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Convenient synthesis of perfluoroalkyltrifluoroborates

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(bpy = 2,2'-bipyridine).

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| A R T I C L E I N F O | A B S T R A C T |
|--|--|
| In memoriam: Nobel laureate George Olah. | Perfluoroalkyltrimethoxyborates were converted into the corresponding perfluoroalkyltrifluoroborates in high |
| Keywords: | yield by the action of potassium bifluoride in acidic media, i.e. in hydrochloric acid (37%), glacial acetic acid, |
| Perfluoroalkyltrifluoroborates | and trifluoroacetic acid as well as in acidic ionic liquids. These low-cost methods avoid the use of toxic and |
| Nucleophilic fluorination | corrosive hydrofluoric acid or anhydrous HF (aHF). Potassium and sodium perfluoroalkyltrifluoroborates are |
| Brønsted acid catalysis | highly valuable starting materials for the preparation of low viscosity ionic liquids and organic salts with |
| Ionic liquids | $[R_FBF_3]^-$ anions, in general, and for the synthesis of further perfluoroalkylborate anions, for example per- |
| Olah reagent | fluoroalkylcyanofluoroborates $[R_FBF_{3-n}(CN)_n]^-$ (n = 1–3). Furthermore, complex metal cations are accessible |

1. Introduction

Potassium and sodium perfluoroalkyltrifluoroborates are convenient starting materials for the synthesis of organic salts [1] and ionic liquids with perfluoroalkyltrifluoroborate anions $[R_{\rm p}BF_2]^-$ [2–8]. The strong changes of the properties of monoperfluoroalkyltrifluoroborates versus tetrafluoroborates are nicely exemplified by a comparison of the properties of the respective ionic liquids (ILs). In contrast to tetrafluoroborate ILs that are often hydrophilic, e.g. EMIM[BF4], ILs based on perfluoroalkyltrifluoroborate anions are much more hydrophobic and they exhibit much lower viscosities [8]. Similar to tetrafluoroborates, perfluoroalkyltrifluoroborates are valuable starting materials for further derivatizations. Recently, we have developed convenient syntheses of inorganic and organic salts including very lowviscosity ILs with monoperfluoroalkylcyanofluoroborate anions of the general formula $[R_FBF_{3-n}(CN)_n]^-$ (n = 1, 2, 3) starting from perfluoroalkyltrifluoroborates [9,10]. The chemistry of alkyl- and perfluoroalkyltrifluoroborates was reviewed several times in the past demonstrating the high synthetic value and importance of this class of compounds [11-16].

The potassium salt $K[CF_3BF_3]$ was prepared for the first time in the early sixties of the last century via a two-step procedure from $(CH_3)_3SnCF_3$ and boron trifluoride followed by metathesis with KF in water (Scheme 1) [17]. This reaction was the first example for the successful preparation of a perfluoroalkyltrifluoroborate.

Later, Molander et al. have improved the synthesis of potassium trifluoromethyltrifluoroborate $K[(CF_3BF_3)]$ by using $(CH_3)_3SiCF_3$ (Ruppert-Prakash reagent) as a source for the trifluoromethyl group and the readily available and easy to handle trimethoxyborane (Scheme 2A) [18]. Nowadays, $(CH_3)_3SiCF_3$ is commercially available, which makes this synthesis the method of choice for the preparation monotrifluoromethylboron compounds.

with the weakly coordinating $[R_FBF_3]^-$ counterions, as exemplified by the synthesis of $[Cu(bpy)_3][C_2F_5BF_3]$

Many trifluoromethylboron derivatives possess a limited thermal stability due to the tendency to eliminate difluorocarbene [11,17,19]. Especially three coordinate trifluoromethylboron compounds are very labile, e.g. the free Lewis acids $(CF_3)_{3-x}BF_x$ (x = 0–1) are unknown and any attempts to trap these Lewis acids remained unsuccessful [20]. The aminotrifluoromethylboranes $CF_3B{N(CH_3)_2}_2$ and $(CF_3)_2BN(CH_3)_2$ are thermally more robust but still decompose at relatively low temperatures (140 °C) under elimination of difluorocarbene [21]. In contrast, four coordinate trifluoromethylboron compounds often exhibit unprecedented high thermal and chemical stabilities. The homoleptic tetrakis(trifluoromethyl)borate anion [B(CF₃)₄]⁻ is a very weakly coordinating anion that was successfully used for the stabilization of highly reactive cations [13,22,23]. The very strong Lewis acid $(CF_3)_3B$, which is unknown as free acid [20], is capable in stabilizing reactive groups, e.g. in $[(CF_3)_3BC(O)Hal]^-$ (Hal = F, Cl, Br, I) [24,25] and $[(CF_3)_3BCPnic]^-$ (Pnic = N, P, As) [26].

