 3\,MeOH,$$

$R_F = CF_2{=}CF, CF_3CF{=}CF, C_6F_5$.

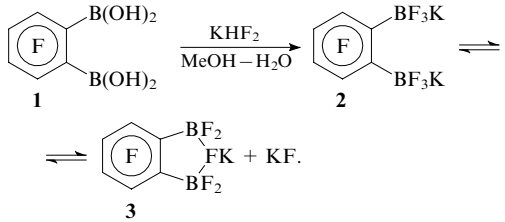
In practice, (polyfluoroorgano)trifluoroborates are often synthesized without isolation of (polyfluoroorgano)-trialkoxyborates, which are characterized by NMR spectroscopy in solution and are then introduced into the reaction with an aqueous MHF_2 solution (M = K, Bu^n_4N). The method is applicable to the synthesis of a wide range of polyfluorinated organotrifluoroborates.[16, 40, 42, 50–55]

$$R_FM + B(OMe)_3 \xrightarrow[-110 \text{ to } -70\ ^\circ C]{Et_2O - C_6H_{14}} M[R_FB(OMe)_3] \xrightarrow[22\ ^\circ C]{KHF_2,\ HF\ (aqueous)} K[R_FBF_3],$$

R_F = n-C_nF_{2n+1} (n = 2–6), n-$C_6F_{13}(CH_2)_2$, RCF=CF (R = F, Cl, H, n-C_nF_{2n+1}, C_3F_7O, n-C_nH_{2n+1}, Ph, Et_3Si), CF_2=CR (R = H, Cl, CF_3), RC≡C [R = CF_3, $(CF_3)_2CF$, C_3F_7, XCF=CF (X = CF_3, n-C_4F_9), C_6F_5], $C_6F_nH_{5-n}$ (n = 1–5), 4-C_5NF_4; M = Li, MgBr.

It should be made several remarks. The formation of aryltrialkoxyborates $M[Ar_FB(OAlk)_3]$ depends on many factors, the nature of the alkyl groups in $B(OAlk)_3$ playing the major role. For example, the reaction of pentafluorophenylmagnesium bromide with $B(OMe)_3$ at −40 °C is completed within 1 h. The arylation of $B(OPr^n)_3$ occurs at the same rate only at −5–0 °C. In the case of $B(OPr^i)_3$, the ^{19}F NMR signals of C_6F_5MgBr appear in the reaction mixture within 4 h at 0 °C.[56] An analogous situation is observed in the case of perfluoroalkylation of $B(OAlk)_3$ with perfluoroalkyltrimethylsilanes (see above).[35] The acidity of the medium plays an important role in the step of the replacement of alkoxy groups by fluorine atoms (fluorodealkoxylation). A 6–8-fold molar excess of KHF_2 in aqueous methanol is sufficient for the synthesis of polyfluoroaryl derivatives. The fluorodealkoxylation of polyfluorinated alkenyl- and alkynyltrialkoxyborates was performed with the use of a KHF_2 solution acidified with 48% HF. Under these conditions, the reaction of perfluoroalkyltrimethoxyborates gives a mixture of $K[C_nF_{2n+1}BF_3]$, $K[C_nF_{2n+1}BF_2(OMe)]$, and $K[C_nF_{2n+1}BF_2(OH)]$, which is transformed into $K[C_nF_{2n+1}BF_3]$ by the dissolution in HF (the concentration was 48%–100%).

Fluorinated arylboronic acids[57] and their esters[56] react with KHF_2 like their unfluorinated analogues[58] to form the corresponding potassium organotrifluoroborates. Let us note the interesting behaviour of tetrafluorophenylene-1,2-diboronic acid (**1**), which reacts with KHF_2 to give bis(trifluoroborate) **2** in the equilibrium with salt **3** and KF.[59]



The reaction of pentafluorophenylboronic acid[60] or its isopropyl ester[61] with $Li[AlH_4]$ affords lithium pentafluorophenylhydroborate $Li[C_6F_5BH_3]$ in 28% and 60% yields, respectively.

$$C_6F_5B(OR)_2 + Li[AlH_4] \xrightarrow[22\ ^\circ C]{Et_2O} Li[C_6F_5BH_3],$$

R = H, Pr^i.

2. Bis(polyfluoroorgano)borates $M[(R_F)_2BXY]$

Known methods for the synthesis of borates $M[(R_F)_2BXY]$ can be classified into three groups: 1) the introduction of two perfluoroorganic substituents by the addition–substitution of ligands in boranes; 2) the disproportionation of the salts $M[R_FBX_3]$; 3) the transformation of compounds containing two fluorinated organic substituents.

The addition of the nucleophile R_F^- to electrophilic borane BXY_2 gives the $[R_FBXY_2]^-$ anion, whose fate depends on the nature of the ligands X and Y and the organic group R_F. Perfluoroalkyllithium $C_nF_{2n+1}Li$ readily reacts with dimethoxychloroborane in diethyl ether at −90 °C (n = 2) or −110 °C (n = 3, 4, 6) to form lithium bis(perfluoroalkyl)dimethoxyborates, whose treatment with KF affords the salts $K[(C_nF_{2n+1})_2B(OMe)_2]$.[39, 53] In this case, the salt $Li[(C_nF_{2n+1})_2B(OMe)_2]$ is easily formed because the $[C_nF_{2n+1}BCl(OMe)_2]^-$ anion readily eliminates Cl^- (in the form of LiCl) to give $C_nF_{2n+1}B(OMe)_2$. The latter reacts with the next $C_nF_{2n+1}Li$ molecule to form $Li[(C_nF_{2n+1})_2B(OMe)_2]$. The less nucleophilic reagent $C_nF_{2n+1}MgBr$ reacts with $ClB(OMe)_2$ only in the presence of THF, and the yields of $K[(C_nF_{2n+1})_2B(OMe)_2]$ (n = 3, 4) are at most 22%–29%.[39]

$$2\ C_nF_{2n+1}Li + ClB(OMe)_2 \xrightarrow[-110\ ^\circ C]{Et_2O} Li[(C_nF_{2n+1})_2B(OMe)_2] + LiCl\downarrow,$$

$$Li[(C_nF_{2n+1})_2B(OMe)_2] + KF \xrightarrow[20\ ^\circ C]{Et_2O} K[(C_nF_{2n+1})_2B(OMe)_2] + LiF\downarrow.$$

(60%–76%)

The reaction of perfluoroalkyllithium with $B(OMe)_3$ stops at the first step because the elimination of MeO^- from the $[C_nF_{2n+1}B(OMe)_3]^-$ anion occurs much more slowly than the elimination of the Cl^- anion from $[C_nF_{2n+1}BCl(OMe)_2]^-$. The reaction rate can be increased by binding the methoxide anion with the appropriated electrophile, for example, with Me_3SiCl. This method was applied to the synthesis of lithium dimethoxyborates containing various perfluoroalkyl groups.[51]

$$Li[C_nF_{2n+1}B(OMe)_3] + Me_3SiCl \xrightarrow{Et_2O} C_nF_{2n+1}B(OMe)_2 + Me_3SiOMe + LiCl,$$

$$C_2F_5Li + C_nF_{2n+1}B(OMe)_2 \longrightarrow Li[C_nF_{2n+1}(C_2F_5)B(OMe)_2],$$

$$Li[C_nF_{2n+1}(C_2F_5)B(OMe)_2] + KF \xrightarrow{Et_2O} K[C_nF_{2n+1}(C_2F_5)B(OMe)_2] + LiF.$$

The dissolution of potassium bis(perfluoroalkyl)dimethoxyborates in hydrofluoric acid gives a mixture of the salts $K[(C_nF_{2n+1})_2B(OX)F]$ (X = H, Me). These products are transformed into difluoroborate $K[(C_nF_{2n+1})_2BF_2]$ only in anhydrous HF.[39, 41, 53]

Unlike perfluoroalkyllithium, more nucleophilic CF_2=CFLi reacts with $ClB(OMe)_2$ to form a mixture of $Li[(CF_2{=}CF)_nB(OMe)_{4-n}]$ (n = 1–4).[50] Individual bis(perfluoroalkenyl)borates were synthesized by the approach applied previously to the synthesis of bis(perfluoroalkyl)borates.[50, 51]

$$Li[CF_2{=}CFB(OMe)_3] + Me_3SiCl \xrightarrow{Et_2O} CF_2{=}CFB(OMe)_2 + Me_3SiOMe + LiCl,$$

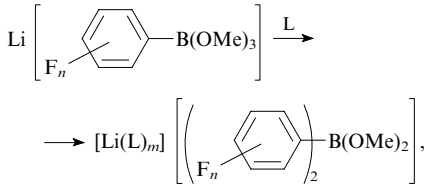
$$CF_2{=}CFLi + CF_2{=}CFB(OMe)_2 \longrightarrow Li[(CF_2{=}CF)_2B(OMe)_2],$$

$$Li[(CF_2{=}CF)_2B(OMe)_2] + 2\,KHF_2 \xrightarrow{H_2O} K[(CF_2{=}CF)_2BF_2] + KF + LiF + 2\,MeOH.$$

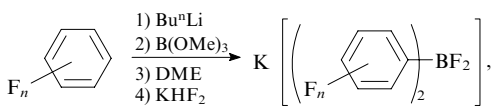
The reaction of pentafluorophenylmagnesium bromide with $B(OAlk)_3$ gives borates containing 1–2 perfluoroaryl groups. Even in the presence of an excess of trialkoxyborane (1.5–2 equiv.), the percentage of bis(pentafluorophenyl)-dialkoxyborates is 10 mol.%–15 mol.% [56] due to the substantial dissociation of the $[C_6F_5B(OR)_3]^-$ anion to $C_6F_5B(OR)_2$ and OR^-. The reaction of an excess of C_6F_5MgBr (2–4 equiv.) with triethoxyborane affords $[MgBr\cdot OEt_2][(C_6F_5)_2B(OEt)_2]$ as the major product, whereas the formation of borates $[(C_6F_5)_3BOEt]^-$ and $[(C_6F_5)_4B]^-$ was not observed (^{11}B NMR spectroscopy).[62]

The reactions considered below do not have the general character, but they are suitable for the synthesis of particular bis(perfluoroorgano)borates.

The disproportionation of polyfluorophenyltrialkoxyborates $M[C_6F_nH_{5-n}B(OAlk)_3]$ is an example. The lithium salts $Li[C_6F_nH_{5-n}B(OMe)_3]$ ($n = 4, 5$) are stable in dichloromethane; however, the replacement of Li^+ by K^+ or $Bu^n_4N^+$, as well as the addition of reagents that form complexes with lithium [tetraethylenediamine (TMEDA), DME, THF, or Et_2O], lead to the formation of bis(polyfluorophenyl)dimethoxyborates.[49,63] The disproportionation has the second order with respect to the $[C_6F_nH_{5-n}B(OMe)_3]^-$ anion and can be used for the preparative synthesis of potassium bis(polyfluorophenyl)difluoroborates.[63]

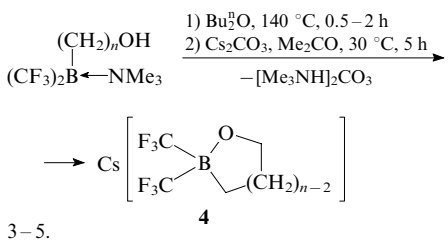


$n = 4, 5$; L is TMEDA, DME, THF, Et_2O.



$n = 4, 5$.

The heating of the complex $HO(CH_2)_n(CF_3)_2B\cdot NMe_3$, which was prepared by the hydroboration of $H_2C{=}CH(CH_2)_{n-2}(CF_3)_2B\cdot NMe_3$ with 9-borabicyclo[3.3.1]nonane (9-BBN) followed by the reaction of the product with hydrogen peroxide in an alkaline solution, results in the intramolecular substitution to give salts **4**.[64]

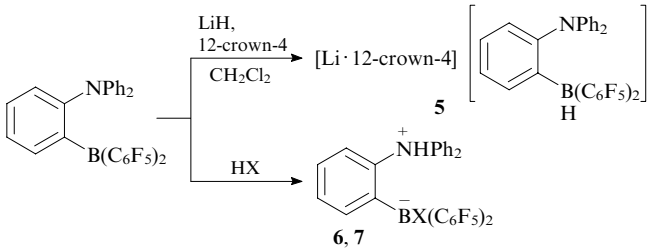


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$n = 3–5$.

A series of fluoroborates $[Et_3NH][R(CF_3)_2BF]$ (R = Et, Bn, Ph, $HC{\equiv}C$, $H_2C{=}CH$) was synthesized by the reaction of the complexes $R(CF_3)_2B\cdot NMe_3$ with the salt $Et_3N\cdot 3\,HF$ at 155–200 °C.[45]

The synthesis of compound **5** is, to the best of our knowledge, the only example of the formation of hydridoborate by the direct addition of the hydride anion to (polyfluoroorgano)borane.[65] In this study, the synthesis of betaines **6** and **7** by the conjugated addition of HCl or water to (2-diphenylaminophenyl)bis(pentafluorophenyl)borane was also described.



X = Cl (**6**), OH (**7**).

3. Tris(polyfluoroorgano)borates $M[(R_F)_3BX]$

Methods for the synthesis of tris(trifluoromethyl)borates $M[(CF_3)_3BX]$ with different ligands X were exhaustively covered in the reviews.[3–5] We will consider the studies published after 2000 and the borates $M[C_nF_{2n+1}(C_mF_{2m+1})_2BX]$ (n, $m = 1–4$, M is an alkali-metal or quaternary ammonium cation). The complexes $C_nF_{2n+1}(C_mF_{2m+1})_2B\cdot NAlk_3$, which are stable under ambient conditions, are important precursors of the latter compounds. The heating of the adduct $(C_2F_5)_3B\cdot NMe_3$ with $Et_3N\cdot 3\,HF$ (200–204 °C, 8 h) followed by the treatment with KOH afforded the salt $K[(C_2F_5)_3BF]$ (in 68% yield).[66] The use of water instead of $Et_3N\cdot 3\,HF$ led to the formation of $[Me_3NH][(C_2F_5)_3BOH]$.[67] It should be noted that in both cases a small amount (3%–6%) of hydridoborate $M[(C_2F_5)_3BH]$ was obtained.

The oxidation of the complexes $C_nF_{2n+1}(C_mF_{2m+1})_2B\cdot NHEt_2$ with ozone in aqueous CsOH affords nitroborates $Cs[C_nF_{2n+1}(C_mF_{2m+1})_2BNO_2]$ ($n = 1, 2, 4$; $m = 1, 2$).[68,69] The reactions of the latter compounds with zinc in an alkaline medium give aminoborates [for example, $Cs[(CF_3)_3BNH_2]$ (Ref. 70)], which can be transformed into diazinidoborates $Cs[(CF_3)_3BN{=}NCF_3]$ with the use of CF_3NO.[69]

The complexes $R_F(CF_3)_2B\cdot NMe_3$ containing unsaturated perfluorinated groups ($R_F = CF_2{=}CF$, $CF_3.CF{=}CF$, or C_6F_5) react with $Et_3N\cdot 3\,HF$ at 165–200 °C to form fluoroborates $[Et_3HN][R_F(CF_3)_2BF]$.[45] The use of Me_4NF instead of $Et_3N\cdot 3HF$ makes it possible to perform the reaction in butanone at 80 °C.[71] The authors hypothesized that there are two mechanisms of the B–N bond cleavage: the thermal dissociation and intermediate formation of the alkylideneborate anion upon the addition of the fluoride ion to the trifluorovinyl group of the complex $CF_2{=}CF(CF_3)_2B\cdot NMe_3$ (**8**). The latter pathway is apparently indirectly confirmed by the results of the study,[72] where complex **8** was treated with silane CF_3SiMe_3 in the presence of $[Me_4N]F$, resulting in the formation of a mixture of the products $[Me_4N][(E)\text{-}CF_3CF{=}CF(CF_3)_2BF]$, $[Me_4N][CF_2{=}CF(CF_3)_2BF]$, and $[Me_4N][(E)\text{-}CF_3CF{=}CF.(CF_3)_3B]$.[72]

The complex $(CF_3)_3B \cdot CO$ (**9**) prepared by the partial hydrolysis of borate $K[(CF_3)_4B]$ with concentrated sulfuric acid is another source of the salts $M[(CF_3)_3BX]$.[73,74] The carbon atom of the carbonyl ligand in complex **9** is a highly reactive electrophilic centre. The reaction with liquid ammonia gives a mixture of the salts $[NH_4][(CF_3)_3BC(O)NH_2]$, $[NH_4][(CF_3)_3BCN]$, and $[NH_4]_2[\{(CF_3)_3BC(O)\}_2NH]$ depending on the reaction conditions.[75] The reaction of complex **9** with potassium or caesium fluorides in liquid SO_2 affords fluoroacylborates $M[(CF_3)_3BC(O)F]$ (M = K, Cs),[76] but the reactions with other alkali metal halides give mixtures of products.[77] Haloacylborates $M[(CF_3)_3BC(O)Hal]$ (Hal = Cl, Br, I) were synthesized through tetraalkylammonium and tetraalkylphosphonium halides.[77] The haloacyl group in $[Ph_4P][(CF_3)_3BC(O)Hal]$ is easily transformed into the phosphaethynyl and arsaethynyl groups in the reaction with $K[X(SiMe_3)_2]$ to form the salts $[Ph_4P][(CF_3)_3BC{\equiv}X]$ (X = P, As).[78] In anhydrous HF, $(CF_3)_3B \cdot CO$ reacts with KF to give fluoroborates $K[(CF_3)_3BF]$ and $K[C_2F_5BF_3]$.[79] The reaction with $Co_2(CO)_8$ under CO affords the salt $[Co(CO)_5][(CF_3)_3BF]$.[80]

The complex $K[(CF_2{=}CF)_3BF]$ is the only representative of tris(perfluoroalkenyl)borates. This complex was prepared by the treatment of a solution of $(CF_2{=}CF)_3B$, which was prepared *in situ* from $(CF_2{=}CF)_2SnBu^n_2$ and BCl_3 in CH_2Cl_2, with an excess of anhydrous KF.[50]

The reactions of tris(pentafluorophenyl)borane (**10**) and related perfluoroarylboranes with neutral and negatively charged nucleophiles were extensively investigated in the studies of metallocene catalysts for the homogeneous olefin polymerization. In this section, we consider the preparative methods for the synthesis of the salts $M[(Ar_F)_3BX]$.

The reactions of $(C_6F_5)_3B$ and tris(nonafluorobiphenyl-2-yl)borane $[(2\text{-}C_{12}F_9)_3B]$ with trityl chloride in toluene gave the salts $[Ph_3C][(C_6F_5)_3BF]$ and $[Ph_3C][(2\text{-}C_{12}F_9)_3BF]$, respectively.[81] The reactions of trityl chloride,[82] 1-butyl-3-methylimidazolium chlorides ([BMIM]Cl), Bu^n_4P, or Ph_4P (Ref. 83) with borane **10** give the corresponding tris(pentafluorophenyl)chloroborates in good yields.[82]

$$(C_6F_5)_3B\ (\mathbf{10}) + Ph_3CX \xrightarrow[22\ ^\circ C,\ 2\ h]{PhMe\ or\ CH_2Cl_2} [Ph_3C][(C_6F_5)_3BX],$$

X = F (68%), Cl (42%).

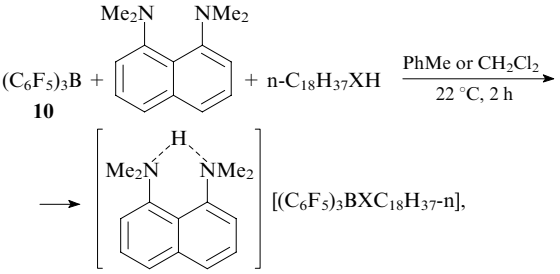
Several methods are available for the synthesis of tris(pentafluorophenyl)hydroxyborates $M[(C_6F_5)_3BOH]$. For example, the salt $[K \cdot DB\text{-}18\text{-}crown\text{-}6][(C_6F_5)_3BOH]$ was synthesized by the reaction of powdered KOH with borane **10** in the presence of dibenzo-18-crown-6 (DB-18-crown-6).[84] The salt $[BMIM][(C_6F_5)_3BOH]$ was prepared by mixing chloroborate $[BMIM][(C_6F_5)_3BCl]$ with a suspension of anhydrous LiOH in CH_2Cl_2 (22 °C, 12 h).[83] Hydroxyborates $[R_3NH][(C_6F_5)_3BOH]$ can be synthesized in quantitative yields by the hydrolysis of siloxyborates $[R_3NH][(C_6F_5)_3BOSi{\equiv}]$ (hereinafter, Si≡ is the silicon atom located either on the SiO_2 surface or involved in the siloxane cluster).[85] Triorganoammonium salts of tris(pentafluorophenyl)hydroxyborates[85,86] and an ^{17}O isotope-labeled sample[87] are produced in high yields by the deprotonation of borane complex **10** with water.

$$(C_6F_5)_3B\ (\mathbf{10}) + R_3N + H_2O \xrightarrow[22\ ^\circ C,\ 2\ h]{PhMe} [R_3NH][(C_6F_5)_3BOH],$$

R_3N = $PhMe_2N$ (55%), Et_3N (72%).

$$(C_6F_5)_3B \cdot 3\,H_2{}^{17}O + Et_3N \xrightarrow[22\ ^\circ C,\ 2\ h]{PhMe} [Et_3NH][(C_6F_5)_3B{}^{17}OH].$$

The reactions with the use of alcohols or thiols instead of water give tris(pentafluorophenyl)alkoxyborates and -alkylthioborates.[85,88–90] Trialkylamines, *N*,*N*-dialkylanilines, or 1,8-bis(dimethylamino)naphthalene can be used as bases; however, the complex $(C_6F_5)_3B \cdot py$ rather than the expected borate is formed in the presence of pyridine.[85] It should be taken into account that the reaction in toluene can afford the corresponding toluene-solvated tris(pentafluorophenyl)alkoxyborate.[85]



X = O, S.

$$(C_6F_5)_3B\ (\mathbf{10}) + PhMe_2N + Pr^iOH \xrightarrow[22\ ^\circ C,\ 2\ h]{PhMe} [PhMe_2NH][(C_6F_5)_3BOPr^i] \cdot 0.5\,PhMe.$$

The salt with the unsolvated anion was quantitatively synthesized by the alcoholysis of siloxy borate.[85]

$$[R_3NH][(C_6F_5)_3BOSi{\equiv}] + Pr^iOH \longrightarrow [R_3NH][(C_6F_5)_3BOPr^i]\ (100\%)$$

Anions containing oxygen-bridged boron atoms are produced in the reaction of borane **10** and triethylamine with the complex $(C_6F_5)_3B \cdot OH_2$ or borinic acid $(C_6F_5)_2BOH$.[86]

$$(C_6F_5)_3B\ (\mathbf{10}) + Et_3N \xrightarrow{CH_2Cl_2}$$

$$\xrightarrow{(C_6F_5)_3B \cdot OH_2} [Et_3NH][(C_6F_5)_3B(\mu\text{-}OH)B(C_6F_5)_3]$$

$$\xrightarrow{(C_6F_5)_2BOH} [Et_3NH][(C_6F_5)_3BOB(C_6F_5)_2]\ (100\%)$$

The reactions of borane **10** with silanols in the presence of tertiary amines give silyloxyborates in high yields.[85,91]

$$(C_6F_5)_3B\ (\mathbf{10}) + R'_3N + ROH \xrightarrow[22\ ^\circ C,\ 2\ h]{PhMe} [R'_3NH][(C_6F_5)_3BOR],$$

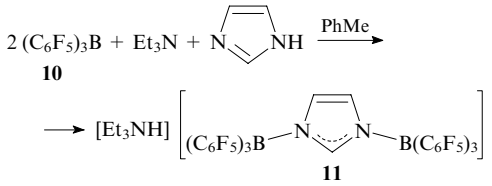
R'_3N = $PhEt_2N$: ROH = Ph_3SiOH (97%), (cyclo-C_5H_9)$_7Si_8O_{12}OH$ (57%);
ROH = (cyclo-C_5H_9)$_7Si_8O_{12}OH$: R'_3N = $PhMe_2N$ (63%), Et_3N (38%);
ROH = (cyclo-C_5H_9)$_7Si_7O_9(OH)_3$: R'_3N = $PhMe_2N$ (59%), Et_3N (65%).

The treatment of dehydroxylated SiO_2 under the same conditions results in the formation of the borate centres $[PhEt_2NH][(C_6F_5)_3BOSi{\equiv}]$ on the substrate surface.[91]

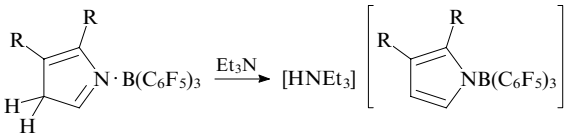
The reactions of borane **10** with anions of a number of oxygen-containing acids were investigated. The structure of the reaction product with $[Me_4N]OAc$ depends on the ratio of the reactants. Thus, the reaction of equimolar amounts of the reactants in CH_2Cl_2 affords borate $[Me_4N].[AcO\{B(C_6F_5)_3\}]$ in 80% yield, whereas the reaction with 2 equiv. of borane **10** produces borate $[Me_4N].[AcO\{B(C_6F_5)_3\}_2]$ (70%).[92] These borates exist in solutions of carboxylic acids [AcOH,[92] n-$C_{17}H_{35}CO_2H$ (Refs 93–95)] and borane **10** in CH_2Cl_2 at temperatures below −30 °C; the heating of these reactants leads (as a result of the replacement of the boron atom by hydrogen) to the formation of C_6F_5H presumably through the hydrodeboration of acid $H[C_nH_{2n+1}CO_2\{B(C_6F_5)_3\}_m]$ (n = 1, 17; m = 1, 2).[92] The reaction of the complex $(C_6F_5)_3B\cdot OEt_2$ with nitrates and bisulfates was investigated.[82] In the former case, the formation of borates with the B—O bond was not observed, whereas the reaction with bisulfate gives the stable salt.

$$(C_6F_5)_3B\cdot OEt_2 + [PhMe_2NH][HSO_4] \xrightarrow[22\ ^\circ C,\ 12\ h]{CH_2Cl_2} [PhMe_2NH][(C_6F_5)_3BOSO_3H]$$
(67%)

Unlike the reaction of borane **10** with KOH, the reaction with a suspension of sodium amide in diethyl ether affords the salt $[Na(OEt_2)_4][(C_6F_5)_3B-NH_2-B(C_6F_5)_3]$ containing the bridging nitrogen atom in the anion in high yield. However, the reaction of borane **10** with lithium dimethylamide or dimethylphosphide under the same conditions gives a mixture of unidentified products. Attempts to deprotonate the complexes $(C_6F_5)_3B\cdot NHMe_2$ and $(C_6F_5)_3B\cdot PHCy_2$ (Cy is cyclohexyl) also failed.[96] The reasons for these differences remain unclear. The reactions of borane **10** with pyrrolyllithium,[97] lithium imidazolide,[98] or potassium imidazolide[99] were described; in these reactions, the latter compounds act as bidentate nucleophiles. Analogously, salt **11** is produced in the reaction of borane **10** with imidazole in the presence of triethylamine.[99]



Salts with pyrrole and indole ligands can be synthesized according to a similar procedure. The initially formed neutral compounds {*N*-[tris(pentafluorophenyl)borane]-5*H*-pyrrole and *N*-[tris(pentafluorophenyl)borane]-3*H*-indole} contain mobile hydrogen atoms at the sp^3-hybridized carbon atoms and are easily deprotonated with triethylamine; for example:[100]



R = H; R–R is benzo.

The reactions of borane **10** with the ambidentate anions SCN^- and CN^- were examined in the studies.[82, 101, 102] It was found that the thiocyanate anion is coordinated to the boron atom through the nitrogen atom.

$$(C_6F_5)_3B + KSCN + 18\text{-crown-6} \xrightarrow[22\ ^\circ C]{PhMe} [K\cdot 18\text{-crown-6}][(C_6F_5)_3BNCS]$$
10

The reaction with cyanide anions occurs differently. The reactions of borane **10** with mercury(II) cyanide[102] or $K_2[M(CN)_4]$ [M = Ni,[82, 101] Pt (Ref. 82)] give compounds, in which the boron atom is coordinated by the nitrogen atom, whereas the treatment of borane **10** with KCN affords borate with the bridging cyanide.[82, 102]

$$(C_6F_5)_3B\cdot OEt_2 + K_2[M(CN)_4] \xrightarrow[22\ ^\circ C,\ 2\ h]{CH_2Cl_2} K_2[(C_6F_5)_3B—NC—M\{CN—B(C_6F_5)_3\}_3]$$
(80%)

M = Ni, Pt.

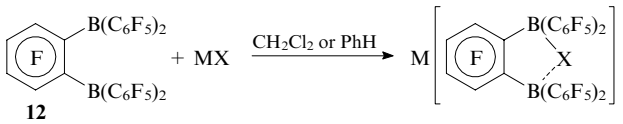
$$2\,(C_6F_5)_3B + KCN + 18\text{-crown-6} \xrightarrow[22\ ^\circ C]{PhMe} [K\cdot 18\text{-crown-6}][(C_6F_5)_3B(\mu\text{-}CN)B(C_6F_5)_3]$$
10

By contrast, the boron atom in the compound $[Me_3Si(\mu\text{-}NC)B(C_6F_5)_3]$ is coordinated by the carbon atom; this coordination mode is retained in the anion after the treatment with potassium chloride.[102]

$$(C_6F_5)_3B + Me_3SiCN \xrightarrow[22\ ^\circ C]{CH_2Cl_2} [Me_3Si(\mu\text{-}CN)B(C_6F_5)_3] \xrightarrow[PhMe,\ 22\ ^\circ C]{KCl,\ 18\text{-crown-6}} [K\cdot 18\text{-crown-6}][(C_6F_5)_3BCN]$$
10 (77%)

In the study,[102] the seeming paradox was attributed to the rapid equilibrium between Me_3SiCN and Me_3SiNC.

A series of studies on the reactions of nucleophiles with diborane 1,2-$C_6F_4[B(C_6F_5)_2]_2$ (**12**) deserve special mention. This diborane reacts with 1 equiv. of KF or $[Ph_3C][BF_4]$ to form stable salts corresponding to the addition of one fluoride anion.[103, 104] This reaction occurs upon mixing of diborane **12** with Ph_3CCl in benzene at 25 °C, but the salt of this anion with the $[PhCMe_2]^+$ cation is decomposed in dichloromethane at temperatures above −80 °C to form 1,3,3-trimethyl-1-phenylindan, the starting diborane, and HCl.[105] The reactions with RO^- anion donors give salts containing the bridging oxygen atom between two boron atoms.[103, 104, 106, 107]



MX = (KF + 18-crown-6), $[Ph_3C][BF_4]$, Ph_3CCl, $PhMe_2CCl$, Ph_3COMe, $Ph_3COC_6F_5$, (KOH + 18-crown-6).

The salts formed by the $[K\cdot 18\text{-crown-6}]^+$ (see Ref. 104) or $[Ph_3C]^+$ cations[103] are stable in the solid state and in dichloromethane. The salt with the $[(Bu^n_3Sn)_2OMe]^+$ cation is decomposed at temperatures above −60 °C to form unidentified products, although the anion remains intact.[106] A similar process is observed in the reaction of diborane **12** with methanol in dichloromethane. The addition of MeOH

to a solution of diborane **12** at −80 °C results in the formation of the salt $[(MeOH)_nH][1,2\text{-}C_6F_4\{B(C_6F_5)_2\}_2.(\mu\text{-}OMe)]$ (^1H and ^{19}F NMR spectroscopic data). If $n \leqslant 2$, the decomposition of this salt at temperatures above −60 °C affords boranes $(C_6F_5)_2BOMe$ and $(1,2,3,4\text{-}F_4C_6H)B(C_6F_5)_2$. However, this salt is stable in an excess of methanol ($n \gg 2$) even at room temperature.[107]

(Tetraorgano)borates $M[(R_F)_3BR]$ containing three polyfluoroorganic groups are represented in the modern literature exclusively by perfluoroaryl derivatives. Many reports on these salts are associated with investigations of the activation of metallocene catalysts. These processes are important for the design of catalytic systems, but their use for the preparative synthesis of $M[(C_6F_5)_3BR]$ is hardly reasonable.

One of the evident routes to the synthesis of borates $M[(C_6F_5)_3BR]$ is based on the reactions of organolithium compounds with borane **10**.[108–114]

$$\underset{\mathbf{10}}{(C_6F_5)_3B} + RLi \xrightarrow{Et_2O \text{ or } Et_2O-C_6H_{14}} Li[(C_6F_5)_3BR].$$

R	Ref.
Me, Et, Pr^i, Bu^tCH_2	109, 113
Bu^n	111, 112
Ph	108

In the short communication,[114] the synthesis of $[Li(THF)_4][(C_6F_5)_3BR]$ (R = cyclo-C_5H_5, inden-1-yl) by the reaction of cyclopentadienyl- or indenyllithium with $(C_6F_5)_3B$ in THF at 22 °C (quantitative yields) was described without experimental details. The deprotonation of these borates with butyllithium at −78 °C affords the salts $[Li(THF)_4]_2[(C_6F_5)_3B(\text{cyclo-}C_5H_4)]$.

The lithium salts are, as a rule, not purified and are transformed into quaternary ammonium salts by the exchange with $[R_4N]X$ in water or into tritylium salts by the reaction with Ph_3CCl in CH_2Cl_2. In a benzene solution of $[Ph_3C][(C_6F_5)_3BBu^n]$, the redistribution of the substituents at the boron atoms occurs at a substantial rate to give borates $[Ph_3C][(C_6F_5)_4B]$ and $[Ph_3C][(C_6F_5)_2BBu^n_2]$.[112] In the study,[109] the authors reported that they synthesized the salts $[Ph_3C][(C_6F_5)_3BR]$ contaminated with triphenylmethane, particularly, in the case of R = Et or Pr^i. This fact was attributed to the β-elimination of the proton from the alkyl group of alkyltris(pentafluorophenyl)borate by the carbocation Ph_3C^+.

In the study,[115] several examples of the formation of zwitterionic borates were given. The reaction of borane **10** with methylenetriphenylphosphorane produces compound **13**. A similar product is generated from benzylidenetriphenylphosphorane at −10 °C, but an increase in the temperature leads to the formation of products corresponding to the replacement of the hydrogen atom in the *para* position of the benzylidene moiety and the fluorine atom in one of the pentafluorophenyl groups.

$$\underset{\mathbf{10}}{(C_6F_5)_3B} + H_2C{=}PPh_3 \xrightarrow[40\ ^\circ C,\ 6\ h]{PhMe} \underset{\mathbf{13}\ (89\%)}{(C_6F_5)_3\bar{B}CH_2\overset{+}{P}Ph_3}$$

$$\underset{\mathbf{10}}{(C_6F_5)_3B} + PhCH{=}PPh_3 \xrightarrow{PhMe}$$

$$\xrightarrow[-10\ ^\circ C,\ 1\ h]{} (C_6F_5)_3\bar{B}CHPh\overset{+}{P}Ph_3 \quad (74\%)$$

$$\xrightarrow[55\ ^\circ C,\ 24\ h]{} Ph_3\overset{+}{P}CH_2\text{–}C_6H_4\text{–}\bar{B}(C_6F_5)_3 +$$

$$+\ Ph_3\overset{+}{P}CH\text{–}C_6H_3F\text{–}\bar{B}F(C_6F_5)_2$$
(Ph)

The unusual method for the synthesis of the salts $M[(R_F)_3BR]$ was described in the study.[67] The complex $(C_2F_5)_3B\cdot NMe_3$ reacts with alkynes HC≡CR (R = Ph, C_6H_4Me-4, $SiPr^i_3$) in tributylamine to form tris(pentafluoroethyl)alkynylborates $[Bu^n_3HN][(C_2F_5)_3BC{\equiv}CR]$ in moderate yields. The salts $M[(C_2F_5)_3BC{\equiv}CPh]$ can add water at the triple bond to give keto borates $M[(C_2F_5)_3BCH_2C(O)Ph]$.[67]

4. Tetrakis(polyfluoroorgano)borates $M[(R_F)_4B]$

Lithium tetrakis(pentafluorophenyl)borate is the first representative of tetrakis(perfluoroorgano)borates. It was synthesized in 1964 by the reaction of pentafluorophenyllithium with $(C_6F_5)_3B$.[116] This borate was used for the synthesis of the potassium and tetraethylammonium salts by the exchange of the cations in aqueous solutions of KCl, KNO_3, or $[Et_4N]Cl$ (the procedures were described in the study [117]).

$$\underset{\mathbf{10}}{(C_6F_5)_3B} + C_6F_5Li \xrightarrow[-78-22\ ^\circ C]{C_5H_{12} \text{ or } Et_2O-C_6H_{14}} Li[(C_6F_5)_4B].$$

The more convenient method for the synthesis of tetrakis(polyfluoroaryl)borates is based on the reaction of polyfluoroaryllithium directly with boron trichloride. The reaction is performed by the addition of a solution of BCl_3 in hexane or pentane to a solution of Ar_FLi generated from a solution of Ar_FH (or Ar_FBr) and Bu^nLi in a diethyl ether–hexane mixture. This method was used for the synthesis of lithium salts of tetraarylborates containing substituents in the tetrafluorophenyl ring (70%–80% yields).[118–121] Then the salts were transformed into ammonium or tritylium salts (80%–95% yields).

$$4\text{-}RC_6F_4X \xrightarrow[2)\ 1/4\ BCl_3,\ C_6H_{14}]{1)\ Bu^nLi,\ Et_2O-C_6H_{14},\ -78\ ^\circ C} [Li(OEt_2)_n][(4\text{-}RC_6F_4)_4B],$$

X = H, Br; R = F (70%–75%), $SiMe_2Bu^t$ (74%), $SiPr^i_3$ (72%), CF_3 (83%), $CF(C_6F_5)_2$.

$$[Li(OEt_2)_n][(4\text{-}RC_6F_4)_4B] + Ph_3CCl \xrightarrow{C_5H_{12} \text{ or } C_6H_{14}}$$
$$\longrightarrow [Ph_3C][(4\text{-}RC_6F_4)_4B] + LiCl + n\,Et_2O,$$

R = F (75%–95%), $SiMe_2Bu^t$ (86%), $SiPr^i_3$ (82%), CF_3 (95%), $CF(C_6F_5)_2$ (91%).

$$[Li(OEt_2)_n][(4\text{-}RC_6F_4)_4B] + [PhMe_2NH]Cl \xrightarrow{H_2O}$$
$$\longrightarrow [PhMe_2NH][(4\text{-}RC_6F_4)_4B] + LiCl + n\,Et_2O,$$

R = F (>90%), CF_3 (95%).

The synthesis of the salt $Tl[(C_6F_5)_4B]$ (85% yield) by the reaction of $Li[(C_6F_5)_4B]$ with HCl in diethyl ether followed by the treatment with TlOEt was described.[122]

The reaction of 1,4-dibromotetrafluorobenzene with 2 equiv. of Bu^nLi gave 1,4-dilithiotetrafluorobenzene, whose treatment with tris(pentafluorophenyl)borane (2 equiv.) afforded the salt $Li_2[1,4\text{-}(C_6F_5)_3.BC_6F_4B(C_6F_5)_3]$.[123]

The synthesis of the salt $[Me_4N][(C_6F_5)_4B]$ (15% yield) by the reaction of C_6F_5MgBr with $Na[BF_4]$ in diethyl ether (22 °C, 16 h) followed by the cation exchange with $[Me_4N]Cl$ in water was documented.[124] However, according to the results of the study,[125] the pentafluoroarylation stops at the step of the formation of $Na[(C_6F_5)_2BF_2]$.

Tetrakis(trifluorovinyl)borates $M[(CF_2{=}CF)_4B]$ were synthesized by two methods. One method is based on the reaction of BCl_3 with $(CF_2{=}CF)_2SnBu^n_2$ in the presence of alkali metal or (better) ammonium chlorides.[126]

$$2\,(CF_2{=}CF)_2SnBu^n_2 + BCl_3 + MCl \xrightarrow[20\ ^\circ C,\ 2\ h]{CH_2Cl_2} M[(CF_2{=}CF)_4B] + 2\,Cl_2SnBu^n_2,$$

M = Li (30%), K (26%), Cs (25%), Me_4N (92%), Bu^n_4N (85%), $BnMe_3N$ (80%–98%).

Another method involves the addition of a solution of BCl_3 in hexane to a cold solution of an excess of trifluorovinyllithium. The lithium salt is transformed into the potassium or tetramethylammonium salt without isolation by mixing in an aqueous solution of KF or $[Me_4N]F$.[50]

$$CF_2{=}CFLi \xrightarrow[2)\ KF,\ H_2O]{1)\ BCl_3,\ Et_2O-C_6H_{14},\ -78\ldots20\ ^\circ C} K[(CF_2{=}CF)_4B].\quad (76\%)$$

This method was used[127] also for the synthesis of potassium tetrakis(trifluoropropynyl)borate $K[(CF_3C{\equiv}C)_4B]$ from $CF_3C{\equiv}CLi$.

Attempts to synthesize tetrakis(perfluoroalkyl)borates by this method failed. The salts $M[(CF_3)_4B]$ were synthesized by bubbling ClF or ClF_3 through a solution of $M[B(CN)_4]$ in anhydrous HF.[128]

$$M[B(CN)_4] + 4\,ClF_3 \xrightarrow[-78\ldots20\ ^\circ C]{HF\ (anhydrous)} M[(CF_3)_4B] + 2\,Cl_2 + 2\,N_2,$$

M = Ag, Li, NH_4.

$$[NH_4][(CF_3)_4B] + \frac{1}{2}\,M_2CO_3 \xrightarrow{H_2O} M[(CF_3)_4B] + NH_3 + \frac{1}{2}\,H_2O + \frac{1}{2}\,CO_2,$$

M = Li, Na, K (87%), Rb, Cs.

The photolysis of the salt $Cs[(CF_3)_3BN{=}NR_F]$ (λ = 254 nm, 30 h; the conversion was 60%) afforded a mixture of $Cs[(CF_3)_3BF]$ and $Cs[(CF_3)_3BR_F]$ ($R_F = CF_3$, C_2F_5); however, this method is not preparatively significant.[128]

III. Synthesis of (polyfluoroorgano)boranes

Among representatives of this class of compounds, polyfluorinated aromatic derivatives of three-coordinate boron were studied in most detail. Polyfluoroalkenylboranes were less well studied, and only R_FBX_2 (X = F, OAlk) and $C_nF_{2n+1}B(NAlk_2)_2$ are known in the series of polyfluoroalkyl and polyfluoroalkynyl compounds.