The comparably low thermal and chemical stability of trifluoromethyl compounds is not only limited to boron but is observed for

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¹ https://go.uniwue.de/finze-group.

A \

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E)

 $(CH_3)_3SnCF_3 + BF_3 \xrightarrow{20 \text{ °C}, 1 \text{ h}} [(CH_3)_3Sn][CF_3BF_3] \xrightarrow{KF/Water, 100 \text{ °C}, 30 \text{ min}}_{-(CH_3)_3SnF} K[CF_3BF_3] \text{ Scheme 1. First synthesis of } K[CF_3BF_3] [17].$

G.A. Molander et al., Organometallics, 22 (2003) 3313-3315.

B)

$$C_nF_{2n+1}I \xrightarrow{\text{EtMgBr}} C_nF_{2n+1}MgBr \xrightarrow{0} C_nF_{2n+1}MgBr \xrightarrow{1} B(OCH_3)_3 = 2 KHF_2(aq), 40\% HF, 10 °C, overnight \\ -2 CH_3OH \xrightarrow{1} K[C_nF_{2n+1}BF_2(OCH_3)] \xrightarrow{40\% HF, r. t., 4 h} -CH_3OH \xrightarrow{1} K[C_nF_{2n+1}BF_3] = 10 °C, overnight \\ -CH_3OH \xrightarrow{1} CH_3OH \xrightarrow{1} CH$$

H.-J. Frohn et al., Z. Anorg. Allg. Chem, 627 (2001) 15-16.

C)

$$C_2F_5H \xrightarrow{n-BuLi} C_2F_5Li \xrightarrow{B(OCH_3)_3} Li[C_2F_5B(OCH_3)_3] \xrightarrow{48\% \text{ HF, } 20 \degree \text{C, } 16 \text{ h}} Li[C_2F_5BF_3] \xrightarrow{13 \text{ CH}_3OH} Li[C_2F_5BF_3]$$

A.A. Kolomeitsev et al., Tetrahedron Lett., 44 (2003) 8273-8277.

$$\begin{array}{c} \textbf{D} \\ C_{n}F_{2n+1}H & \xrightarrow{t-BuLi} \\ n = 3, 4, 6 \end{array} \xrightarrow{t-BuLi} C_{n}F_{2n+1}Li & \xrightarrow{B(OCH_{3})_{3}} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 3 \ h} & \text{Li}[C_{n}F_{2n+1}B(OCH_{3})_{3}] & \xrightarrow{KF} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 3 \ h} & \text{Li}[C_{n}F_{2n+1}B(OCH_{3})_{3}] & \xrightarrow{KF} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 3 \ h} & \text{Li}[C_{n}F_{2n+1}B(OCH_{3})_{3}] & \xrightarrow{KF} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 3 \ h} & \text{Li}[C_{n}F_{2n+1}B(OCH_{3})_{3}] & \xrightarrow{KF} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 3 \ h} & \text{Li}[C_{n}F_{2n+1}B(OCH_{3})_{3}] & \xrightarrow{KF} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 3 \ h} & \text{Li}[C_{n}F_{2n+1}B(OCH_{3})_{3}] & \xrightarrow{KF} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 3 \ h} & \text{Li}[C_{n}F_{2n+1}B(OCH_{3})_{3}] & \xrightarrow{KF} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 3 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 3 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C, \ 24 \ h} & \begin{array}{ther} \\ \underbrace{ther, -110}_{to \ 20 \ ^{\circ}C,$$

N.Yu. Adonin et al., Z. Anorg. Allg. Chem, 633 (2007) 647-652.

A.A. Kolomeitsev et al., Tetrahedron Lett., 44 (2003) 8273-8277.

$$(CH_3)_3SiC_3F_7 + B(OCH_3)_3 + KF \xrightarrow{r.t.}_{DME} K[C_3F_7B(OCR_3)_3] + C_3F_7H + K[B(OCH_3)_4] + (CH_3)_3SiF_{Yield: 24\%}$$

N.Yu. Adonin et al., Z. Anorg. Allg. Chem, 633 (2007) 647-652.

G)

$$(C_{2}F_{5})_{3}P \xrightarrow{n-BuLi, -60 \ ^{\circ}C} Li[BuP(C_{2}F_{5})_{3}] \xrightarrow{B(OCH_{3})_{3}} Li[C_{2}F_{5}B(OCH_{3})_{3}] \xrightarrow{1) \ 48\% \ HF, r.t, \ 10 \ h}{2) \ KHF_{2}, r.t, \ 10 \ h} \xrightarrow{K[C_{2}F_{5}BF_{3}]} KF[C_{2}F_{5}BF_{3}] \xrightarrow{F_{2}F_{2}F_{3}} KF[C_{2}F_{5}BF_{3}]$$

U. Welz-Biermann et al., WO 2003/087113, Merck Patent GmbH, Darmstadt, Germany.

H)

$$(C_{2}F_{5})_{3}P=O \xrightarrow{KF, B(OCH_{3})_{3}} F(C_{2}F_{5}B(OCH_{3})_{3}) \xrightarrow{aHF, r.t, 1 h} F(C_{2}F_{5}BF_{3}) \xrightarrow{K[C_{2}F_{5}BF_{3}]} F(C_{2}F_{5}BF_{3})$$

N. Ignatyev et al., WO 2003/087020, Merck Patent GmbH, Darmstadt, Germany.

Scheme 2. Syntheses of monoperfluoroalkyltrifluoroborates $M[C_nF_{2n+1}BF_3]$ (M = cation).

many compounds with CF₃-E bonds

(E = Si [27–30], Sn [30–35], Ge [33,36,37], Cd [38–40]), e.g. for $(CF_3)_3PF_2$ [41] and $(CF_3)_3P$ [42]). In contrast, the C_2F_5 -E analogues, for example with E = B [20,43], P [44] and group 14 elements [29,45–53], are thermally and chemically significantly more stable.

The first syntheses of perfluoroalkylfluoroborates with longer perfluoroalkyl chains $M[(C_nF_{2n+1})_xBF_{3\cdot x}]$ (M = cation; $n \ge 2$; x = 1–3)

have been developed in the earlier 2000's. Typical protocols for the preparation of monoperfluoroalkyltrifluoroborates are based on the addition of a perfluoroalkyl group to boron containing synthons (Scheme 2**B**–**H**) [43,54–58], followed by fluorination with metal bifluorides [54,57,59], aqueous HF [18,54,55,57], aHF [58,59], or other fluorinating reagents, for example BF₃ and perfluoroacylfluorides $R_FC(O)F$ [60], or $C_6F_5IF_2$ [61]. The perfluoroalkylalkoxyborates that



are formed as intermediates can either be isolated (Scheme 2C–E) or can be subsequently fluorinated to result in the corresponding perfluoroalkyltrifluoroborates $M[C_nF_{2n+1}BF_3]$ (M = cation; Scheme 2B, C, G, H). Perfluoroalkyl iodides [54], perfluoroalkyltrimethylsilanes [18,55,56], 1H-perfluoroalkanes [55,56], tris(perfluoroalkyl)phosphines (R_F)₃P [43,44,57,62], and tris(perfluoroalkyl)phosphine oxides (R_F)₃P = O [43,58] were used as source of perfluoroalkyl groups in the synthesis of perfluoroalkyltrialkoxyborates $M[(C_nF_{2n+1})B(OR)_3]$ (M = cation, R = alkyl group, n \geq 2; Scheme 2).