1. Polyfluoroorgano(halo)boranes R_FBHal_2 and bis(polyfluoroorgano)(halo)boranes $(R_F)_2BHal$

Methods for the synthesis of perfluorinated aryl(halo)boranes and alkenyl(halo)boranes published before 2002 were partially discussed in the publication[7] and were analyzed in detail in the review.[16] Hence, we will describe only the most important preparative methods for the synthesis of these compounds and consider more recent publications.

Data on iodoboranes R_FBI_2 and $(R_F)_2BI$ are lacking in the literature. Bromoboranes and chloroboranes can be synthesized in good yields from boron trihalides and tin, mercury,[16] or copper[129] derivatives. The replacement of the fluorine atom by bromine in $1,2\text{-}(BF_2)_2C_6F_4$ (BBr_3, toluene, 60 °C) was described;[59] however, the report on the synthesis of $(C_6F_5)_2BBr$ by the redistribution of the ligands in $(C_6F_5)_3B$ and BBr_3 (toluene–hexane, −78–22 °C)[114] was a mistake.[130] The method, which is successfully used in the case of hydrocarbons for the synthesis of aryldichloroboranes and aryldibromoboranes by the reaction of $BHal_3$ with $ArSiAlk_3$,[131,132] proved to be inefficient in the synthesis of (perfluoroaryl)dihaloboranes.[56,104]

$$C_6F_5MAlk_n + BHal_3\ (excess) \longrightarrow C_6F_5BHal_2 + HalMAlk_n,$$

$MAlk_n = SnMe_3$, $SnMe_2C_6F_5$, $SnBu^n_2C_6F_5$, HgMe, HgEt, HgBr; Hal = Cl, Br.

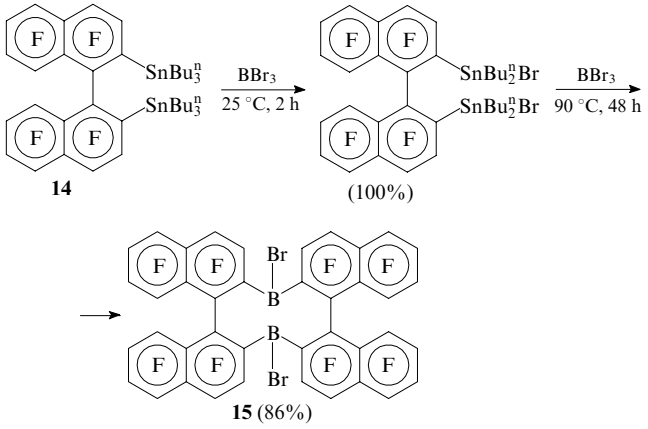
$$(C_6F_5)_2SnMe_2 + BCl_3 \xrightarrow[120\ ^\circ C,\ 48\ h]{} (C_6F_5)_2BCl + Cl_2SnMe_2,\quad (68\%)$$

$$(CF_2{=}CF)_2Hg + BCl_3 \xrightarrow[4\ ^\circ C,\ 1\ h]{xylene} (CF_2{=}CF)_2BCl + HgCl_2,\quad (41\%)$$

$$[Cu(C_6F_5)]_4 + 4\,BHal_3 \xrightarrow[-78-22\ ^\circ C]{CH_2Cl_2} 4\,C_6F_5BHal_2 + 4\,CuHal,$$

Hal = Cl (57%), Br (62%).

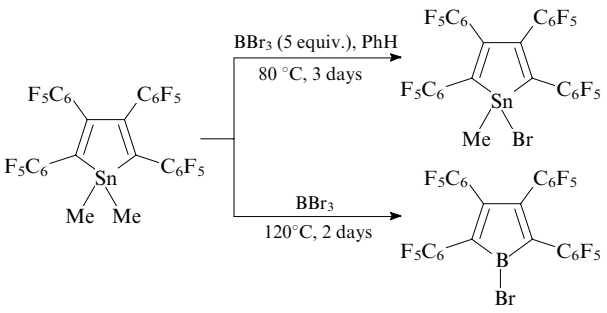
In the series of sterically hindered stannanes, the bromodealkylation is the main pathway. For example, the reaction of 2,2′-bis(tributylstannyl)perfluoro-1,1′-binaphthyl (**14**) with an excess of BBr_3 at 25 °C results in the cleavage of the $Sn-C_4H_9$ bond rather than of the $Sn-C_{10}F_6$ bond. The prolonged heating of the reaction product leads to the intermolecular condensation to form 1,6-diboracyclodecane derivative **15**.[133]



14 (100%)

15 (86%)

A similar situation was observed in the synthesis of bromoborole **16**, which was obtained only after prolonged heating of the organotin precursor with an excess of BBr_3 in the absence of a solvent.[134]



16 (77%)

Analogous reactions of copper and tin derivatives with boron trifluoride either do not occur or give fluoroboranes in low yields.[16] The defluorination of the salts $K[R_FBF_3]$ with a fluoride anion acceptor is the method of choice for the synthesis of (perfluoroorgano)difluoroboranes R_FBF_2. Solutions of polyfluorinated aryldifluoroboranes and alkenyldifluoroboranes[16, 53, 59] in chlorohydrocarbons (CH_2Cl_2), fluorohydrocarbons [$CF_3CH_2CHF_2$ (PFP), $CF_3CH_2CF_2CH_3$ (PFB)], or fluorochlorocarbons ($CFCl_3$, $CF_2ClCFCl_2$) are prepared by bubbling BF_3 through a suspension of $K[R_FBF_3]$ at a temperature from -50 to -30 °C followed by the separation of a solution of borane from the $K[BF_4]$ precipitate.

$$K[R_FBF_3] + BF_3 \xrightarrow[-50 \text{ to } -30\ ^\circ C]{\text{solv}} R_FBF_2 + K[BF_4],$$

$R_F = C_6F_nH_{5-n}$ ($n = 0-5$), RCF=CF (R = F, H, Cl, Alk, Ph, C_nF_{2n+1}), CF_2=CR (R = H, Cl, CF_3), $C_6F_{13}C_2H_4$;
solv is the solvent.

Solutions of perfluorinated acetylenic derivatives of boron can be synthesized in a similar way.[135]

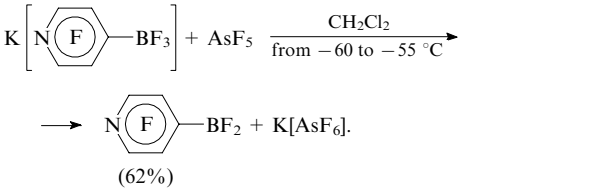
$$K[R_FC{\equiv}CBF_3] + BF_3 \xrightarrow[-40 \text{ to } -25\ ^\circ C]{\text{PFP or PFB}} R_FC{\equiv}CBF_2 + K[BF_4],$$

R_F = CF_3 (93%), C_3F_7 (95%), $(CF_3)_2CF$ (92%), (*E*/*Z*)-CF_3CF=CF (91%), (*E*/*Z*)-C_4F_9CF=CF (100%), C_6F_5 (96%).

The synthesis of fluoroboranes containing stronger electron-withdrawing organic groups requires the use of stronger Lewis acids.[53, 79, 136]

$$K[C_nF_{2n+1}BF_3] + AsF_5 \xrightarrow[-40 \text{ to } -20\ ^\circ C]{CH_2Cl_2,\ CFCl_3,\ \text{PFP or PFB}} C_nF_{2n+1}BF_2 + K[AsF_6],$$

n = 3, 6.



(62%)

The resulting (perfluoroorgano)difluoroboranes are used in subsequent reactions, but, if necessary, boranes can be isolated by distillation[56] or the defluorination of fluorborates can be performed in the absence of a solvent.[79] According to calculations, trifluoromethyldifluoroborane readily undergoes the 1,2-shift of the fluorine atom

$$CF_3BF_2 \longrightarrow :CF_2 + BF_3,$$

and attempts to detect the latter compound in the reaction of $K[CF_3BF_3]$ with AsF_5 failed.[79] The earlier data on the generation of CF_3BF_2 (Refs 137 and 138) seem to be mistaken. Data on bis(perfluoroalkyl)haloboranes and bis(perfluoroalkenyl)haloboranes are lacking in the literature.

2. (Polyfluoroorgano)boronic acids $R_FB(OH)_2$, bis(polyfluoroorgano)borinic acids $(R_F)_2BOH$, and their anhydrides and esters

The synthesis of polyfluorinated organoboronic acids and diorganoborinic acids is based on the hydrolysis of the corresponding haloboranes, alkoxyboranes, or alkoxyborates. Pentafluorophenylboronic (**17**) and bis(pentafluorophenyl)borinic (**18**) acids were synthesized by the hydrolysis of chloroboranes with an equimolar amount of water in acetone[139, 140] or toluene.[141]

$$(C_6F_5)_{3-n}BCl_n + n\,H_2O \xrightarrow[-78\ ^\circ C]{Me_2CO} (C_6F_5)_{3-n}B(OH)_n + n\,HCl,$$

17, **18**

n = 1 (**18**, 49%), 2 (**17**, 89%).

Acid **18** was synthesized according to the modified procedure by the hydrolysis of the reaction mixture prepared from $(C_6F_5)_2SnMe_2$ and BCl_3, *i.e.*, without the intermediate isolation of chloroborane.[142]

$$(C_6F_5)_2SnMe_2 \xrightarrow[2)\ 2\ M\ HCl]{1)\ BCl_3,\ 100\ ^\circ C,\ 2\ h} (C_6F_5)_2BOH.$$

18 (27%)

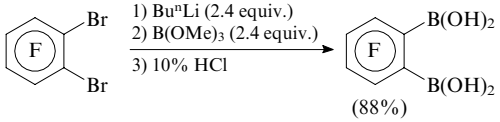
The hydrolysis of a mixture of alkoxyborane and alkoxyborate, which was prepared from polyfluoroarylmagnesium halide (polyfluoroaryllithium) and trialkoxyborane, with a dilute hydrochloric or sulfuric acid followed by the extraction of the product is a more convenient and efficient method. This method was used for the synthesis and isolation of fluorine-containing arylboronic[53, 59, 143, 144] and diarylborinic acids.[53, 142, 145]

$$Ar_FM \xrightarrow{B(OAlk)_3\ (>1\ \text{equiv.})} Ar_FB(OAlk)_2 + M[Ar_FB(OAlk)_3] \xrightarrow{HCl\ (\text{aqueous})} Ar_FB(OH)_2,$$

$Ar_F = C_6F_nH_{5-n}$ ($n = 1-5$), 4-C_5NF_4; M = MgBr, Li.

$$Ar_FM \xrightarrow{B(OAlk)_3\ (0.5\ \text{equiv.})} Ar_FB(OAlk)_2 + M[Ar_FB(OAlk)_3] \xrightarrow{HCl\ (\text{aqueous})} (Ar_F)_2BOH,$$

Ar_F = C_6F_5, 3,4,5-$F_3C_6H_2$, 4-C_5NF_4; M = MgBr, Li.



(88%)

It should be noted that the prolonged stirring of a solution of the salt $Li[Ar_FB(OMe)_3]$ (Ar_F = 2,3,4,6-F_4C_6H, 2,3,5,6-F_4C_6H, C_6F_5) in DME at 20 °C followed by the hydrolysis affords bis(polyfluorophenyl)borinic acids $(Ar_F)_2BOH$, whereas acids $Ar_FB(OH)_2$ are present as

impurities. Attempts to prepare isomeric acid (2,3,4,5-$F_4C_6H)_2BOH$ according to this procedure failed.[49, 63]

3,3,3-Trifluoropropen-2-ylboronic acid was isolated in 90% yield after the treatment of the products, which were synthesized by the reaction of $CF_3CBr{=}CH_2$ with Mg and $B(OAlk)_3$ in THF, with hydrochloric acid, and it is stable under moisture conditions.[146] Perfluorinated alkenylboronic acids **19** and (*E*)-**20** were synthesized by the acid hydrolysis of the corresponding trimethoxyborates. These acids are relatively easily decomposed, and attempts to isolate the *Z* isomer from the reaction mixture failed.[41]

$$CF_2{=}CFLi \xrightarrow[2)\ 10\%\ HCl]{1)\ B(OMe)_3} CF_2{=}CFB(OH)_2,$$
19

$$Li[CF_3CF{=}CFB(OMe)_3] \xrightarrow{10\%\ HCl} CF_3CF{=}CFB(OH)_2,$$
20

(*Z*)-**20** (0%), (*E*)-**20** (51%).

The reaction of $CF_2{=}C(CF_3)BF_2$ with water gave $CF_2{=}CHCF_3$ rather than acid, but the hydrolysis conditions were not described in the study.[147]

Polyfluoroarylboronic acid anhydrides $(Ar_FBO)_3$ (triarylboroxines) are often formed as impurities in the synthesis of the corresponding acids and can be identified by ^{11}B NMR spectroscopy. The synthesis of $(C_6F_5BO)_3$ (**21**) upon recrystallization of acid **17** or 1,3,2-dioxaborolane-4,5-dione [C_6F_5(cyclo-BOC(O)C(O)O)] from toluene[140] and by the reaction of $C_6F_5B{=}NBu^t$ with benzophenone (−30 °C, 24 h) was documented.[148] According to other data, polyfluorinated phenylboronic acids 2,6-$F_2C_6H_3B(OH)_2$, 2,4,6-$F_3C_6H_2B(OH)_2$, $C_6F_4HB(OH)_2$, and $C_6F_5B(OH)_2$ crystallize from boiling toluene without dehydration, whereas 4-$FC_6H_4B(OH)_2$, 2,4-$F_2C_6H_3B(OH)_2$, and 3,4,5-$F_3C_6H_2B(OH)_2$ give the corresponding fluorine-containing phenylboroxines.[143] The simple and efficient method for the quantitative transformation of arylboronic acids into anhydrides is based on the treatment with an excess of $SOCl_2$ in diethyl ether.[143]

$$3\,Ar_FB(OH)_2 + 3\,SOCl_2 \xrightarrow[20\ ^\circ C]{Et_2O} (Ar_FBO)_3 + 3\,SO_2 + 6\,HCl,$$

Ar_F = C_6F_5, 2,3,5,6-F_4C_6H, 3,4,5-$F_3C_6H_2$, 4-FC_6H_4.

Tetrakis(pentafluorophenyl)diboroxine was synthesized by the reaction of acid **18** with $(C_6F_5)_2BCl$ (**22**) in toluene (25 °C).[141] Anhydride $(CF_3CH_2CH_2BO)_3$ was prepared by heating the acid over calcined Al_2O_3 *in vacuo* or by the azeotropic distillation of water with benzene.[149] Polyfluorinated alkylboronic and alkenylboronic acid anhydrides were not described in the literature.

The reactions of the reagents R_FM with an excess of trialkoxyborane generally produce mixtures of (polyfluoroorgano)dialkoxyboranes and (polyfluoroorgano)trialkoxyborates, whose ratio depends on the nature of R_F and M and the reaction conditions.[39, 46, 53, 56] In the reactions with organomagnesium nucleophiles, esters $R_FB(OAlk)_2$ are formed as the major products and can be isolated by distillation. For example, trifluorovinyl(dialkoxy)boranes,[150, 151] 3,3,3-trifluoropropyl(dibutoxy)borane,[149] and 2-perfluoropropyl-1,3,2-benzodioxaborole $C_3F_7B(1,2\text{-}O_2C_6H_4)$ (Ref. 152) were synthesized. The latter compound was prepared through the formation of perfluoropropyllithium, and the absence of the corresponding borate was attributed to the cyclic nature of the compound.

$$CF_2{=}CFMgI + B(OAlk)_3 \xrightarrow[-70-22\ ^\circ C]{Et_2O} CF_2{=}CFB(OAlk)_2,$$

Alk = Pr^n (22%), Bu^n (30%).

Another approach is based on the reaction of a solution or a suspension of (polyfluoroorgano)trialkoxyborate with trimethylchlorosilane,[35, 46, 49–51] methanesulfonyl chloride, or methylating agents.[35]

$$M[R_FB(OAlk)_3] \xrightarrow{E} R_FB(OAlk)_2,$$

E = Me_3SiCl; M = Li; R_F = C_6F_5, $CF_2{=}CF$, C_nF_{2n+1} (n = 3, 4, 6); Alk = Me; E = Me_3SiCl, $MeSO_2Cl$, CF_3SO_2OMe, TsOMe; M = K; R_F = CF_3, C_2F_5; Alk = Me, Et.

The esterification of polyfluorinated organoboronic acids or the transesterification of their esters with alcohols is of limited preparative value because of the low nucleophilicity of the boron atom and the tendency to undergo hydrodeboration. This method is applicable when the fluorine atoms are remote from the boron atom and the hydrodeboration does not occur.[149]

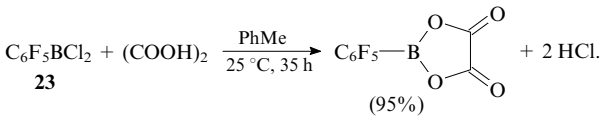
$$CF_3CH_2CH_2B(OH)_2 + 2\,EtOH \xrightarrow[\Delta]{PhH} CF_3CH_2CH_2B(OEt)_2 + 2\,H_2O.$$

The reaction of $(C_6F_5)_2BOH$ with MeOH (1 equiv.) in CD_2Cl_2 (20 °C, 4 h) in the presence of activated molecular sieves 3 Å gives ester $(C_6F_5)_2BOMe$, but the reported ^{19}F NMR spectra clearly showed the concurrent formation of the hydrodeboration product of C_6F_5H.[153] The synthesis of perfluoro-2-phenyl-1,3,2-benzodioxaborole (87% yield) by refluxing acid **17** with tetrafluoropyrocatechol in toluene was described, but the product was characterized only by the melting point.[154] *meso*-2-(Pentafluorophenyl)-4,5-diphenyl-1,3,2-dioxaborolane was synthesized in a similar way from acid **17** and *meso*-1,2-diphenyl-1,2-ethanediol.[155] Under these conditions, acid **17** does not react with amino alcohols [2-amino-1,2-diphenylethanol and diphenyl(pyrrolidin-2-yl)methanol], but its ester $C_6F_5B(OMe)_2$ gives the corresponding 2-pentafluorophenyl-1,3,2-oxazaborolidine derivatives (the yields were not reported and attempts to purify the products failed).[155] The interpretation of these results should be considered with caution because (a) commercial product **17** was stored under strictly anhydrous conditions and, consequently, it could exist partially or completely as the anhydride (see above); (b) the reactions of amino alcohols were performed not with pure ester $C_6F_5B(OMe)_2$ but with the solid substance prepared by the concentration of a suspension of $C_6F_5B(OMe)_2$ and [MgBr][$C_6F_5B(OMe)_3$] in THF (see also Ref. 56).

The reactions of O-nucleophiles (alcohols and phenols) with chloro(organo)boranes are more efficient. For example, pentafluorophenylchloroboranes easily form esters in the reactions with pentafluorophenol[156] or oxalic acid.[140]

$$(C_6F_5)_{3-n}BCl_n + n\,C_6F_5OH \xrightarrow[0-25\ ^\circ C]{CH_2Cl_2} (C_6F_5)_{3-n}B(OC_6F_5)_n + n\,HCl,$$

n = 1 (64%), 2 (62%).