Potassium bifluoride KHF₂ is the reagent of choice for the conversion of alkyl-, aryl-, including pentafluorophenyl- and alkenyltrialkoxyborates as well as boronic acid derivatives R-B(OH)2 into the corresponding organotrifluoroborate anions $[R-BF_3]^-[12,14,15].$ However, the fluorination power of aqueous KHF₂ is not sufficient to convert perfluoroalkyl- and perfluoroalkenyltrialkoxyborates into perfluoroalkyl- and perfluoroalkenyltrifluoroborates. H.-J. Frohn et al. have noticed that fluorination of $Li[RCF = CFB(OCH_3)_3]$ with KHF₂ in aqueous methanol remains incomplete and results in a mixture of K $[RCF = CFBF_n(OCH_3)_{3-n}]$ [63]. The full replacement of all methoxy groups by fluorine requires subsequent treatment with aqueous HF (40%). Similarly, the conversion of K[C₃F₇BF₂(OCH₃)], which was obtained from MgBr[C3F7B(OCH3)3] and KHF2, into K[C3F7BF3] was achieved by treatment with hydrofluoric acid (40%). This synthesis can be carried out as a one-pot, two-step procedure [54]. Pentafluoroethyltrimethoxyborates $M[C_2F_5B(OCH_3)_3]$ (M = Li, MgBr) were converted into the corresponding potassium pentafluoroethyltrifluoroborates K[C₂F₅BF₃] with aqueous HF (48%) and KHF₂ [57] or by treatment of K[C₂F₅B(OCH₃)₃] with aHF [58]. Substitution of methoxy groups by fluorine in K[(C₂F₅)₂B(OCH₃)₂] requires even harsher conditions. Treatment of $K[(C_2F_5)_2B(OCH_3)_2]$ with hydrofluoric acid (52%) for 4 days at ambient temperature did not result in full conversion. Subsequent treatment with aHF at 20 °C for 24 h resulted in the formation of K[(C₂F₅)₂BF₂] in 57% yield [59].

The protocols described above are not convenient for practical applications in that they rely on the use of either aqueous or anhydrous HF, which is very toxic, corrosive, and requires special equipment because it cannot be handled in glassware. Herein we describe alternative procedures that avoid the use of anhydrous HF and that can be performed in usual laboratory glass equipment.

2. Results and discussion

In the fluorination process, the conversion of trimethoxyborates M $[R_FB(OCH_3)_3]$ into the corresponding trifluoroborates M $[R_FBF_3]$ by the action of KHF₂/HF(aq), hydrofluoric acid does not only serve as a source of fluoride but, more importantly, as Brønsted acid. Protonation of the oxygen atom of the methoxy groups [63] facilitates the substitution of OCH₃ by fluorine (Scheme 3).

However, hydrofluoric acid is a weak acid [64] with a p K_a of 3.45 at 25 °C [65]. It is less acidic than HCl (p $K_a = -2.20$) and HBr (p $K_a = -4.70$). Probably, the weak acidity of hydrofluoric acid is the reason for the incomplete substitution of the methoxy groups of K [(C₂F₅)₂B(OCH₃)₂] by fluorine in hydrofluoric acid (52%). Full exchange of OCH₃ by fluorine can only be achieved by the much stronger acid aHF [59]. It is worth to notice that the replacement of the first methoxy group by fluorine takes place with potassium bifluoride in

Scheme 3. Mechanism of the Brønsted acid activated replacement of a methoxy group at boron by a fluorine substituent.

hydrofluoric acid. However, the conversion of $[(C_2F_5)_2BF(OCH_3)]^$ into $[(C_2F_5)_2BF_2]^-$ and similarly of $[C_2F_5BF_2(OCH_3)]^-$ into $[C_2F_5BF_3]^-$ requires more acidic conditions [59,63].

The disadvantages in the preparation of perfluoroalkyltrifluoroborates via all literature known procedures have stimulated us to develop a more convenient protocol for the conversion of perfluoroalkyltrimethoxyborates into the corresponding perfluoroalkyltrifluoroborates. Surprisingly, we have found that aqueous HF can be replaced by common mineral acids, for instance by 37% HCl or other acids in combination with KHF₂ as fluoride source (Scheme 4) [66].