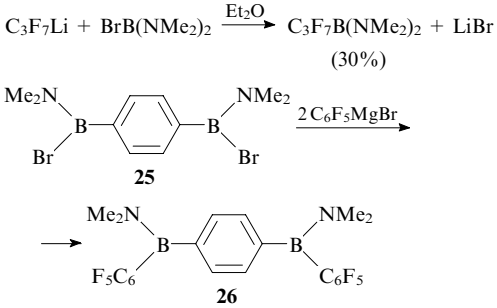


Apparently, dichloroborane **23** reacts in a similar manner with perfluoropinacone in chloroform (25 °C, 4 h), but the structure of perfluoro-2-phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was confirmed only by the boiling point and the IR spectrum.[154]

It should be mentioned special cases of the formation of (perfluoroorgano)boronic acid esters. Thus, the reaction of $(C_6F_5)_2BH$ (**24**) with butanol in benzene gives ester $(C_6F_5)_2BOBu^n$ (Ref. 157). This compound was produced also upon heating (80 °C) of a solution of borane **24** in THF (the cleavage with THF).[158] The heating of the complex $(C_6F_5)_2BF \cdot OEt_2$ (120–130 °C, 5 mm Hg) affords ester $(C_6F_5)_2BOEt$ (40%).[130] The reaction of $(C_6F_5)_3B$ with 2,3-dihydroxynaphthalene in toluene gives ester $C_6F_5B(O_2R)$ (R is 2,3-naphthalidene),[159] whereas the reaction with $Ti(OPr^i)_4$ (22 °C, 24 h) produces ester $(C_6F_5)_2BOPr^i$ (89% yield).[160]

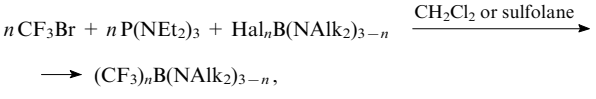
3. (Polyfluoroorgano)boron compounds with the boron–nitrogen bond

Perfluorinated alkyl, alkenyl, and aryl derivatives of three-coordinate boron containing the B–N bond were documented. Perfluoropropylbis(dimethylamino)borane was synthesized by the nucleophilic substitution of halogen in chloro- or bromobis(dimethylamino)borane.[152] The reaction of bromo(dimethylamino)borane **25** gave bis(pentafluorophenyl) derivative **26** in high yield.[161]



The reaction of trifluorovinyllithium with chloropentamethylborazine or 1,3,5-trichlorotrimethylborazine gives the corresponding trifluorovinyl derivatives of borazine.[162] Pentafluorophenyllithium and pentafluorophenylmagnesium bromide react with 1,3,5-trichlorotrimethylborazine in a similar way.[163]

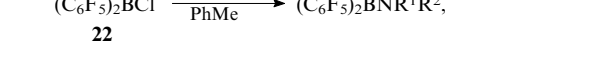
The reaction of bromotrifluoromethane with halo(dialkylamino)borane and $P(NEt_2)_3$ was proposed for the synthesis of trifluoromethyl(dialkylamino)boranes.[164, 165]



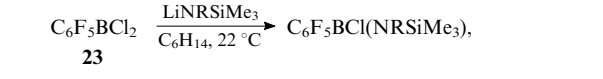
n = 1, 2 (8%–35%); Hal = Cl, Br; Alk = Me, Et, Pr^i, *etc.*

Aminoboranes containing the longer perfluoroalkyl chain cannot be synthesized by this reaction even with the use of an excess of the starting bromo(dimethylamino)borane. Instead, these reactions give complexes of tris(perfluoroalkyl)boron with dialkylamines in low yields; for example, $(C_2F_5)_3B \cdot NHMe_2$ was generated from C_2F_5I, $P(NEt_2)_3$ and Br_2BNMe_2.[66]

The character of the reaction products of pentafluorophenylchloroboranes with N-nucleophiles substantially depends on the nature of the latter compounds and the reaction conditions. Thus, the treatment of chloride **22** or dichloride **23** with an equimolar amount of lithium silylamide affords products of the replacement of the chlorine atom in good yields.[148, 166]

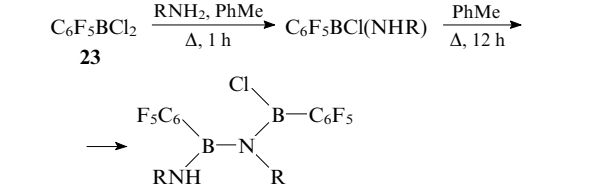


M = H, Li, Na; R^1, R^2 = H, $SiMe_3$.



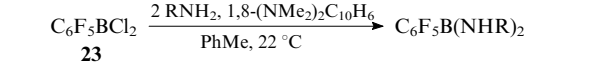
R = $SiMe_3$ (67%), Bu^t (68%), Mes (82%).

The same result was obtained by the refluxing of dichloride **23** with *p*-anisidine or mesidine in toluene for 1 h, but the prolonged boiling leads to the deeper conversion of the reaction product.[167]



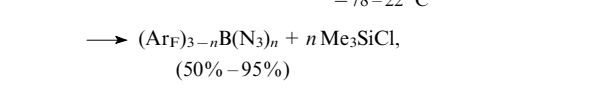
R = 4-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$.

The reactions with the use of an excess of arylamine in the presence of a strong base give pentafluorophenylbis(arylamino)boranes.[167]



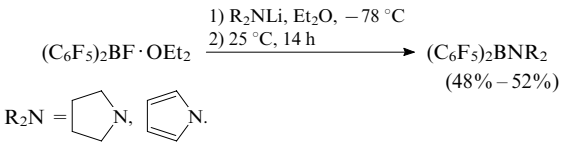
R = 4-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$ (60%).

The chlorine atom at the boron atom was replaced by the azido group with the use of trimethylsilyl azide. The reactions occur under mild conditions and in the absence of bases.[168–170] However, the reaction of dichloride **23** with Me_3SiN_3 in the presence of pyridine affords the complex $C_6F_5B(N_3)_2 \cdot py$.[169]

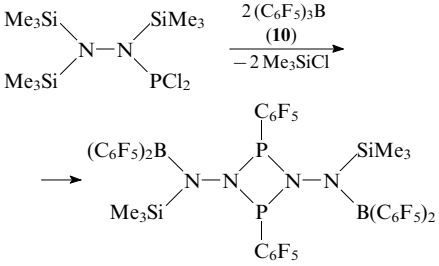


Ar_F = C_6F_5, 2,6-$F_2C_6H_3$, 2-FC_6H_4; n = 1, 2.

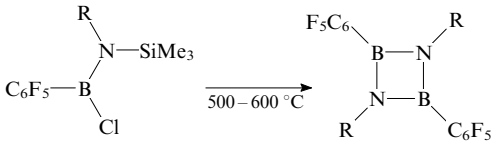
Bis(pentafluorophenyl)-*N*-pyrrolylborane and bis(pentafluorophenyl)-*N*-pyrrolidinylborane were synthesized by the reactions of the corresponding lithium amides with the complex $(C_6F_5)_2BF \cdot OEt_2$ and by the opposite way from C_6F_5Li and *N*-pyrrolidinyldichloroborane.[171]



The reaction of tris(trimethylsilyl)hydrazidodichlorophosphine with borane **10** produces diazaphosphetidine, in which the phosphorus(III) atom is bound to the C_6F_5 group. This reaction can be considered as the formal insertion of the NNP group into the C–B bond.[172]



2,4-Bis(pentafluorophenyl)-1,3,2,4-diazaboretidine derivatives were synthesized by the vacuum pyrolysis of the compounds $C_6F_5BCl(NRSiMe_3)$.[148]



R = Bu^t, $SiMe_3$, Mes.

4. (Polyfluoroorgano)boron compounds with the boron–hydrogen bond

Bis(pentafluorophenyl)borane (**24**) is the only representative of this class of compounds. In solution, this compound exists as a mixture of the monomer and the dimer. This borane was synthesized by two methods: by the reduction of chloride **22** (Ref. 158) and by the reaction of borane **10** with triethylsilane.[157]

$$(C_6F_5)_2BCl \xrightarrow[C_6H_{14}]{Me_2SiHCl \text{ or } Bu^n_3SnH} [(C_6F_5)_2BH]_n,$$
22 **24** (52%–80%)

n = 1, 2.

$$(C_6F_5)_3B \xrightarrow[PhH,\ 60\ ^\circ C,\ 3\ days]{Et_3SiH} [(C_6F_5)_2BH]_n,$$
10 **24** (70%)

n = 1, 2.

5. Polyfluorinated triorganoboranes

a. Triarylboranes and related compounds

The most well-known representative of this class, *viz.*, tris(pentafluorophenyl)borane (**10**), is generally synthesized by the reaction of C_6F_5MgBr or C_6F_5Li with boron trihalides. The choice of the reagents and the solvent plays an important role. The reaction of C_6F_5MgBr with boron trifluoride etherate in diethyl ether gives, in addition to $(C_6F_5)_3B$, a small amount of $(C_6F_5)_2BF\cdot OEt_2$, which cannot be separated by recrystallization but which is decomposed during sublimation to form more volatile $(C_6F_5)_2BOEt$.[130] The yields of borane **10** are 60%–80%.[173, 174] Unlike C_6F_5Li, which can detonate at temperatures above –20 °C, a solution of pentafluorophenylmagnesium bromide is stable in boiling diethyl ether[20] due to which borane **10** can be synthesized in amounts up to 0.5 mol at once.[175]

$$3\ C_6F_5MgBr + BF_3\cdot OEt_2 \xrightarrow[0-22\ ^\circ C]{Et_2O} (C_6F_5)_3B + 3\ MgFBr + Et_2O.$$
10 (60%–80%)

Triarylboranes containing mono-, di-, and trifluorophenyl groups can also be efficiently synthesized through fluorine-containing arylmagnesium halides.[176, 177]

$$Ar_FBr + Mg \xrightarrow[-20-22\ ^\circ C]{Et_2O \text{ or } THF} Ar_FMgBr \xrightarrow[-20-22\ ^\circ C]{BF_3\cdot OEt_2} (Ar_F)_3B,$$

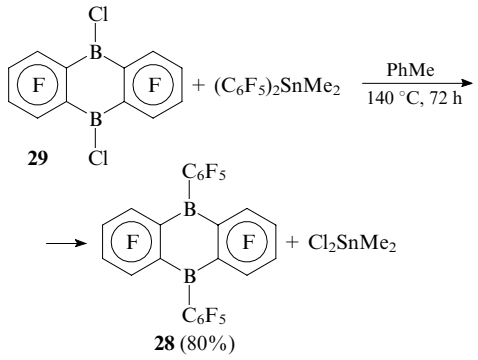
Ar_F = 2-FC_6H_4 (12%), 4-FC_6H_4 (46%), 2,6-$F_2C_6H_3$ (46%), 2,4,6-$F_3C_6H_2$ (57%).

Although pentafluorophenyllithium is very poorly soluble in hydrocarbons, these solvents are employed when it is necessary to avoid the use of coordinating solvents (Et_2O, THF), which can form stable complexes with perfluoroarylboranes. Initially, C_6F_5Li are synthesized by the addition of a solution of Bu^{n}Li in hexane to a cold (–78 °C) solution of C_6F_5Br in a hydrocarbon [pentane, hexane, petroleum ether (40%–70%)]; then a solution of BCl_3 in hexane is added to a suspension of C_6F_5Li. According to another procedure, a suspension of C_6F_5Li is added to a solution of BBr_3 in hexane.[178] Borane **10** was synthesized in 30%–50% yields.[116, 117, 178, 179] Since the work with large amounts of C_6F_5Li is dangerous, this method is suitable for the synthesis of borane **10** and related compounds in amounts not larger than 2–5 g. The syntheses of perfluorinated tris(biphenylil)borane[180, 181] and tris(2-naphthyl)borane[182] can serve as examples.

$$3\ Ar_FLi + BCl_3 \xrightarrow[-78-22\ ^\circ C]{C_5H_{12}-C_6H_{14}} (Ar_F)_3B + 3\ LiCl,$$

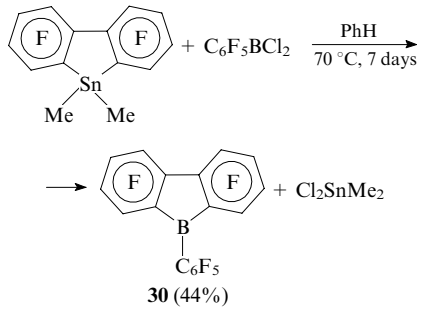
Ar_F = C_6F_5 (30%–50%), 2-$(C_6F_5)C_6F_4$ (91%), 2-$C_{10}F_7$ (26%).

Polyfluorinated triarylboranes containing various aryl groups can be synthesized by the reactions of organometallic nucleophiles with diarylhaloboranes or di(perfluoroaryl)haloboranes. For example, the addition of 2-$Ph_2NC_6H_4Li$ or 2-$(C_6F_5)C_6F_4Li$ to $(C_6F_5)_2BCl$ affords $(C_6F_5)_2B$(2-$Ph_2NC_6H_4$) (73%)[65] and $(C_6F_5)_2B$[2-(C_6F_5).C_6F_4] (37%),[183] respectively. In some cases, the use of etherate $(C_6F_5)_2BF\cdot OEt_2$ (**27**) is more efficient than $(C_6F_5)_2BCl$ due apparently to the too high Lewis acidity of the latter compound. Bis(pentafluorophenyl)mesitylborane was synthesized in 40% yield from mesitylmagnesium bromide and $(C_6F_5)_2BF\cdot OEt_2$.[184] Perfluorinated heterocyclic compound **28** was successfully synthesized by the reaction of 9,10-dichlorooctafluoro-9,10-diboraanthracene (**29**) with bis(pentafluorophenyl)dimethyltin. It was noted[185, 186] that the use of stannanes $C_6F_5SnMe_3$ or $C_6F_5SnBu^n_3$ instead of the above-mentioned tin derivative leads to the formation of the products of the replacement of the chlorine atom by alkyl rather than pentafluorophenyl groups.



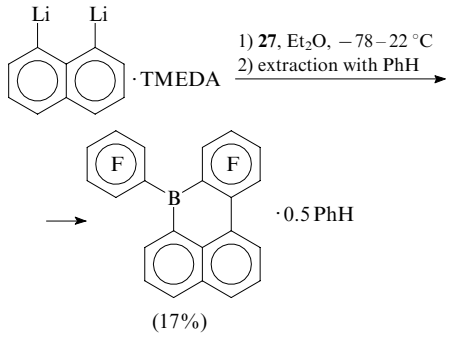
29 **28** (80%)

Perfluoro-9-phenyl-9-borafluorene (**30**) was synthesized in a similar way.[187]



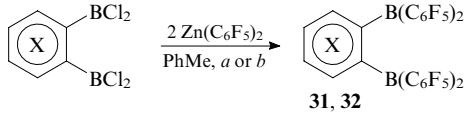
30 (44%)

An attempt to synthesize perfluoro-9,10-diphenyl-9,10-diboraanthracene (**28**) from C_6F_5Li and chloroborane **29** (Refs 185 and 186) led to a complex mixture of products, whereas the reaction of 2,2′-dilithiooctafluorobiphenyl with $C_6F_5BCl_2$ in diethyl ether gave the complex of perfluoro-9-phenyl-9-borafluorene containing a diethyl ether molecule, which was not removed after heating *in vacuo*.[187] The reaction of 1,8-dilithionaphthalene with $(C_6F_5)_2BF \cdot OEt_2$ gives nonafluoro-7-7-bora-7*H*-benzanthracene as the final product, which is formed as a result of the nucleophilic substitution of the fluorine atom in the starting 1-lithio-8-bis(pentafluorophenyl)borylnaphthalene.[188]



(17%)

The synthesis of sterically hindered perfluorinated triarylboranes and boron-containing heterocyclic compounds is based on the reaction of perfluoroaryl(halo)boranes with perfluoroaryl zinc or tin derivatives. For example, arylborane **31** and its perfluorinated analogue **32** were synthesized



31, **32**

(*a*) X = H (**31**); 120 °C, 24 h; 68% yield;
(*b*) X = F (**32**); 80 °C, 12 h; 55% yield.

in good yields by heaing the corresponding chloroboranes and bis(pentafluorophenyl)zinc in toluene.[104]

Sterically hindered pentafluorophenylbis(mesityl)borane was synthesized by heating pentafluorophenylcopper with di(mesityl)bromoborane in toluene (44% yield).[184]

b. Polyfluoroarylboranes with alkyl, alkenyl, and alkynyl groups

Bis(pentadluorophenyl)alkynylboranes can be synthesized by the reaction of chloroborane **22** with bis(alkynyl)dimethylstannane. These compounds are stable at temperatures below −35 °C, but are decomposed at 25 °C.[189]

$$(C_6F_5)_2BCl + \frac{1}{2}(RC{\equiv}C)_2SnMe_2 \xrightarrow[-78-25\ ^\circ C]{C_6H_{14}} (C_6F_5)_2BC{\equiv}CR + \frac{1}{2}Cl_2SnMe_2,$$

22

R = Bu^t (85%), Ph (75%), C_6F_5 (~60%).

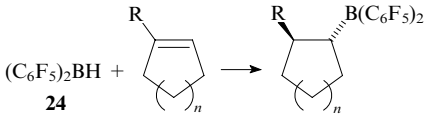
Pentafluorophenyl(alkyl)boranes can be synthesized by the reaction of C_6F_5Li with alkyldichloroboranes. For example, this method was used for the synthesis of the diboron compound $[(C_6F_5)_2B]_2CHCH_2Bu^t$ from $(Cl_2B)_2CHCH_2Bu^t$ and C_6F_5Li.[190] However, the reaction of indenyllithium with $(C_6F_5)_2BCl$ gave a complex mixture of products, and only the use of the complex $(C_6F_5)_2BF \cdot OEt_2$ instead of chloroborane **22** made it possible to synthesize indenyl, fluorenyl, and cyclopentadienylbis(pentafluorophenyl)borane derivatives in 40% – 60% yields.[130]

An alternative approach to the synthesis of alkyl- and alkenylbis(pentafluorophenyl)boranes is based on the hydroboration of alkenes and alkynes with borane $(C_6F_5)_2BH$. The reaction is performed in benzene at 25 °C until the precipitate of borane disappears (several minutes).[157, 158, 191]

$$(C_6F_5)_2BH + R'CH{=}CHR \xrightarrow[25\ ^\circ C]{PhH} (C_6F_5)_2BCR'HCH_2R,$$

24

R′ = H: R = H, Ph, CH_2CH_2Br, $CH_2CH_2CO_2Et$, $(CH_2)_nSiMe_3$ (n = 0, 1, 4);
R′ = Me_3Si: R = 4-XC_6H_4 (X = H, Me, OMe, F).



24

R = Me, n = 1, 2; R is 2-naphthyl, n = 2.

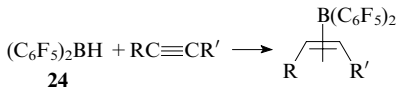
The structures of the products indicate that the reaction is kinetically controlled. Since the reaction is reversible, some bis(pentafluorophenyl)alkylboranes are gradually isomerized into thermodynamically controlled products.[157, 158, 191] The isomerization rate increases with an increase in the size of the substituent R′ in the $(C_6F_5)_2BCR'H$ moiety, and only thermodynamically controlled products, *viz*., boranes $(C_6F_5)_2BCH(SiMe_3)CH_2Ar$, are formed in the case of R′ = Me_3S.[191] The formal hydro-

$$(C_6F_5)_2BH + CHBr{=}CHMe \xrightarrow[25\ ^\circ C]{PhH} \left[\begin{array}{l} \\ BrCH_2{-}CH{-}Me \end{array}\right.\!\!\begin{array}{l} B(C_6F_5)_2 \\ | \\ \end{array}\!\!\left.\right] \longrightarrow (C_6F_5)_2BBr + CH_2{=}CHMe$$

24

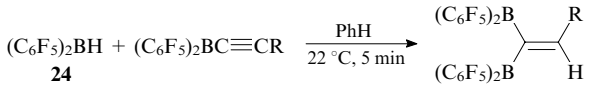
debromination of 1-bromoalkenes can be mentioned as one of other side reactions.

The addition of borane **24** to alkynes occurs in a similar way. The hydroboration of internal alkynes is the non-selective reaction; unsymmetrical substrates give a mixture of bis(pentafluorophenyl)(alken-2-yl)boranes, which remain intact and do not react with borane **24**.[157, 158]



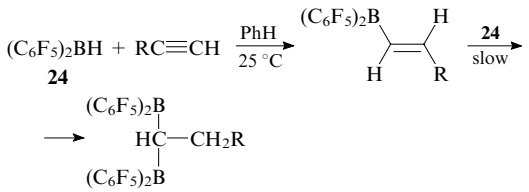
R = R′ = Me, Ph; R = $SiMe_3$: R′ = Ph, Bu^n.

The exceptions are bis(pentafluorophenyl)(alkyn-1-yl)-boranes, whose addition reactions are regiospecific.[189]



R = Bu^t (90%), Ph (80%), C_6F_5 (65%).

The hydroboration of terminal alkynes affords bis(pentafluorophenyl)[(*E*)-alken-1-yl]boranes, which can react with the second equivalent of borane **24** to form 1,1-diborylalkanes, but the secondary hydroboration rate is much slower.

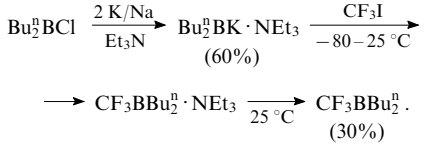


R = Bu^n, Bu^t, $CH_2CH_2CO_2Et$.

As for the preparative value of this method for the synthesis of (pentafluorophenyl)alkenyl- and bis(pentafluorophenyl)alkylboranes, it should be noted that all hydroboration reactions were carried out with 0.15–0.3 mmol of borane **24** in NMR tubes, the reaction products were not isolated, and their structures were determined by NMR spectroscopy. The products were obtained in virtually quantitative yields, and freshly prepared solutions can be used for subsequent transformations.

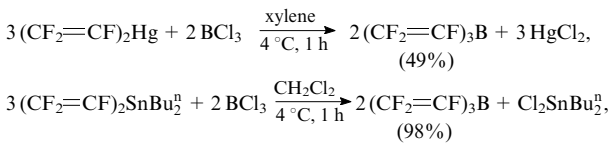
c. Triorganoboranes with polyfluorinated alkyl and alkenyl groups

Triorganoboranes containing only perfluorinated alkyl or alkynyl groups were not described in the literature. The synthesis of trifluoromethyldibutylborane based on the following sequence of reactions was documented:

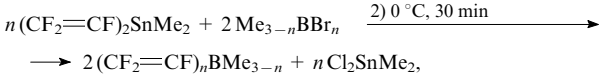


However, the structure of the reaction product was confirmed only by the molecular weight and the boiling point.[138]

Tris(trifluorovinyl)borane can be synthesized by the reaction of BCl_3 with bis(trifluorovinyl)mercury[150] or bis(trifluorovinyl)dialkylstannane[50, 126] or by the reaction of the latter compound with bis(trifluorovinyl)chloroborane.[192]



A similar approach was used for the synthesis of trifluorovinyl(methyl)boranes. Both compounds, $CF_2{=}CFBMe_2$ and $(CF_2{=}CF)_2BMe$, were synthesized in high yields by the low-temperature reaction of stannane $(CF_2{=}CF)_2SnMe_2$ with the corresponding methylbromoborane.[193]



n = 1 (98%), 2 (95%).