Even glacial acetic acid, which is a relatively weak acid, serves as a convenient reaction medium for the fluorination of $K[CF_3B(OCH_3)_3]$ and $K[C_2F_5B(OCH_3)_3]$ with KHF₂. The corresponding trifluoroborates K [CF₃BF₃] and K[C₂F₅BF₃] were obtained in good yields (Scheme 4). Application of trifluoroacetic acid as reaction medium results in the formation of a mixture potassium pentafluoroethyltrifluoroborate K [C₂F₅BF₃] and potassium trifluoroacetate CF₃C(O)OK, which is difficult to separate (see Experimental Section). However, the separation of K [C₂F₅BF₃] and CF₃C(O)OK was achieved by conversion of this mixture into the corresponding EMIM ionic liquids (EMIM = 1-ethyl-3-methylimidazolium) in water, i.e. into EMIM[C₂F₅BF₃] (hydrophobic IL) and EMIM[CF₃C(O)O] (hydrophilic IL) (Scheme 5).

The ionic liquid EMIM[HSO₄] doped with sulfuric acid enabled the combination of the fluorination with a metathesis process to get the ionic liquid EMIM[$C_2F_5BF_3$] in a one-step procedure (Scheme 6).

The room temperature ionic liquid tributylammonium trihydrogenfluoride $[Bu_3NH]H_3F_4$ and Olah reagent (~70% HF/~ 30% pyridine) are also suitable media for the conversion of K[C₂F₅B (OCH₃)₃] into K[C₂F₅BF₃] (Scheme 7A) or Li[C₂F₅B(OCH₃)₃] into PyH [C₂F₅BF₃] (Scheme 7B), which can be easily transformed into different other salts, e.g. EMIM[C₂F₅BF₃], at room temperature.

Furthermore, it is possible to synthesize monoperfluoroalkyltrifluoroborates in a one-pot procedure starting from perfluoroalkyl iodides and trimethoxyborane via an in situ generated Grignard reagent followed by fluorination in hydrochloric acid (37%) with KHF₂ (Scheme 8). As expected, the yield of perfluoroalkyltrifluoroborates diminished with increasing length of the perfluoroalkyl chain [67].

The potassium salts of monoperfluoroalkyltrifluoroborates are highly valuable starting compounds. They can be used for example for the preparation of ionic liquids such as $\text{EMIM}[C_2F_5BF_3]$ (Scheme 5). Furthermore, they are reagents for the synthesis of coordination compounds, which is demonstrated by the preparation of the copper(II) complex salt [Cu(bpy)_3][C_2F_5BF_3]_2. Upon dropwise addition of an aqueous solution of K[C_2F_5BF_3] into an aqueous solution of [Cu(bpy)_3][NO_3)_2, pale blue [Cu(bpy)_3][C_2F_5BF_3]_2 precipitates that was

| | KHF ₂ | KIR-BE-1 | + 3CH_OH |
|-----------------|---|--------------------|----------|
| K[KFD(OOH3)3] | acid | | 0013011 |
| R _F | Acid | Yield, % | 6: |
| CF ₃ | CH ₃ C(O)O | H 82 | |
| C_2F_5 | 37% HCI CH ₃ C(O)O HCI(q)/DM | 71 H 51 E 87 | |

Scheme 4. Conversion of perfluoroalkyltrimethoxy- into perfluoroalkyltrifluoroborates by the action of KHF_2 in acidic reaction media.

$$K[C_{2}F_{5}B(OCH_{3})_{3}] \xrightarrow{KHF_{2}/CF_{3}C(O)OH} K[C_{2}F_{5}BF_{3}] + CF_{3}C(O)OK$$

$$+ EMIM Ci - KCI$$

$$EMIM[C_{2}F_{5}BF_{3}] + EMIM[CF_{3}C(O)O]$$

$$Yield: 76\%$$

 $\label{eq:scheme 5. One-pot synthesis of the hydrophobic ionic liquid EMIM[C_2F_5BF_3] starting from potassium pentafluoroethyltrimethoxyborate K[C_2F_5B(OCH_3)_3].$

$$K[C_2F_5B(OCH_3)_3] \xrightarrow{KHF_2} EMIM[HSO_4]/H_2SO_4 EMIM[C_2F_5BF_3]$$

Yield: 70%

Scheme 6. One-pot synthesis of the hydrophobic ionic liquid $\rm EMIM[C_2F_5BF_3]$ in the acidic ionic liquid $\rm EMIM[HSO_4]$ doped with sulfuric acid.