IV. Synthesis of complexes of (polyfluoroorgano)boranes with bases

Unlike non-fluorinated analogues, (polyfluoroorgano)boranes are strong Lewis acids. In the series of perfluoroalkylfluoroboranes, the affinities for the fluoride anion ($-\Delta E$) are as follows (kJ mol^{-1}):

406.4 ($C_4F_9BF_2$) > 402.6 ($C_3F_7BF_2$) >

> 401.9 [$(C_2F_5)(CF_3)CFBF_2$] > 392.6 (CF_3BF_2) > 329.7 (BF_3);

533.9 [$(CF_3)_3B$] > 460.8 [$(CF_3)_2BF$].[79]

The wider scale of changes in the affinity for the fluoride anion (in pF^- units) was reported in the study:[194]

9.98 [$(CF_3)_3CBF_2$] > 9.67 ($C_3F_7BF_2$) >

> 9.61 [$(CF_3)_2CFBF_2$] > 9.40 (CF_3BF_2) >

> 8.90–9.00 ($CF_3CF{=}CFBF_2$) ~ 8.90 ($CF_3C{\equiv}CBF_2$) >

> 8.51 ($C_6F_5BF_2$) > 8.03 ($CF_2{=}CFBF_2$) > 7.88 (BF_3) >

> 6.89 ($MeC{\equiv}CBF_2$) > 6.77 ($PhBF_2$) >

> 6.46–6.71 ($C_nH_{2n+1}BF_2$) >

> 6.26–6.35 ($MeCH{=}CHBF_2$).

For a number of (perfluooroorgano)boranes, the experimental dependences of the decrease in the Lewis acidity were determined:

$(2\text{-}C_6F_5C_6F_4)_3B$ > $(2\text{-}C_{10}F_7)_3B$ > **30** > $(C_6F_5)_3B$ ≫

≫ 9-methylperfluoro-9-borafluorene >

> $(C_6F_5)_2BMe$,[187]

28 > $(2\text{-}C_{10}F_7)_3B$ > $(C_6F_5)_3B$ > $(2\text{-}C_6F_5C_6F_4)_3B$,[185]

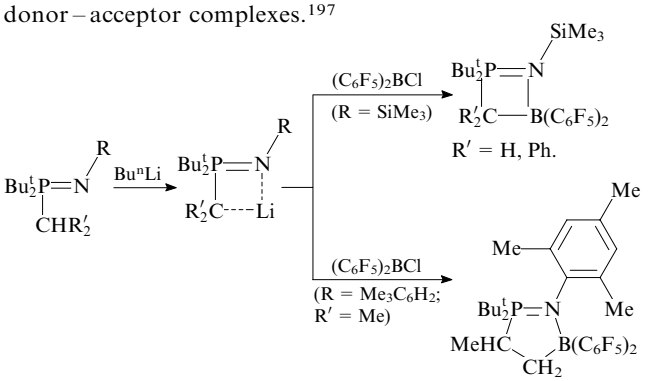
BCl_3 > $CF_2{=}CFBCl_2$ > $(CF_2{=}CF)_2BCl$ >

> $(CF_2{=}CF)_3B$ > BF_3.[195]

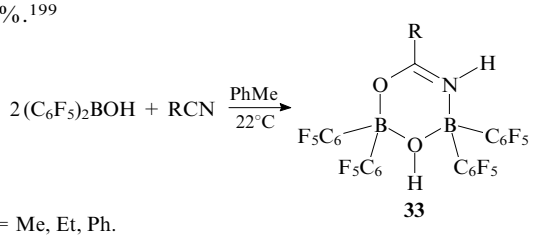
The neutral complexes $(R_F)_nBX_{3-n}\cdot$Base are generally synthesized by the reaction of borane $(R_F)_nBX_{3-n}$ with a base in solution. Exceptions are the complexes of perfluor-

oalkylboranes, which were synthesized by other methods (see below). Here, we consider only the main methods for the synthesis of complexes of (polyfluoroorgano)boranes with bases, the data, which were not included in the previous reviews, and the new results.

Data on the complexes $(R_F)_nBX_{3-n}\cdot Base$ (X = F, Cl, Br, OR, NR_2, n = 1, 2; $R_F \neq C_mF_{2m+1}$) are scarce although donor–acceptor interactions between certain boranes and bases in solution were detected by NMR spectroscopy.[156] The complexes $RCF{=}CFBF_2\cdot OEt_2$ [R = F, (*Z*)-CF_3], which were synthesized by the addition of diethyl ether to a solution of perfluoroalkenylboranes in CH_2Cl_2, were identified by ^{19}F NMR spectroscopy but were not isolated.[196] Difluoroborane $C_6F_5BF_2$ forms complexes with acetonitriles[16] and 4-methylpyridine.[178] The reaction of a twofold excess of C_6F_5MgBr with $BF_3\cdot OEt_2$ in diethyl ether gave $(C_6F_5)_2BF\cdot OEt_2$, which was isolated in 70% yield.[130] Chloroborane $(C_6F_5)_2BCl$ reacts with lithiated phosphinimines $(LiCR'_2)Bu^t_2PNR$ (R = $SiMe_3$, 2,4,6-$Me_3C_6H_2$; R′ = H, Ph, Me) to give four- and five-membered cyclic donor–acceptor complexes.[197]



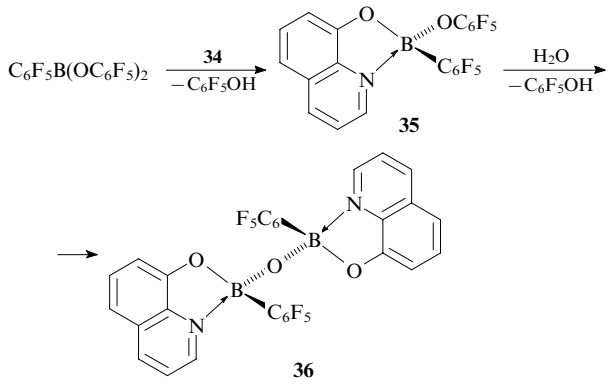
Polyfluorophenylboronic acids are transformed into polyfluorobenzenes in the presence of bases, but the mechanism of hydrodeboration is unknown (see Section VI).[198] Bis(pentafluorophenyl)borinic acid slowly reacts with nitriles in toluene to form product **33** in yields higher than 90%.[199]



33

R = Me, Et, Ph.

The reaction of 8-hydroxyquinoline (**34**) with $C_6F_5B(OC_6F_5)_2$ gives compound **35**, which is readily hydrolyzed to form product **36**.[200]



35 **36**

Partially fluorinated triorganoboranes can form complexes with strong bases [Et_2O,[130] Me_3N,[193] Bu^tNH_2 (Ref. 130)].

$$R(C_6F_5)_2B + Et_2O \longrightarrow R(C_6F_5)_2B\cdot OEt_2,$$

R is fluoren-9-yl, 9-$SiMe_3$-fluoren-9-yl.

$$R(C_6F_5)_2B + NH_2Bu^t \longrightarrow R(C_6F_5)_2B\cdot NH_2Bu^t,$$

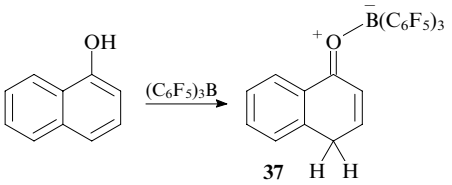
R is fluoren-9-yl, inden-9-yl.

$$(CF_2{=}CF)_nBMe_{3-n} + Me_3N \longrightarrow (CF_2{=}CF)_nBMe_{3-n}\cdot NMe_3,$$

n = 1, 2.

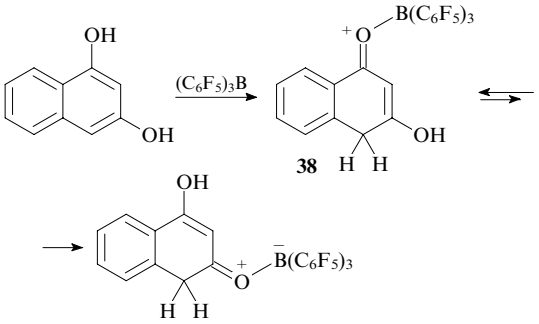
The complexation of bases with tris(pentafluorophenyl)borane and related perfluorinated triorganoboranes was studied in most detail; this process was comprehensively considered in the review.[12] Let us illustrate the main pathways of the reactions by a number of examples.

1-Naphthol reacts with $(C_6F_5)_3B$ similarly to carbonyl compounds[201] and forms complex **37** at the oxygen atom of the keto form.



37

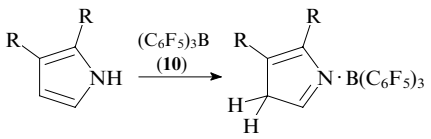
In the presence of two OH groups in positions 1 and 3 of the naphthalene ring, there is the equilibrium in solution, which is strongly shifted toward complex **38**.[159]



38

Complexes of borane **10** with carboxylic acid vinyl esters are transformed into chelate complexes **39**.[202] The reaction proceeds through intermediate compound **40**, whose treatment with 1,8-bis(dimethylamino)naphthalene in an excess of borane **10** gives complex **41** (Scheme 1).[202]

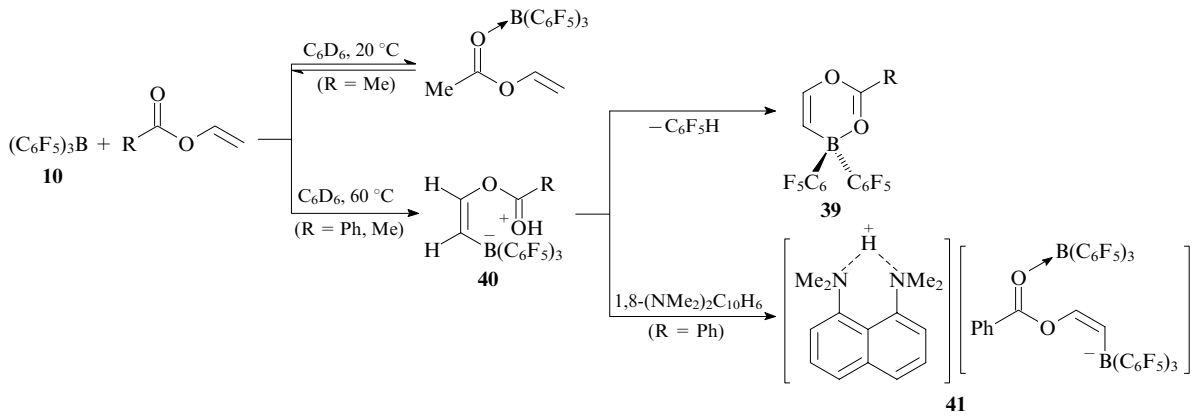
Borane **10** forms stable complexes with nitrogen-containing heterocycles (substituted imidazoles,[203] pyrrole, and indole[100]); for example:



R = H, R–R is benzo.

The reaction of $(C_6F_5)_3B$ with nitriles affords solid high-melting-point compounds, in which the boron atom is coordinated by the nitrogen atom.[204] The polydentate molecules ICN, NH_2CN, and 1,3,5-$C_3N_3H_3$ molecules react with borane **10** in a similar way, but the complexes

Scheme 1



of borane **10** with trihalotriazines 1,3,5-$C_3N_3X_3$ (X = Cl, F) (weak bases) were not detected.[205]

$$(C_6F_5)_3B + RCN \xrightarrow[22\ ^\circ C]{C_5H_{12}\ or\ CH_2Cl_2} (C_6F_5)_3B\cdot NCR,$$

10

R = Me (94%), 4-MeC_6H_4 (92%), 4-$O_2NC_6H_4$ (96%), I (90%), NH_2 (70%).

The coordination of borane **10** with isonitriles occurs at the carbon atom.[204]

$$(C_6F_5)_3B + RNC \xrightarrow[22\ ^\circ C]{C_5H_{12}} (C_6F_5)_3B\cdot CNR,$$

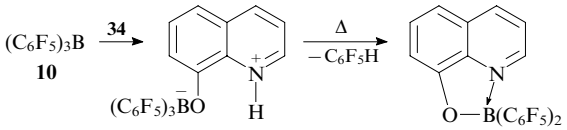
10

R = Bu^t (89%), 2,6-$Me_2C_6H_3$ (95%).

The reaction of borane **10** with phosphines [PH_3,[206] PBu^tH_2,[207] PMe_3,[208] PCp_2H, PCy_2H, PBu^n_3, $PCyH_2$, PEt_2H, PCy_3,[209] and PPh_3 (Ref. 204); Cp = η-C_5H_5] occurs by the usual mechanism and gives the complexes $(C_6F_5)_3B\cdot PR_3$; however, the reactions of borane **10** with sterically hindered phosphines PR_3 (R = Pr^i, Cy) and PR_2H (R = Bu^t, Mes) are accompanied by the nucleophilic substitution of the fluorine atom in the pentafluorophenyl group of borane followed by the migration of the fluorine atom to the boron atom to form stable zwitterions.[210] Analogously, the heating of borane **10** with phosphines PCp_2H, PCy_2H, PBu^n_3, and PPh_3, PCy_3 at 130 °C for 24 h results in the formation of the salts 4-$R_2R'P^+$. .$C_6F_4B^-(C_6F_5)_2F$.[209]

The anomalous pathway of the reaction of $(C_6F_5)_3B\cdot THF$ with sterically hindered phosphines was attributed to the steric factor. Since the typical complex with $(C_6F_5)_3B$ cannot be formed, the competitive nucleophilic cleavage of THF occurs to give the zwitterion.[211]

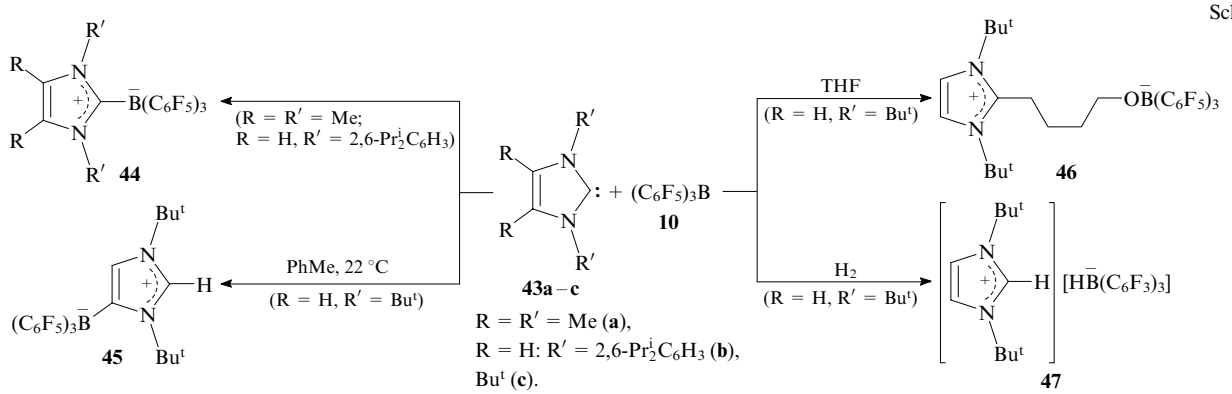
The fact that the coordination of the 'hard' boron atom (acceptor) by the 'hard' donor atom is more favourable is clearly manifested in the formation of the complexes of borane **10** with phosphinimines $R_3P{=}NH$ (R = Pr^i, Bu^t)[212] or phosphine oxides R_3PO,[213–215] in which the boron atom is coordinated exclusively by nitrogen or oxygen atoms, respectively. The initial formation of the zwitterion from borane **10** and 8-hydroxyquinoline (**34**)[200] followed by the elimination of pentafluorobenzene upon heating and the formation of complex **42** is another example.

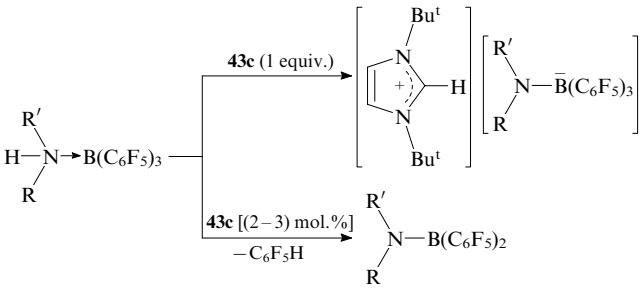


The complexation of $(C_6F_5)_3B$ with N-heterocyclic carbenes (NHC) is a special case.[216–221] The results of this process substantially depend on the nature of NHC. The reactions of borane **10** with carbenes **43a** (Ref. 222) and **43b** (Ref. 223) give complexes **44**. The reaction of carbene **43c** with $(C_6F_5)_3B$ at 22 °C in toluene affords complex **45** with abnormal carbene.[224] In the reaction with $(C_6F_5)_3B$ in THF, carbene **43c** acts like sterically hindered phosphines (see above) to form the corresponding zwitterion **46**;[224] the reaction at low temperatures under a hydrogen atmosphere gives stable salt **47** (Scheme 2).[223,224]

Carbene **43c** is a strong base and can abstract protons from the complexes $(C_6F_5)_3B\cdot NHRR'$ (R = H, Et, Ph; R′ = H, Et, Bu^t, Ph) to form the corresponding salts. Unexpectedly, carbene **43c** appeared to catalyze the protolytic cleavage of one C–B bond, resulting in the formation of pentafluorobenzene and aminoborane $(C_6F_5)_2BNRR'$.[223]

Scheme 2





For the sake of completeness, let us consider data on complexes of perfluoroalkylboranes with amines; these data were described in detail in the reviews.[3–5]

Most of the known methods for the synthesis of the complexes $(CF_3)_3B\cdot NHAlk_2$ or $(CF_3)_3B\cdot NAlk_3$ are based on the reaction of an excess of trifluoromethylating agents [for example, CF_3Br and $P(NEt_2)_3$ or CF_3I and tetrakis(dimethylamino)ethylene (TDMAE)] with halo(amino)boranes Hal_2BNAlk_2 (Hal = Cl, Br; Alk = Me, Et, Pr^i, *etc.*). The reaction product $(CF_3)_3B\cdot NHAlk_2$ is easily transformed into $(CF_3)_3B\cdot NAlk_3$ by the alkylation, for example, with MeI and aqueous alkaline.[225–228]

$$Br_2BNMe_2 \xrightarrow[2)\ H_3O^+]{1)\ CF_3I-TDMAE} (CF_3)_3B\cdot NHMe_2.$$

The perfluoroethylation of borane Br_2BNMe_2 with C_2F_5I and TDMAE affords the complex $(C_2F_5)_3B\cdot NHMe_2$ in 12% yield.[68] The use of aminophosphine $P(NEt_2)_3$ instead of TDMAE results in an increase in the yield of $(C_2F_5)_3B\cdot NHMe_2$ to 50%–60%.[66]

The method of choice for the synthesis of complexes of alkylamines with perfluorotrialkylboranes containing longer perfluoroalkyl groups involves the perfluoroalkylation of borane Cl_2BNEt_2 with nucleophiles $C_nF_{2n+1}Li$. The reactions with C_2F_5Li and C_3F_7Li give the complexes $(C_nF_{2n+1})_3B\cdot NHEt_2$ in 90% and 75% yields, respectively.

$$3\ C_nF_{2n+1}Li + Cl_2BNEt_2 \xrightarrow[-110\ ^\circ C]{Et_2O} Li[(C_nF_{2n+1})_3BNEt_2] + 2\ LiCl\downarrow,$$

n = 2, 3.

$$Li[(C_nF_{2n+1})_3BNEt_2] + HCl \xrightarrow[20\ ^\circ C]{Et_2O-H_2O} (C_nF_{2n+})_3B\cdot NHEt_2 + LiCl\downarrow,$$

n = 2 (90%), 3 (75%).

The reactions with $C_nF_{2n+1}Li$ containing the longer perfluorocarbon chain give aminoboranes $(C_nF_{2n+1})_2BNEt_2$ (n = 4, 6), which is attributed to the steric hindrance at the boron atom. The use of dimethylaminodichloroborane instead of Cl_2BNEt_2 made it possible to synthesize the complexes $(C_nF_{2n+1})_3B\cdot NHMe_2$ in 50% (n = 4) and 59% (n = 6) yields.[229]

$$2\ C_nF_{2n+1}Li + Cl_2BNEt_2 \xrightarrow[-110\ ^\circ C]{Et_2O} (C_nF_{2n+1})_2BNEt_2 + 2\ LiCl\downarrow,$$

n = 4, 6.

$$3\ C_nF_{2n+1}Li + Cl_2BNMe_2 \xrightarrow[-110\ ^\circ C]{Et_2O} Li[(C_nF_{2n+1})_3BNMe_2] + 2\ LiCl\downarrow,$$

n = 4, 6.