characterized by elemental analysis, multinuclear NMR spectroscopy and single-crystal X-ray diffraction. In Fig. 1 one formula unit of [Cu (bpy)₃][C₂F₅BF₃]₂ is depicted. The bond parameters of the [C₂F₅BF₃]⁻ anion are close to the ones reported earlier for [2MOP][C₂F₅BF₃] (2MOP = 2-methyl-3-oxazolidine-1'-spiropyrrolidinium) [68]. The copper(II) center in the [Cu(bpy)₃]²⁺ cation that is located on a twofold axis shows a distorted octahedral coordination. The distortion is a consequence of the chelating 2,2'-bipyridine ligand that does not allow 90° angles for N1…Cu1…N1' and N2…Cu1…N1' and it is due to the Jahn-Teller distortion, which is evident from the strongly different Cu…N distances of 229.3(2) pm compared to 202.6(2) and 204.7(2) pm.

3. Experimental part

3.1. Materials and methods

Perfluoroalkyl iodides were purchased from chemicals suppliers: C_2F_5I from P&M (Moscow, Russia) and C_3F_7I and C_4F_9I from ABCR. B (OCH₃)₃ was obtained from Sigma-Aldrich and dried with sodium metal, distilled, and stored under argon. Olah reagent (~70% HF/~ 30% pyridine) was purchased from Sigma-Aldrich and used as received. [Bu₃NH]H₃F₄ was prepared from anhydrous HF (4 eq) and tributylamine (1 eq) at -78 °C.

The perfluoroalkyltrifluoroborates were characterized by NMR spectroscopy and the data are in agreement to those reported in the literature. The NMR spectra were recorded in acetone- d_6 on a Bruker Avance 200 spectrometer at ¹H: 199.9 MHz, ¹¹B: 64.1 MHz, and ¹⁹F: 188.1 MHz or on a Bruker DPX 400 spectrometer at ¹H: 400.1 MHz, ¹¹B: 128.4 MHz, and ¹⁹F: 376.5 MHz with deuterium lock. CFCl₃ and BF₃·Et₂O were used as external references for the ¹⁹F and ¹¹B NMR spectra, respectively. The signal of the residual proton of acetone- d_6 at 2.05 ppm was used as reference for the ¹H NMR spectra.

All reactions were carried out in standard glass equipment without visible etching of the glass surface after the reactions.

A)

$$K[C_2F_5B(OCH_3)_3] \xrightarrow{[Bu_3NH]H_3F_4}{- 3 CH_3OH} K[C_2F_5BF_3]$$

Yield: 46%

3.2. Synthesis of perfluoroalkyltrifluoroborates M[R_FBF₃]

3.2.1. Preparation of potassium trifluoromethyltrifluoroborate K[CF₃BF₃]

K[CF₃B(OCH₃)₃] (1.0 g, 4.7 mmol) was added to a solution of KHF₂ (2.4 g, 31 mmol) in glacial acetic acid (25 mL). The reaction mixture was stirred at 50 °C for one hour and then for 3 h at 80 °C. All volatiles were removed in fine vacuum. The residue was diluted with acetone and neutralized by the addition of potassium carbonate. The precipitate was filtered off. The filtrate was concentrated to a few milliliters and the addition of CH₂Cl₂ (20 mL) resulted in the formation of solid K [CF₃BF₃], which was filtered off and dried in vacuum. Yield: 82% (680 mg, 3.86 mmol). ¹¹B NMR (64 MHz, acetone-d₆): δ – 0.45 (m). ¹⁹F NMR (188 MHz, acetone-d₆): δ – 75.80 (q, ²J_{F,B} = 32.7 Hz, CF₃, 3F), – 155.63 (q, ¹J_{F,B} = 39.7 Hz, BF₃, 3F).