The complexes $R_F(CF_3)_2B\cdot NHMe_2$ were synthesized by the reactions of (perfluoroorgano)iodides[68] and TDMAE with bis(trifluoromethyl)dimethylaminoborane.

$$C_nF_{2n+1}I + (CF_3)_2BNMe_2 \xrightarrow[2)\ H_3O^+]{1)\ TDMAE,\ CH_2Cl_2} C_nF_{2n+1}(CF_3)_2B\cdot NHMe_2,$$

n = 2 (60%), 4 (63%).

$$C_6F_5I + (CF_3)_2BNMe_2 \xrightarrow[2)\ H_3O^+]{1)\ TDMAE,\ CH_2Cl_2} C_6F_5(CF_3)_2B\cdot NHMe_2,$$

$$C_6F_5(CF_3)_2B\cdot NHMe_2 \xrightarrow[2)\ MeI]{1)\ KOH} C_6F_5(CF_3)_2B\cdot NMe_3.$$

The possibility of the perfluoroalkenylation according to this procedure was not reported, but the complexes $R_FCF{=}CF(CF_3)_2B\cdot NHMe_2$ were synthesized by the reaction of $(CF_3)_2BNMe_2$ with perfluoroalkenyllithium, which was generated *in situ* from RCF_2CFH_2 and Bu^{t}Li.[45,71]

$$RCF_2CFH_2 + (CF_3)_2BNMe_2 \xrightarrow[2)\ H^+]{1)\ Bu^tLi\ (2\ equiv.)} RCF{=}CF(CF_3)_2B\cdot NHMe_2,$$

R = F, (*Z*/*E*)-CF_3.

V. NMR spectra of perfluorinated organoboron compounds

NMR spectroscopy is one of the most fast and informative methods for the detection and analysis of the structures of organic compounds in the liquid phase. Data from ^{11}B and ^{19}F NMR spectroscopy are important for polyfluorinated organoboron compounds, whereas ^1H and ^{13}C NMR spectroscopy is of limited use. The reference data on ^{11}B and ^{19}F NMR spectroscopy are available in the monographs.[230,231] Compilations of the NMR spectra of borates $M[(C_nF_{2n+1})_2BXY]$ (M = K, Me_4N; X = OMe, OH, F; Y = OMe, F),[39] $K[R_FBF_3]$,[55] and $M[(CF_2{=}CF)_nBX_{4-n}]$ (M = Li, K; X = OMe, F; n = 1–4)[50] were published. Here, we briefly outline the principal characteristics of ^{11}B, ^{13}C, and ^{19}F NMR spectra necessary for the identification of perfluorinated organoboron compounds.

In many cases, the differences in the chemical shifts in the ^{11}B NMR spectra of hydrocarbon and perfluorocarbon organoboron compounds are at most 2–3 ppm. In the series of (perfluoroorgano)boranes R_FBX_2, the δ(B) values are 16–24 ppm (X = F), 21–26 ppm (X = OH, OR), and 30–50 ppm (X = Cl, Br, NR_2, N_3). Bis(perfluoroorgano)-boranes $(R_F)_2BX$ are characterized by the δ(B) values of 30–60 ppm. The signals of polyfluorinated triorganoboranes are observed at 45–75 ppm; in the series of $(C_6F_5)_2BR$, a strong shielding of the boron atom is detected after the replacement of the saturated substituent (R = Alk) by unsaturated groups, the shielding being decreased in the series (R)

aryl ≈ alkenyl > alkynyl.

The formation of complexes of boranes with neutral or negatively charged bases causes substantial upfield shifts of the ^{11}B NMR signal compared to the starting boranes. For example, δ(B) for $C_6F_5BF_2$, $C_6F_5BF_2\cdot 4\text{-}MeC_5H_4N$,[178] and $[C_6F_5BF_3]^-$ are 23, 4, and 2 ppm, respectively, whereas the

signals of $(C_6F_5)_3B$ and $(C_6F_5)_3B \cdot NCMe$ are observed at 59 and −10 ppm. Polyfluorinated tetraorganoborates containing aryl, alkyl, or alkenyl groups, which formally correspond to the addition of $[R']^-$ to R_3B, are characterized by the presence of the ^{11}B NMR signal in the region from −12 to −20 ppm.

The ^{19}F NMR spectra of organofluoroboranes show broadened signals in the region from −70 to −95 ppm (−BF_2) and at −30 ppm (>BF). The positions and width of these signals are very sensitive to the presence of admixtures of bases. For example, in the presence of traces of moisture the signals are shifted upfield, which is accompanied by a substantial broadening (up to hundreds of Hz). This is attributed to the formation of an equilibrium mixture of borane and its complex with a base. For example, the signals δ(F) of the BF_2 group of boranes $C_nF_{2n+1}BF_2$, $CF_2{=}CFBF_2$, and $C_6F_5BF_2$ are shifted upfield by 60–100 ppm upon the complexation with Et_2O, Me_3N, and MeCN. The transformation of $(C_6F_5)_2BF$ into $(C_6F_5)_2BF \cdot OEt_2$ or $(C_6F_5)_2BF \cdot NCMe$ is also accompanied by the shielding of the fluorine atom [$\Delta\delta$(F) of the BF group is 121 and 147 ppm, respectively].

The chemical shift δ(F) of the BF_n groups in the spectra of organofluoroborates $M[(R_F)_nBF_{3-n}]$ depends on the nature and the number (n) of the groups R_F. In the spectra of the salts $K[R_FBF_3]$, the chemical shift δ(F) of the BF_3 groups is (ppm): −133 ($R_F = C_6F_5$), −137 ($R_F = C{\equiv}CC_nF_{2n+1}$), −143 ($R_F = CF{=}CFC_nF_{2n+1}$), and −152 ($R_F = C_nF_{2n+1}$). An increase in the number of trifluorovinyl groups in $K[(CF_2{=}CF)_nBF_{3-n}]$ leads to a change in δ(F) of the BF_n group from −143 (n = 1) to −164 (n = 2) and −212 ppm (n = 3).[50]

The quadrupole moment of the ^{11}B nucleus leads to the broadening of the ^{11}B and ^{19}F NMR signals of the BF_2 and BF groups, and the direct measurement of the spin–spin coupling constants $^1J(B,F)$ often presents problems. In compounds containing four-coordinate boron atom (organofluoroborates and complexes of organofluoroboranes with bases), the signals of these groups are substantially more narrow, which allows the estimation of the constants $^1J(B,F)$ and $^2J(B,F)$. The latter are usually equal to 20–35 Hz. The $^1J(B,F)$ values vary in the ranges of 30–70 Hz: 31–33 Hz ($M[R_FC{\equiv}CBF_3]$),[55] 38–43 Hz ($M[R_FBF_3]$),[55] 57–66 Hz ($M[(R_F)_2BF_2]$),[39,63] 54 Hz ($M[(CF_2{=}CF)_3BF]$,[50] and 59–68 Hz ($M[(C_nF_{2n+1})_3BF]$) (Refs 66 and 128) In the NMR spectra of the complexes of fluoroboranes with nitrogen-containing bases, the $^1J(B,F)$ values vary from 48–51 Hz [$C_6F_5BF_2 \cdot NC_5H_4Me$-4,[178] $CF_3BF_2 \cdot NMe_3$ (Ref. 232)] to 55–61 Hz [$(C_6F_5)_2BF \cdot NCMe$, $(CF_3)_2BF \cdot NHMe_2$ (Ref. 233)].

Tables 1–4 give the spectroscopic characteristics (^{11}B and ^{19}F NMR) of typical boranes and borates.

It is often difficult to detect the ^{13}C NMR signal of the C-1 atom in the spectra of polyfluorinated organoboron compounds because of the large relaxation time of the nucleus, the quadrupole broadening caused by the field of the adjacent boron atom, the multiplicity due to the large spin–spin coupling constants $^nJ(C,F)$ (n = 1–3) and, as a consequence, the long time of the NMR experiment. This problem is easier for derivatives of four-coordinate boron. Table 4 gives the ranges of the constants $^1J(C\text{-}1,B)$ estimated from the $^{13}C\{^{19}F\}$ NMR spectra of (perfluoroorgano)borates. It is interesting that the constants $^1J(C\text{-}1,B)$ in the spectra of trifluoromethylborates $M[(CF_3)_nBX_{3-n}]$ are

Table 1. Chemical shifts in the ^{11}B and ^{19}F NMR spectra of (perfluoroorgano)(halo)boranes and -borates.

Compound	Solvent (temperature)	δ(B) /ppm	δ(F) /ppm [a]	Ref.
$C_3F_7BF_2$	CD_2Cl_2 (−50 °C)	16.0	−76.5 (BF_2), −81.8 ($3F^3$), −129.5 ($2F^2$), −134.5 ($2F^1$)	136
$CF_2{=}CFBF_2$	CH_2Cl_2	21.8	−87.1 (BF_2), −72.1 ($1F^{2trans}$), −99.0 ($1F^{2cis}$), −207.2 ($1F^1$)	196
$C_3F_7C{\equiv}CBF_2$	PFP (−20 °C)	15.5	−72.2 (BF_2), −79.1 ($3F^5$), −100.6 ($2F^3$), −125.6 ($2F^4$)	135
$C_6F_5BF_2$	CH_2Cl_2	22.8	−74.4 (BF_2), −129.0 ($2F^{2,6}$), −143.8 ($1F^4$), −161.3 ($2F^{3,5}$)	56
$CF_2{=}CFBCl_2$	$CFCl_3$	31.3 [b]	−71.6 ($1F^{2trans}$), −87.9 ($1F^{2cis}$), −184.5 ($1F^1$)	234
$C_6F_5BCl_2$	C_6D_6	52.3	−129.9 ($2F^{2,6}$), −146.6 ($1F^4$), −162.4 ($2F^{3,5}$)	129
$C_6F_5BBr_2$	C_6D_6	53.3	−130.3 ($2F^{2,6}$), −147.4 ($1F^4$), −161.9 ($2F^{3,5}$)	129
$(CF_2{=}CF)_2BF$	$C_6D_5CD_3$	49.9	–	193
$(CF_2{=}CF)_2BCl$	$C_6D_5CD_3$	49.9	–	193
$(CF_2{=}CF)_2BBr$	$C_6D_5CD_3$	57.0	–	193
$(C_6F_5)_2BF$	CH_2Cl_2	–	−29.2 (BF), −130.9 ($4F^{2,6}$), −145.2 ($2F^4$), −161.9 ($4F^{3,5}$)	16
$(C_6F_5)_2BCl$	C_6D_6	59.1	−129.6 ($4F^{2,6}$), −143.9 ($2F^4$), −160.4 ($4F^{3,5}$)	157
$CF_3BF_2 \cdot NMe_3$	Et_2O	−0.6	−173.4 (BF_2), −71.2 ($3F^1$)	232
$CF_2{=}CFBF_2 \cdot OEt_2$	CH_2Cl_2	–	−149.0 (BF_2), −94.3 ($1F^{2trans}$), −118.8 ($1F^{2cis}$), −199.7 ($1F^1$)	196
$C_6F_5BF_2 \cdot NCMe$	CD_2Cl_2	–	−136.5 (BF_2), −136.3 ($2F^{2,6}$), −155.8 ($1F^4$), −164.4 ($2F^{3,5}$)	16
$(C_6F_5)_2BF \cdot OEt_2$	C_6D_6	12.4	−150.0 (BF), −134.5 ($4F^{2,6}$), −154.5 ($2F^4$), −163.0 ($4F^{3,5}$)	130
$(C_6F_5)_2BF \cdot NCMe$	CD_2Cl_2	–	−176.0 (BF), −136.1 ($4F^{2,6}$), −156.4 ($2F^4$), −164.0 ($4F^{3,5}$)	16
$K[C_3F_7BF_3]$	CD_3CN	−0.6	−152.1 (BF_3), −80.2 ($3F^3$), −127.3 ($2F^2$), −133.6 ($2F^1$)	136
$K[CF_2{=}CFBF_3]$	CD_3CN	0.7	−143.4 (BF_3), −101.2 ($1F^{2trans}$), −124.0 ($1F^{2cis}$), −195.7 ($1F^1$)	46
$K[C_3F_7C{\equiv}CBF_3]$	MeCN	−2.6	−136.6 (BF_3), −80.3 ($3F^5$), −95.3 ($2F^3$), −126.9 ($2F^4$)	55
$K[C_6F_5BF_3]$	CD_3CN	1.8	−133.4 (BF_3), −135.2 ($2F^{2,6}$), −160.7 ($1F^4$), −165.3 ($2F^{3,5}$)	56
$Cs[(CF_3)_3BF]$	MeCN	−7.3	−230.0 (BF), −69.0 ($12F^1$)	235
$Cs[(CF_3)_3BCl]$	MeCN	−12.7	−65.8 ($12F^1$)	235
$Cs[(CF_3)_3BBr]$	MeCN	−14.9	−64.3 ($12F^1$)	235

[a] In Tables 1–3, the notations mF^n refer to the F atoms bound to C atoms; m is the number of equivalent F atoms, the index n indicates the position of the corresponding CF_x group with respect to the B atom. [b] In $C_6D_5CD_3$.[193]

Table 2. Chemical shifts in the ^{11}B and ^{19}F NMR spectra (ppm) of selected perfluorinated organoboron compounds containing the B–O, B–N, and B–H bonds.

Compound	Solvent	δ(B)	δ(F)	Ref.
$C_3F_7B(OMe)_2$	CH_2Cl_2	21.5	−81.3 ($3F^3$), −127.9 ($2F^2$), −128.8 ($2F^1$)	51
$C_6F_5B(OH)_2$	Et_2O	26.2	−132.1 ($2F^{2,6}$), −155.1 ($1F^4$), −163.4 ($2F^{3,5}$)	143
$(C_6F_5BO)_3$	Et_2O	18.6	−132.4 ($6F^{2,6}$), −154.1 ($3F^4$), −163.7 ($6F^{3,5}$)	143
$C_6F_5B(OMe)_2$	CH_2Cl_2	26.1	−132.8 ($2F^{2,6}$), −153.8 ($1F^4$), −162.6 ($2F^{3,5}$)	49
$(C_6F_5)_2BOBu^n$ (see [a])	$CDCl_3$	39.5	−132.7 ($4F^{2,6}$), −149.2 ($2F^4$), −161.1 ($4F^{3,5}$)	157
$(C_6F_5)_2BH$ (see [b])	C_6D_6	60.1	−130.5 ($4F^{2,6}$), −143.4 ($2F^4$), −161.7 ($4F^{3,5}$)	158
$[(C_6F_5)_2BH]_2$ (see [b])	C_6D_6	18.0	−134.8 ($8F^{2,6}$), −148.0 ($4F^4$), −160.7 ($8F^{3,5}$)	158
$C_6F_5B(N_3)_2$	C_6D_6	34.6	−131.7 ($2F^{2,6}$), −147.7 ($1F^4$), −160.6 ($2F^{3,5}$)	169
$Li[C_3F_7B(OMe)_3]$ (see [c])	MeCN	1.1	−79.3 ($3F^3$), −126.4 ($2F^2$), −125.3 ($2F^1$)	36
$K[(C_3F_7)_2B(OMe)_2]$ (see [d])	MeCN	−1.3	−79.3 ($6F^3$), −124.4 ($4F^2$), −123.3 ($4F^1$)	39
$Li[CF_2{=}CFB(OMe)_3]$	Et_2O	2.5	−100.0 ($1F^{2trans}$), −123.2 ($1F^{2cis}$), −194.0 ($1F^1$)	50
$Li[(CF_2{=}CF)_2B(OMe)_2]$	Et_2O	1.2	−99.6 ($2F^{2trans}$), −123.1 ($2F^{2cis}$), −192.8 ($2F^1$)	50
$Li[(CF_2{=}CF)_3BOMe]$	Et_2O	−7.6	−99.0 ($3F^{2trans}$), −122.8 ($3F^{2cis}$), −191.9 ($3F^1$)	50
$Li[CF_3C{\equiv}CB(OMe)_3]$	Et_2O	0.8	−47.6 ($3F^3$)	55
$Li[(CF_3C{\equiv}C)_2B(OMe)_2]$	Et_2O	−4.0	−47.8 ($6F^3$)	55
$Li[C_6F_5B(OMe)_3]$ (see [e])	CH_2Cl_2	4.2	−143.9 ($2F^{2,6}$), −158.9 ($1F^4$), −163.9 ($2F^{3,5}$)	48
$Li[C_6F_5BH_3]$ (see [f])	D_2O	−36.0	−131.9 ($2F^{2,6}$), −162.7 ($1F^4$), −164.9 ($2F^{3,5}$)	61
$K[(C_6F_5)_2B(OMe)_2]$ (see [g])	CH_2Cl_2	2.0	−143.1 ($4F^{2,6}$), −160.2 ($2F^4$), −164.7 ($4F^{3,5}$)	49
$Cs[(CF_3)_3BH]$ (see [h])	D_2O	−22.2	−58.7 ($9F^1$)	236
$Cs[(CF_3)_3BOH]$	H_2O	−10.6	−68.0 ($9F^1$)	236

[a] δ(H) = 3.77 ($2H^1$), 1.41 ($2H^2$), 1.32 ($2H^3$), 0.79 ($3H^4$). [b] δ(H) = 4.2 (BH). [c] δ(H) = 3.18 (OMe). [d] δ(H) = 3.23 (OMe). [e] δ(H) = 3.21 (OMe). [f] δ(H) = 1.11 (BH_3). [g] δ(H) = 3.02 (OMe). [h] δ(H) = 1.41 (BH).

Table 3. Chemical shifts in the ^{11}B and ^{19}F NMR spectra (ppm) of selected triorganoboranes and tetraorganoborates containing perfluorinated organic groups.

Compound	Solvent	δ(B)	δ(F)	Ref.
$(C_6F_5)_2BEt$ (see [a])	$CDCl_3$	74.9	−130.7 ($4F^{2,6}$), −147.7 ($2F^4$), −161.2 ($4F^{3,5}$)	157
Z-$(C_6F_5)_2BCH{=}CHBu^n$ (see [b])	$CDCl_3$	58.1	−130.1 ($4F^{2,6}$), −148.7 ($2F^4$), −161.5 ($4F^{3,5}$)	157
$(C_6F_5)_2BC{\equiv}CBu^t$ (see [c])	C_6D_6	48.5	−129.1 ($4F^{2,6}$), −146.5 ($2F^4$), −161.8 ($4F^{3,5}$)	189
$(C_6F_5)_2BPh$ (see [d])	C_6D_6	60.6	−130.9 ($4F^{2,6}$), −149.5 ($2F^4$), −162.1 ($4F^{3,5}$)	129
$(C_6F_5)_3B$	C_6D_6	59.4	−130.1 ($6F^{2,6}$), −143.0 ($3F^4$), −161.4 ($6F^{3,5}$)	129
$CF_2{=}CFBMe_2$ (see [e])	$C_6D_5CD_3$	72.7	−79.6 ($1F^{2trans}$), −94.6 ($1F^{2cis}$), −184.5 ($1F^1$)	193
$(CF_2{=}CF)_3B$	CH_2Cl_2	45.7	−72.7 ($3F^{2trans}$), −90.8 ($3F^{2cis}$), −186.5 ($3F^1$)	126
$(C_6F_5)_3B{\cdot}NCMe$	C_6D_6	−10.3	−134.7 ($6F^{2,6}$), −154.8 ($3F^4$), −163.2 ($6F^{3,5}$)	204
$K[(CF_3)_4B]$	MeCN	−18.9	−61.6 ($12F^1$)	128
$K[(CF_2{=}CF)_4B]$	MeCN	−20.7	−99.3 ($4F^{2trans}$), −123.6 ($4F^{2cis}$), −181.3 ($4F^1$)	126
$Li[(C_6F_5)_3BBu^n]$ (see [f])	C_6D_6 + THF	−12.6	−131.7 ($6F^{2,6}$), −165.5 ($3F^4$), −167.9 ($6F^{3,5}$)	111
$M[(C_6F_5)_4B]$ (see [g])	C_6D_5Cl	−16.3	−131.6 ($8F^{2,6}$), −161.3 ($4F^4$), −165.9 ($8F^{3,5}$)	237

[a] δ(H) ($CDCl_3$) = 1.77 (CH_2), 0.93 (Me); [b] δ(H) (C_6D_6) = 6.83 ($1H^1$ and $1H^2$), 2.07 ($2H^3$), 1.24 and 1.17 ($2H^4$ and $2H^5$), 0.79 ($3H^6$); [c] δ(H) (C_6D_6) = 1.19 (Me); [d] δ(H) (C_6D_6) = 7.53 ($2H^{2,6}$), 7.25 ($1H^4$), 7.11 ($2H^{3,5}$); [e] δ(H) ($C_6D_5CD_3$) = 0.06 (Me); [f] δ(H) (C_6D_6 + THF) = 1.67 (br, $2H^1$), 1.53 and 1.28 ($2H^2$ and $2H^3$), 0.93 ($3H^4$) (br is a broad signal); [g] M = $Cp'_2Zr(OBu^t)L$ (Cp' = cyclo-C_5H_4Me; L = $CH_2{=}CH_2$, $CH_2{=}CHMe$, $CH{\equiv}CMe$, $CMe{\equiv}CMe$).

Table 4. Spin–spin coupling constants ^1J(C-1,B) for selected (perfluoroorgano)borate anions.

Anion	^1J(C-1,B)/Hz	Ref.
$[C_nF_{2n+1}BF_3]$	87–90	55
$[C_nF_{2n+1}CF{=}CFBF_3]$	87–90	55
$[C_nF_{2n+1}C{\equiv}CBF_3]$	99–106	55
$[C_6F_5BF_3]$	75	56
$[(C_nF_{2n+1})_2BF_2]$	70–76	39
$[(CF_3)_3BX]$ [a]	75–83	236
$[(CF_3)_4B]$	74	128
$[(CF_2{=}CF)_4B]$	62	50

[a] X = H, F, Cl, Br, CN, COF, NC, OH.

18–20 Hz larger than those in the spectra of perfluoroalkylborates containing longer perfluoroalkyl chains.

VI. Reactivity of polyfluorinated organoboron compounds

This section considers the reactions accompanied by the C–B bond cleavage and the reactions of (polyfluoroorgano)boranes and -borates with organic derivatives of transition metals. Our task is simplified because some aspects of the reactivity were considered in previous reviews (see the Introduction).

1. Hydrodeboration in acidic and basic media

Data on the transformations of polyfluorinated organic compounds of boron in acidic media are scarce. The C–B bond cleavage in perfluoroalkylborane $C_3F_7B(NMe_2)_2$,[152] as well as in perfluoroalkenylboranes $CF_2{=}C(CF_3)BF_2$ (see Ref. 147) and $CF_2{=}CFB(OBu^n)_2$ (see Ref. 150), easily occurs in the presence of water or dilute aqueous alkaline solutions, and the treatment of $Bu^tCH{=}C[B(C_6F_5)_2]_2$ in benzene with water leads to the fast and regiospecific $B-C_{alkene}$ bond cleavage.[238]

$$C_3F_7B(NMe_2)_2 \xrightarrow{\text{NaOH (aqueous)}} C_3F_7H, \quad (100\%)$$

$$CF_2{=}C(CF_3)BF_2 + H_2O \longrightarrow CF_2{=}CHCF_3 + HOBF_2,$$

$$CF_2{=}CFB(OBu^n)_2 \xrightarrow{0.1\ \text{M KOH}} CF_2{=}CFH + B(OH)_3,$$

$$Bu^tCH{=}C[B(C_6F_5)_2]_2 + 2H_2O \longrightarrow$$

$$\longrightarrow Bu^tCH{=}CH_2 + 2(C_6F_5)_2BOH.$$

The hydrodeboration of a series of polyfluorinated phenylboronic acids $C_6F_nH_{5-n}B(OH)_2$ ($n = 2-5$) in the presence of bases [MeOH; H_2O (33%)–MeOH, KOH (1 equiv.) in the H_2O (33%)–MeOH system; pyridine; D_2O (9%)–pyridine] was investigated.[198] In all cases, the reactions give arenes Ar_FH or Ar_FD. It should be noted that the hydrodeboration rate is determined not only by the number of fluorine atoms, but also by their arrangement with respect to the $B(OH)_2$ group. Thus, the rate constants of hydrodeboration ($k \times 10^2$, min^{-1}) for isomeric tetrafluorophenylboronic acids in a 9% D_2O solution in pyridine (32 °C) are 6.0 [2,3,5,6-$F_4C_6HB(OH)_2$], 0.83 [2,3,4,6-$F_4C_6HB(OH)_2$], and 0.009 [2,3,4,5-$F_4C_6HB(OH)_2$]. Under these conditions, pentafluorophenylboronic acid is completely decomposed within a time shorter than 3 min.[198] The formation of C_6F_5H (90%) from $C_6F_5B(OH)_2$ and diethylamine in DMF (25 °C, 24 h) was documented.[239]

For comparison, let us note that the degree of hydrodeboration of acids $PhB(OH)_2$ and Ph_2BOH in 1.5 M NaOH is at most 30% after heating at 70 °C for one week.[240]

The hydrodeboration of $(C_6F_5)_2BOH$ in CD_2Cl_2 in the presence of 1,8-bis(dimethylamino)naphthalene was studied by ^1H and ^{19}F NMR spectroscopy in the temperature range from −100 to 25 °C. At temperatures below −10 °C, the intermediate [cyclo-$(C_6F_5)_6B_3O_3H_2]^-$ and [cyclo-$(C_6F_5)_5.B_3O_3H]^-$ anions were detected, and these anions gave C_6F_5H upon heating.[241] The treatment of a solution of $(C_6F_5)_2BOH$ in CD_2Cl_2 with methanol also leads to the partial hydrodeboration.[153]

The reactions of tris(pentafluorophenyl)borane with nucleophiles are generally not accompanied by the C–B bond cleavage (see Sections II and IV); however, borane **10** is slowly decomposed with water under rather drastic conditions.[141] Trifluorovinyl(methyl)boranes react in a similar way.[193]

$$\underset{\mathbf{10}}{(C_6F_5)_3B} \xrightarrow[\text{PhMe, 100 °C}]{H_2O} (C_6F_5)_3B{\cdot}OH_2 \xrightarrow[-C_6F_5H]{} (C_6F_5)_2BOH,$$

$$(CF_2{=}CF)_nBMe_{3-n} \xrightarrow[\text{(in an ampoule), 120 °C, 24 h}]{H_2O} \underset{(100\%)}{CF_2{=}CFH},$$

$n = 1, 2.$

Salts of (perfluoroorgano)trimethoxyborates undergo hydrodeboration in water and organic bases.[36, 41, 48, 49] Lithium salts in which the oxygen atoms of the methoxy groups are coordinated to the lithium cation are least prone to hydrodeboration. The addition of the competitive ligand TMEDA or the replacement of lithium by potassium leads to a substantial increase in the rate of hydrodeboration of borates $[R_FB(OMe)_3]^-$ giving R_FH.

$$Li[R_FB(OMe)_3] \longrightarrow R_FH.$$

R_F	Ref.
C_nF_{2n+1}	36
$C_nF_{2n+1}CF{=}CF$	41
$C_6F_nH_{5-n}$	48, 49

In some cases, the hydrodeboration rate of $Li[R_FB(OMe)_3]$ depends on the structure of R_F. Thus, Li[(*E*)-$CF_3CF{=}CFB(OMe)_3$] is quite stable in $(CD_3)_2CO$ and CD_3CN, whereas the salts $Li[RCF{=}CFB(OMe)_3]$ [R = F, (*Z*)-CF_3] are rapidly decomposed in these solvents to give $RCF{=}CFD$.[41]

The conditions of hydrodeboration of potassium (polyfluoroorgano)trifluoroborates $K[R_FBF_3]$ ($R_F = C_6F_5$, $XCF{=}CF$ (X = F, Cl, C_3F_7O, C_2F_5, C_4F_9, Bu^n), and C_6F_{13}) in acids (100% AcOH, 100% CF_3CO_2H, 25%–100% HF) and of particular (perfluoroorgano)difluoroboranes R_FBF_2 [$R_F = C_6F_5$, $CF_2{=}CF$, $CClF{=}CF$, (*Z*)-$C_2F_5CF{=}CF$, (*E*)-$C_4F_9CF{=}CF$, and C_6F_{13}] in anhydrous HF were investigated[242, 243] and considered in the review.[16] We only mention that the hydrodeboration rate of polyfluorinated organotrifluoroborates decreases in the series

$$K[(E)\text{-}Bu^nCF{=}CFBF_3] > K[(Z/E)\text{-}C_3F_7OCF{=}CFBF_3] \approx$$

$$\approx K[CF_2{=}CFBF_3] \geqslant K[(Z/E)\text{-}ClCF{=}CFBF_3] \approx$$

$$\approx K[C_6F_5BF_3] > K[(Z)\text{-}C_2F_5CF{=}CFBF_3] \geqslant$$

$$5\,K[(E)\text{-}C_4F_9CF{=}CFBF_3] \gg K[n\text{-}C_6F_{13}BF_3],$$

which is similar to that for hydrocarbon analogues:

$$K[(Z/E)\text{-}Bu^nCH{=}CHBF_3] > K[PhBF_3] >$$

$$> K[Bu^nBF_3] \approx K[(n\text{-}C_8H_{17})BF_3].^{243}$$

2. Hydroxydeboronation

The replacement of the boron atom by hydroxyl (hydroxydeboronation) is widely used in organic synthesis for the preparation of alcohols and phenols and the transformation of the C=C moiety into CH–C(OH).[244] These reactions are also typical of polyfluorinated organoboranes. Thus, $C_6F_5B(OH)_2$ reacts with 85% H_2O_2 in the absence of a solvent to give C_6F_5OH in 91% yield.[139] Perfluoro-1,1′-binaphthyl-2,2′-diol was synthesized in 90% yield from substituted 1,6-dibromo-1,6-diboracyclodecane (**15**) and 30% H_2O_2 (THF, 25 °C, 30 min).[133]

In some cases, it is more convenient to perform the hydroxydeboronation without isolation of intermediate boranes. For example, tetrafluorophenols RC_6F_4OH (R = F, 2-H, 4-H, 4-$F_3CC_6F_4O$) were synthesized in 40%–55% yields by the addition of RC_6F_4Li to $B(OMe)_3$ followed by the treatment of the resulting solution with 50%–85% H_2O_2 at $\leqslant -10$ °C.[245, 246]

The two-step hydration of polyfluoroalkenes $R_FCH{=}CH_2$ by the addition of boranes HBXY followed by the hydroxydeboronation (oxidation) with hydrogen peroxide in an alkaline medium was investigated. The

addition of boranes containing electron-withdrawing substituents occurs very rapidly and gives 2-dihaloborylalkanes (the ^{11}B NMR signal at 60.4 ppm), whose hydroxydeboronation affords polyfluoroalkan-2-ols.[247, 248]

$$R_FCH{=}CH_2 \xrightarrow[C_6H_{14},\ 22\ ^\circ C]{HBX_2} [R_FCH(BX_2)Me] \xrightarrow[Et_2O]{H_2O_2,\ NaOH} R_FCH(OH)Me,\ (82\%-90\%)$$

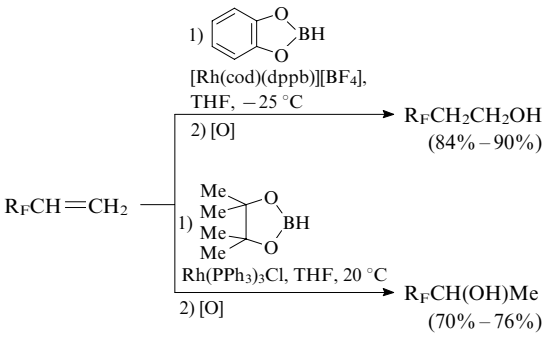
$R_F = CF_3$, n-C_4F_9, n-C_6F_{13}, C_6F_5; X = Cl, Br.

The addition of dialkylboranes $HBAlk_2$ [Alk = Cy, Am^i (Am^i is isoamyl)] to $R_FCH{=}CH_2$ occurs slowly, and 9-BBN reacts only with $C_6F_5CH{=}CH_2$ (THF, 22 °C, 96 h). The reactions of di(cyclohexyl)borane give 1-polyfluoroalkylboranes, which are transformed into polyfluoroalkan-1-ols without isolation. The addition of di(isoamyl)borane followed by the hydroxydeboronation affords a mixture of 1- and 2-polyfluoroalkanols,[247, 248] which is attributed to the disproportionation of $HBAm^i_2$.[248]

$$R_FCH{=}CH_2 \xrightarrow{HBCy_2} [R_FCH_2CH_2BCy_2] \xrightarrow[Et_2O]{H_2O_2,\ NaOH} R_FCH_2CH_2OH,$$

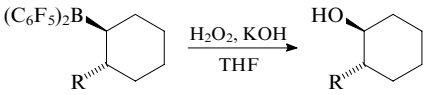
R_F = n-C_6F_{13}, C_6F_5.

It should be noted that the hydroboration of alkenes $R_FCH{=}CH_2$ with catecholborane or pinacolborane occurs by different pathways depending on the presence of neutral or cationic rhodium catalysts.[249, 250]



$R_F = CF_3$, n-C_4F_9, n-C_6F_{13}, C_6F_5; cod is cycloocta-1,5-diene, dppb is 1,2-bis(diphenylphosphino)benzene; [O] = NaOH + H_2O_2, THF.

Bis(pentafluorophenyl)alkylboranes and -alkenylboranes (see Section III) are easily transformed into alcohols and aldehydes, respectively, in the reactions with an alkaline solution of H_2O_2. The fate of the $(C_6F_5)_2B$ moiety was not reported in the study.[157]



R = Me, 1-naphthyl.

$$RCH{=}CHB(C_6F_5)_2 \xrightarrow[THF]{H_2O_2,\ KOH} RCH_2CHO,$$

R = n-C_9H_{19} (67%), Ph (49%).

3. Replacement of the boron atom by xenon(II, IV), iodine(III, V), and bromine(III) atoms

The ability to transfer organic groups R_F from the boron atom to xenon(II, IV), iodine(III, V), and bromine(III) atoms is one of remarkable properties of polyfluorinated organoboron compounds. First organoxenon compounds were synthesized in 1989.[251, 252]

$$\underset{\mathbf{10}}{(C_6F_5)_3B} + XeF_2 \xrightarrow[-50\ \text{to}\ -30\ ^\circ C]{CH_2Cl_2\ \text{or MeCN}} [C_6F_5Xe][(C_6F_5)_{4-n}BF_n],$$

n = 1, 2.

Less fluorinated triarylboranes, up to $(C_6FH_4)_3B$ and $(CF_3C_6H_4)_3B$, are also involved in this reaction;[176, 253–255] the reaction with BPh_3 gives a complex mixture of products due apparently to instability of the phenylxenonium salt. (Polyfluoroorgano)difluoroboranes proved to be more appropriate substrates. The latter compounds are more available than triarylboranes, and the resulting $[BF_4]^-$ anions are less nucleophilic than $[(Ar_F)_{4-n}BF_n]^-$, which is reflected in the higher stability of the salts $[R_FXe][BF_4]$. The preparative method was developed for the synthesis of salts of polyfluoroorganic derivatives of xenon(II) containing aryl, alkenyl, and alkynyl groups and salts of pentafluorophenylxenon(IV) based on boranes R_FBF_2.

$$R_FBF_2 + XeF_2 \xrightarrow[-60\ \text{to}\ -30^\circ C]{solv} [R_FXe][BF_4],$$

solv: CH_2Cl_2, $CF_3CH_2CHF_2$, $CF_3CH_2CF_2Me$;
$R_F = C_6F_nH_{5-n}$ (n = 1–5), RCF=CF (R = F, H, Cl, Alk, Ph, C_nF_{2n+1}), $CF_2{=}CR$ (R = H, Cl, CF_3), $CR{\equiv}C$ (R = C_nF_{2n+1}, $(CF_3)_3CF$, $CF_3CF{=}CF$, n-$C_4F_9CF{=}CF$, C_6F_5).

$$C_6F_5BF_2 + XeF_4 \xrightarrow[-55\ ^\circ C]{CH_2Cl_2} [C_6F_5XeF_2][BF_4].$$

Attempts to synthesize diorganoxenon derivatives by this method failed because of the high Lewis acidity of (perfluoroorgano)difluoroboranes. For example, the reaction of $C_6F_5BF_2$ with C_6F_5XeF affords the salt $[C_6F_5Xe][C_6F_5BF_3]$, whereas the reaction of C_6F_5XeF with $(C_6F_5SiF_3)$, which is a weaker acceptor of fluoride anions, gives $(C_6F_5)_2Xe$.[256] It is interesting that the rate of xenonodeboronation (the replacement of the boron atom with xenon) of (E)-$C_nF_{2n+1}CF{=}CFBF_2$ is 2–4 times lower than that of the Z isomer, which is attributed to the steric hindrance in the transition state.[257]

The reaction of arylborane **10** with iodine trifluoride occurs like the reaction with xenon difluoride to give the bis(pentafluorophenyl)iodinium salt.[258] This method was used for the synthesis of numerous symmetrical and unsymmetrical poly- and perfluorinated iodonium salts containing aryl, alkenyl, and alkynyl groups at the iodine atom. In addition to high yields and the simplicity of the isolation of the reaction products, this method is interesting because iodonium salts can be synthesized in two complementary ways, *viz.*, by the reactions $(R_FBF_2 + RIF_2)$ and $(R_FIF_2 + RBF_2)$. Unlike the xenonodeboronation, the iododeboronation of (Z)- and (E)-perfluoroalkenyldifluoroboranes with difluoroiodanes RIF_2 occurs at virtually equal rates.

$$(C_6F_5)_3B + IF_3 \xrightarrow[-78\ ^\circ C]{CH_2Cl_2} [(C_6F_5)_2I][(C_6F_5)_nBF_{4-n}],$$
10 (68%)

$n = 0-3$.

$$R_FBF_2 + RIF_2 \xrightarrow[-60\ \text{to}\ 0\ ^\circ C]{\text{solv}} [(R_F)RI][BF_4],$$

solv: CH_2Cl_2, $CFCl_3$, $CF_3CH_2CHF_2$, $CF_3CH_2CF_2Me$;
$R_F = C_6F_nH_{5-n}$ ($n = 0-5$), 4-C_5NF_4, $R'CF{=}CF$ ($R' = F$, C_nF_{2n+1}), $R'C{\equiv}C$ ($R' = Bu^t$, CF_3, $(CF_3)_3C$), n-C_6F_{13};
$R = C_6F_nH_{5-n}$ ($n = 0-5$), 4-C_5NF_4, $(CF_3)_2CFCF{=}CF$, C_4F_9, CF_3CH_2.

The further progress in the use of (perfluoroorgano)difluoroboranes in the synthesis of organic derivatives of polyvalent halogens can be illustrated by the synthesis of iodine(V) (Ref. 259) and bromine(III) (Ref. 260) salts.

$$C_6F_5BF_2 + C_6F_5IF_4 \xrightarrow[-40-20\ ^\circ C]{CH_2Cl_2} [(C_6F_5)_2IF_2][BF_4],$$
(64%)

$$C_3F_7C{\equiv}CBF_2 + C_6F_5BrF_2 \xrightarrow[-40-20\ ^\circ C]{CF_3CH_2CF_2H} [C_3F_7C{\equiv}C(C_6F_5)Br][BF_4].$$

The use of perfluorinated organoboron compounds in the xenonodeboronation,[261–263] iododeboronation, and bromodeboronation[264] was discussed in more detail in the reviews covering the literature up to 2007–2008.

4. Cross-coupling reactions

Cross-coupling reactions of organoboron compounds with carbon electrophiles catalyzed by palladium complexes (Suzuki–Miyaura reaction) are among important achievements in synthetic organic chemistry of the last two decades.[265,266] Organoboron compounds containing various organic groups are used as reagents, but only a few examples with the involvement of polyfluoroorganic derivatives of boron were described. To understand the factors responsible for this situation recall that the mechanism of cross-coupling reactions involves the oxidative addition, transmetallation, and reductive elimination. Initially, an organic electrophile (for example, RHal) reacts with Pd^0 to form an organic palladium(II) complex. The reaction of the latter with nucleophilic organoboron reagents leads to the transfer of the organic group from the boron atom to the Pd atom (transmetallation) to form the Pd^{II} complex with two organic ligands. The reductive elimination of Pd^0 from the latter complex affords the cross-coupling product, and the catalytic cycle is closed.[267] The nucleophilicity of polyfluorinated organoboron compounds is substantially lower (compared to their unfluorinated and weakly fluorinated analogues) due to the cumulative effect of several fluorine atoms, and it is the main (but not the only) difficulty in the use of (polyfluoroorgano)boron reagents in cross-coupling reactions.

Mono-, di-, and 3,4,5-trifluorophenylboronic acids are involved in the palladium-catalyzed cross-coupling like other arylboronic acids.[268–271] First attempts to introduce pentafluorophenyl groups with the use of $C_6F_5B(OH)_2$ under similar conditions (catalyst, solvent, base) failed.[268,269,271] The problem was solved by introducing special additives. Thus, 2-(polyfluorophenyl)pyridines were synthesized by the reactions of 2,4,6-$F_3C_6H_2B(OH)_2$ and $C_6F_5B(OH)_2$ with 2-iodopyridine in the presence of $[Pd(PPh_3)_4]$, Bu^tOK, and Ag_2O in DME at 70–90 °C in 32% and 76% yields, respectively.[272] However, the reaction of $C_6F_5B(OH)_2$ with 2-bromothiophene under these conditions gave only trace amounts of 2-(pentafluorophenyl)thiophene.[273] The yield of the latter was increased to 20% (in DME) or 68% (in DMF) when potassium phosphate was used instead of Bu^tOK. This improvement made it possible to synthesize a series of 2-pentafluorophenyl- and 2,5-bis(pentafluorophenyl)thiophenes and -selenophenes in 42%–84% yields.[273] The cross-coupling of $C_6F_5B(OH)_2$ with iodobenzene in the presence of $[Pd(PPh_3)_4]$, Bu^tOK, and Ag_2O (DME, 70 °C) afforded 2,3,4,5,6-pentafluorobiphenyl in 40% yield, and the yield was increased to 60%–90% when caesium fluoride was used instead of Bu^tOK.[274] Under these conditions, the reaction of $C_6F_5B(OH)_2$ with 2,8-diiodo-6,6,12,12-tetrafluoroindeno[3,2-*b*]fluorene gave 2,8-bis(pentafluorophenyl)-6,6,12,12-tetrafluoroindeno[3,2-*b*]fluorene in 62% yield.[275] The use of the $Pd_2(dba)_3-2PBu^t_3$ catalyst (dba is dibenzylideneacetone) combined with CsF and Ag_2O is more efficient, as was shown by the synthesis of substituted biphenyls $C_6F_5C_6H_4X$ from $C_6F_5B(OH)_2$ and aryl bromides XC_6H_4Br (X = H, 2-Me, 3-Me, 4-Me, 3-OMe, 4-OMe, 4-F, 4-CO_2Et, 4-NO_2, 4-CF_3)[274] and by the synthesis of 2,12-bis(pentafluorophenyl)-7-phenyl-5,6,8,9-tetrahydrobenzo[*c*,*h*]acridine from the corresponding dibromide.[276] It is possible to use PhCl (39% yield) or $PhOSO_2CF_3$ (4% yield) instead of C_6H_5Br, but they are less efficient.[274]

$$C_6F_5B(OH)_2 + ArHal \xrightarrow{a,\ b\ \text{or}\ c} C_6F_5Ar,$$

(*a*) $[Pd(PPh_3)_4]$, Ag_2O, Bu^tOK, Bu^tOH, DME, 70–90 °C;
(*b*) $[Pd(PPh_3)_4]$, Ag_2O, K_3PO_4, DMF, 85 °C;
(*c*) $Pd_2(dba)_3-2PBu^t_3$, Ag_2O, CsF, DMF, 100 °C.

The above-considered reactions occur in the presence of Lewis bases and silver(I) oxide in anhydrous aprotic solvents. Here, bases play a dual role. On the one hand, they form 'ate' complexes with arylboronic acids, thus increasing the nucleophilicity of the reagent. On the other hand, under basic conditions, polyfluorophenylboronic acids $C_6F_nH_{5-n}B(OH)_2$ ($n \geqslant 3$) undergo hydrodeboration (the replacement of the boron atom by hydrogen),[198] resulting in a decrease in the yields of cross-coupling products. In addition, bases, such as Bu^tOK, can react with pentafluorophenyl-containing products to give the derivatives 4-$Bu^tOC_6F_4$.[272–274] The role of Ag_2O is to transform the initially formed neutral Pd^{II} aryl complex into the cationic intermediate.[277] Due to the high reactivity of the latter, the cross-coupling of polyfluorophenylboronic acids occurs more rapidly than the competitive hydrodeboration.

The influence of the moisture that is present in the solvent on the course of the reaction is less evident. All successful syntheses were carried out under anhydrous conditions and, moreover, commercial pentafluorophenylboronic acid was generally used without additional purification, *i.e.*, the presence of boroxine $(C_6F_5BO)_3$ and its amount in the reagent were not controlled. It should be noted that acids $C_6F_nH_{5-n}B(OH)_2$ ($n \geqslant 3$) readily eliminate water to give boroxines $(C_6F_nH_{5-n}BO)_3$.[143] Presumably, the hydrodeboration rate of the latter in basic media is lower than that of the corresponding acids, and this is favourable for the alternative cross-coupling.

The further progress in the introduction of polyfluoroorganic moieties into organic molecules was made due to the use of individual (polyfluoroorgano)borates $M[R_FBX_3]$ [$R_F = CF_2{=}CF$, X = F; $R_F = C_6F_nH_{5-n}$ ($n = 3-5$);

X = OMe, F], which became available in the last decade.[30, 48, 49, 56] The advantages of these salts are that they are more stable under the reaction conditions and are more nucleophilic than the corresponding arylboronic acids. For example, in the presence of $[Pd(PPh_3)_4]$ or $Pd(OAc)_2$, the reactions of the salts of polyfluorinated aryltrimethoxyborates $Li[C_6F_5B(OMe)_3]$, $Li[C_6F_4HB(OMe)_3]$, $Li[3,4,5\text{-}F_3C_6H_2B(OMe)_3]$, and $4\text{-}FC_6H_4I$ afforded a series of polyfluorinated biphenyls $4\text{-}FC_6H_4C_6F_nH_{5-n}$. The cross-coupling occurs in satisfactory yields in low-polarity (DME) and nonpolar (toluene) anhydrous solvents at 80–100 °C in the absence of bases or silver(I) compounds, although the addition of Ag_2O leads to a slight increase in the yield of $4\text{-}FC_6H_4C_6F_5$ in the reaction of $Li[C_6F_5B(OMe)_3]$ with $4\text{-}FC_6H_4I$.[48]

$$Li[C_6F_nH_{5-n}B(OMe)_3] + ArI \xrightarrow{a \text{ or } b} C_6F_nH_{5-n}Ar,$$

(*a*) $[Pd(PPh_3)_4]$, PhMe, 100 °C; (*b*) $Pd(OAc)_2$, DME, 80 °C.

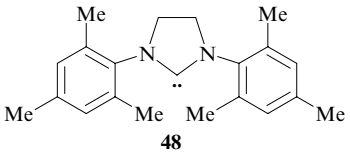
The possibility of the use of potassium organotrifluoroborates in palladium-catalyzed cross-coupling reactions was shown for the first time in the synthesis of biaryl and styrenes from $K[RBF_3]$ (R is aryl or alkenyl) and arenediazonium tetrafluoroborates.[278–280] Under these conditions [$Pd(OAc)_2$, dioxane, 20 °C], the salt $K[C_6F_5BF_3]$ remains intact. However, in the presence of $[Pd(PPh_3)_4]$, the carbon electrophiles $[4\text{-}XC_6H_4N_2][BF_4]$ are arylated with borates $K[C_6F_nH_{5-n}BF_3]$ (n = 3–5) (DME, 20 °C) to form polyfluorinated biphenyls in 20%–60% yields.[281]

$$K[C_6F_nH_{5-n}BF_3] + [ArN_2][BF_4] \xrightarrow[20\ ^\circ C]{[Pd(PPh_3)_4],\ DME} C_6F_nH_{5-n}Ar,$$

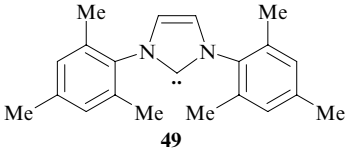
Ar = $4\text{-}XC_6H_4$ (X = CO_2Et, F, NO_2, OMe, H, Me); n = 3–5.

The cross-coupling of $K[C_6F_5BF_3]$ with less electrophilic aryl iodides $4\text{-}XC_6H_4I$ occurs under more drastic conditions [$Pd(OAc)_2$, $2\,PPh_3$, toluene, 100 °C] and requires the presence of Ag_2O and K_2CO_3.[281, 282] This method was used for the synthesis of 2,3,4,5,6-pentafluorobiphenyls[282] and 3,3′-bis(pentafluorophenyl)binaphthyl derivatives.[283] The palladium-catalyzed polyfluoroarylation of aryl bromides affords products in moderate yields (25%–40%),[282] although the cross-coupling with less fluorinated and unfluorinated aryltrifluoroborates generally gives better results.[284, 285]

It should be noted that these reactions were carried out in degassed solvents and under an inert atmosphere. The improved catalyst stable to atmospheric oxygen and moisture was prepared *in situ* from $[Pd(PPh_3)_2Cl_2]$ and SIMes·HCl (**48**·HCl) or IMes·HCl (**49**·HCl) (precursors



48



49

$$K[C_6F_5BF_3] + ArHal \xrightarrow{a \text{ or } b} C_6F_5Ar,$$

(*a*) $Pd(OAc)_2 - 2\,PPh_3$, Ag_2O, K_2CO_3, PhMe, 100 °C;
(*b*) $[Pd(PPh_3)_2Cl_2]$, (**48** or **49**)·HCl, Ag_2O, PhMe, 100 °C.

of the corresponding N-heterocyclic carbene ligands). In this case, pentafluorobiphenyls were produced in yields of up to 99%.[57]

Potassium trifluorovinyltrifluoroborate $K[CF_2{=}CF.BF_3]$ is the only representative of polyfluorinated alkenylborate salts examined in cross-coupling reactions. In spite of the low nucleophilicity of the $[CF_2{=}CFBF_3]^-$ anion associated with the presence of the fluorine atom at the C-1 atom, $K[CF_2{=}CFBF_3]$ reacts with $[4\text{-}FC_6H_4N_2][BF_4]$ in the presence of $[Pd(PPh_3)_4]$ (dioxane, 20 °C) to give $4\text{-}FC_6H_4CF{=}CF_2$.[281]

$$K[CF_2{=}CFBF_3] + [ArN_2][BF_4] \xrightarrow[20\ ^\circ C]{[Pd(PPh_3)_4],\ dioxane} CF_2{=}CFAr.$$

The cross-coupling reaction with less electrophilic $4\text{-}FC_6H_4I$ occurs in toluene (100 °C) in the presence of the $Pd(OAc)_2 - 2\,PPh_3$ catalysts and additives of Ag_2O and K_2CO_3 and gives tetrafluorostyrene in 76% yield.[282]

$$K[CF_2{=}CFBF_3] + 4\text{-}FC_6H_4I \xrightarrow[PhMe,\ 100\ ^\circ C]{Pd(OAc)_2 - 2\,PPh_3,\ Ag_2O,\ K_2CO_3} CF_2{=}CF(C_6H_4F\text{-}4).$$
(76%)

The possibility of the use of derivatives of other transition metals (except for palladium) as catalysts for cross-coupling reactions and the reactivity of polyfluorinated alkyl-, alkenyl-, and alkynylboronic acids, the corresponding borinic acids, and their esters remain unknown.

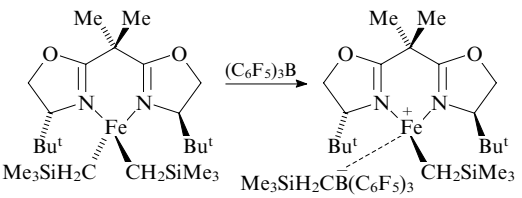
5. Reactions of perfluorinated organoboron compounds with organic derivatives of transition metals

The use of perfluorinated organoboron compounds for the design of metallocene catalysts for the homogeneous olefin polymerization from organic derivatives of transition metals was considered in the reviews.[10, 12, 286] Several typical examples illustrating these reactions are given below.

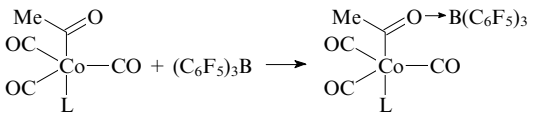
The reactions of the alkyl derivatives of transition metals L_nMAlk (L is the ligand) with $(C_6F_5)_3B$ are accompanied by the elimination of the alkyl group to form the products $[L_nM][Alk(C_6F_5)_3B]$ with different degrees of ionicity of the boron–metal bond. The presence of basic centres with nitrogen, oxygen, and phosphorus atoms has no effect on the reaction pathway.[287]

$$[FeEt_2(bipy)_2] + (C_6F_5)_3B \longrightarrow [FeEt(bipy)_2][EtB(C_6F_5)_3],$$

bipy is bipyridine.

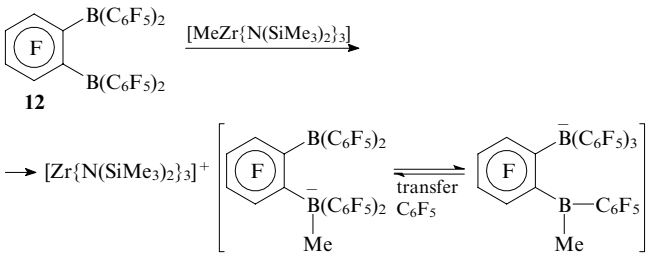


In the presence of carbonyl-containing ligands in the coordination sphere of transition metals, donor–acceptor complexes can be formed.[288]



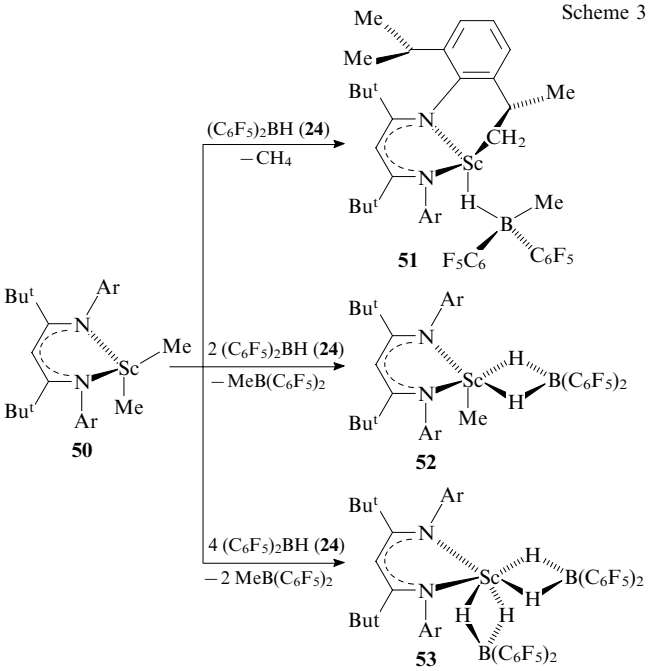
L = PMe_3, $PPhMe_2$, $P(4\text{-}MeC_6H_4)_3$, PPh_3, $P(4\text{-}FC_6H_4)_3$.

The redistribution of the ligands (symmetrization) is less typical of polyfluorinated boron derivatives compared to their hydrocarbon analogues. However, the reaction of diborane **12** with $[MeZr\{N(SiMe_3)_2\}_3]$ is accompanied by the migration of the C_6F_5 group to form borate borane.[289]



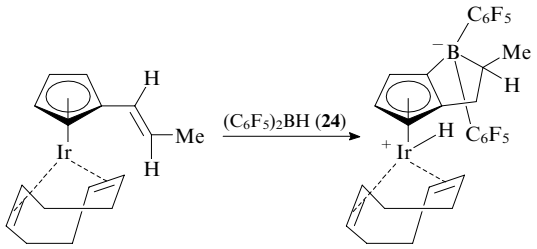
The reactions of boranes $(C_6F_5)_2BH$ and $(C_6F_5)_2BCl$ with organic derivatives of transition metals occur in a different way. For example, the reaction of $LScMe_2$ (**50**) with $(C_6F_5)_2BH$ (1 equiv.) affords scandium derivative **51** and methane. The reaction with 2 equiv. of borane **24** gives complex **52**, whereas the reaction with 4 equiv. of this borane produces complex **53** (Scheme 3).[290]

Scheme 3

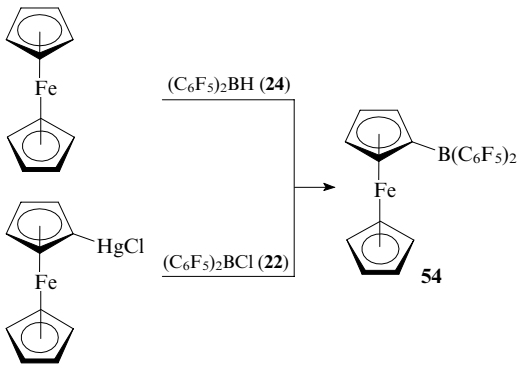


Ar = 2,6-$Pr^i_2C_6H_3$.

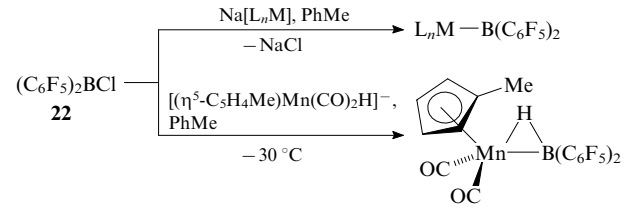
The reaction of $[(cod)Ir(\eta^5\text{-}C_5H_4{-}CH{=}CHMe\text{-}(E))]$ or $[(cod)Ir(\eta^5\text{-}C_5H_4{-}CH_2CH{=}CH_2]$ with $(C_6F_5)_2BH$ (**24**) gives products in which the five-membered boron-containing heterocycle is fused to the cyclopentadienyl ring.[291]



Ferrocene reacts with borane **24** to form borylferrocene **54**, which can also be synthesized from FcHgCl and chloroborane **22** (87%–91% yields).[292]

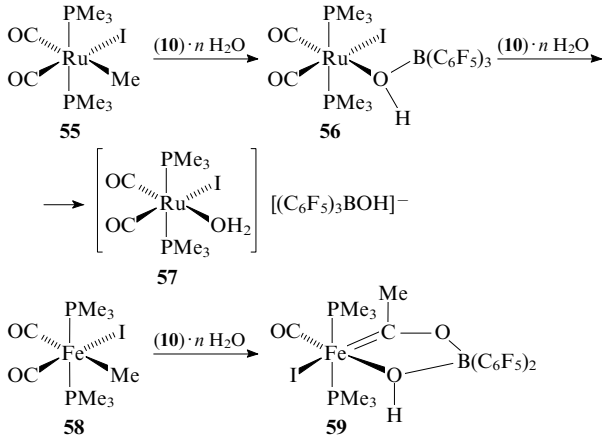


The high electrophilicity of $(C_6F_5)_2BCl$ is responsible for the formation of boryl complexes in the reactions with the nucleophiles $[(\eta^5\text{-}C_5R_5)Fe(CO)_2]^-$ (R = H, Me), $[Mn(CO)_5]^-$, and $[(\eta^5\text{-}C_5H_4Me)Mn(CO)_2H]^-$ (Ref. 293).

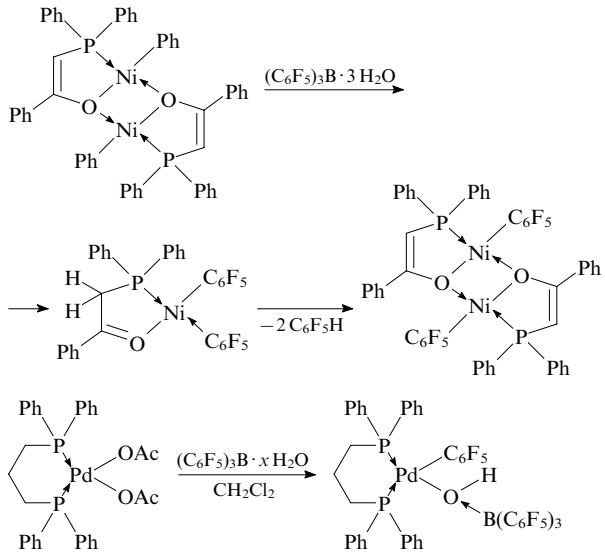


L_nM = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, $(\eta^5\text{-}C_5Me_5)Fe(CO)_2$, $Mn(CO)_6$.

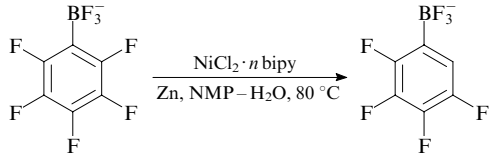
The reactions of transition metal complexes with the complexes $(C_6F_5)_3B\cdot n\,H_2O$ deserve special mention. The latter are strong Brønsted acids, and their reactions generally lead to the elimination of alkyl groups from the metal atom in the form of AlkH. For example, ruthenium complex **55** initially gives product **56**, which is slowly transformed into salt **57**; the reaction of iron complex **58** produces cyclometallated complex **59**.[287]



Unexpectedly, it turned out that the compounds $(C_6F_5)_3B \cdot n\,H_2O$ can serve as pentafluorophenylating reagents. For example, the reactions of Ni (Ref. 294) or Pd (Ref. 295) complexes with $(C_6F_5)_3B$ in the presence of water resulted in the transfer of the C_6F_5 group.



It was shown [296] that the pentafluorophenyltrifluoroborate anion undergoes hydrodefluorination at position 2 in the reaction with the Ni^0 complexes, which is generated *in situ* from nickel chloride, bipyridine, and zinc in *N*-methylpyrrolidone (NMP), to give 2,3,4,5-tetrafluorophenylfluoroborate anions.



VII. Conclusion

The analysis of the published data shows that researchers focus on three types of fluorinated organic compounds of boron. Due to specific properties, each type of compounds finds its own field of practical application. Thus, due to the high Lewis acidity combined with the resistance to oxidation, tris(perfluoroaryl)boranes can be used as acid catalysts in organic synthesis, activators of metallocene and post-metallocene catalysts for the polymerization of unsaturated organic compounds, *etc*.[6, 10, 12, 13, 297] It should be noted that the potential of tris(perfluoroaryl)boranes is not reduced to purely chemical applications. In recent years, it has been reported that these compounds can be used as various additives which, for example, increase the capacity of lithium ion batteries due to dissolution of LiF passivation films.[298]

Most of fluorinated organoborates form weak interactions with highly reactive cationic species in solution and, in addition, are chemically inert. Hence, they are efficient counterions widely used in organometallic chemistry and catalysis.[17, 18] Among fluorinated organoborates, perfluoroalkylborates are of special interest. Due to chemical and electrochemical stability, as well as due to good solubility of most of salts in organic solvents and high conductivity of their solutions, perfluoroalkylborates are considered as promising electrolytes for electrochemical cells and supercondensers.[299–303] Recently, perfluorinated organoborates have found use in the preparation of low-viscosity hydrophobic ionic liquids.[304–309]

The complexes $(R_F)_nBX_{3-n} \cdot$ Base are intermediate in the properties between fluorinated organoboranes and organoborates and are, in most cases, used in the synthesis of both boranes and borates. For particular boranes $(R_F)_nBX_{3-n}$, the complexation with bases is the only possibility of stabilization. In a number of studies, the complexes $(R_F)_nBX_{3-n} \cdot$ Base were employed as individual compounds, for example, for the activation of metallocene and post-metallocene catalysts.[15]

Therefore, fluorinated organic compounds of boron belong to a special class of organoelement compounds, which have unique properties associated with the partial or complete replacement of hydrogens by fluorine atoms in boron-bonded organic groups. The latter fact stimulated the synthesis of unknown fluorinated organic derivatives of boron and the development of new approaches to their synthesis, because most of the methods of classical organoboron chemistry either cannot be used at all or are inefficient in the synthesis of target products. In turn, the solution of these problems called for the development of related fields of chemistry of their precursors, *viz*., fluorinated organic and heteroorganic compounds.

The data presented in the review clearly show the promising directions for the development of the chemistry of fluorinated boron-containing organic compounds and the possibility of the use of these compounds in various fields of science and engineering.

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