3.2.2. Preparation of potassium pentafluoroethyltrifluoroborate K $[C_{2}F_{5}BF_{3}]$

3.2.2.1. Method 1. K[C₂F₅B(OCH₃)₃] (587 mg, 2.24 mmol) and KHF₂ (900 mg, 11.5 mmol) were placed into a glass flask and dissolved in aqueous HCl (37%, 10 mL). The reaction mixture was stirred at room temperature for 3 h. All volatiles were removed in fine vacuum. The solid remainder was extracted with acetonitrile (15 mL) and filtered. After evaporation of the acetonitrile in vacuum the solid K[C₂F₅BF₃] was dried in vacuum. Yield: 71% (360 mg, 1.59 mmol). ¹¹B NMR (64 MHz, acetone-d₆): δ – 0.56 (m). ¹⁹F NMR (188 MHz, acetone-d₆): δ – 84.27 (q, ⁴J_{F,F} = 4.8 Hz, CF₃, 3F), –137.04 (q, ²J_{B,F} = 19.46 Hz, CF₂, 2F), –154.61 (qq, ¹J_{B,F} = 40.8 Hz, ⁴J_{F,F} = 4.9 Hz, BF₃, 3F).

3.2.2.2. Method 2. $K[C_2F_5B(OCH_3)_3]$ (3.30 g, 12.6 mmol) and KHF_2 (6.51 g, 83.3 mmol) were placed into a glass flask and suspended in glacial acetic acid (80 mL). The reaction mixture was stirred at 85 °C for 2.5 h. Additional KHF₂ (2.00 g, 25.6 mmol) was added and the reaction mixture was stirred for one additional hour at 85 °C. All volatiles were removed in vacuum, the residue was treated with potassium carbonate (11 g) and dissolved in acetone (75 mL). The precipitate was filtered off and washed with acetone (25 mL). The combined acetone solutions were concentrated to a few milliliters under reduced pressure. The addition of CH_2Cl_2 (50 mL) resulted in the precipitation of potassium pentafluoroethyltrifluoroborate, which was filtered off and dried in fine vacuum. Yield: 70% (2.00 g, 8.85 mmol).

3.2.2.3. Method 3. $K[C_2F_5B(OCH_3)_3]$ (8.80 g, 33.6 mmol) and KHF_2 (11.5 g, 147 mmol) were placed into a glass flask and dissolved in trifluoroacetic acid (65 mL). The reaction mixture was stirred at room temperature for 2 h. All volatiles were removed in vacuum, the residual solid was extracted with acetonitrile (20 mL), and the suspension was filtered. All volatiles were evaporated in vacuum and the residue was suspended in chloroform (60 mL). The precipitate that consists of a mixture of $K[C_2F_5BF_3]$ and $CF_3C(O)OK$ was filtered off. Yield: 23.5 g; $K[C_2F_5BF_3]:CF_3C(O)OK = ca.$ 1:6. This mixture can be separated by treatment with EMIM Cl in water (see part 3.2.5, Method 2).

3.2.2.4. Method 4. $K[C_2F_5B(OCH_3)_3]$ (200 mg, 0.76 mmol) and KHF_2 (1.00 g, 12.8 mmol) were placed into a glass flask and suspended in 1,2-

Scheme 7. Conversion of pentafluoroethyltrimethoxy- into pentafluoroethyltrifluoroborates by the reaction with the acidic room temperature ionic liquid $[Bu_3NH]H_3F_4$ (A), or with Olah reagent (B).

B) ~70% HF/~30% pyridine

$$\text{Li}[C_2F_5B(\text{OCH}_3)_3] \xrightarrow{\text{Olah reagent}} - 3 \text{ CH}_3\text{OH} \xrightarrow{\text{PyH}^+[C_2F_5BF_3]^-} \xrightarrow{\text{EMIM CI}} \text{EMIM}[C_2F_5BF_3]^- \xrightarrow{\text{EMIM CI}} \text{EMIM}[C_2F_5BF_3]^- \xrightarrow{\text{PyHCI}} \text{PyHCI} \xrightarrow{\text{PyHCI}} \xrightarrow{\text{PyHCI}} \text{PyHCI} \xrightarrow{\text{PyHCI}} \xrightarrow{\text{PyHCI}} \xrightarrow{\text{PyHCI}} \text{PyHCI} \xrightarrow{\text{PyHCI}} \xrightarrow{\text{PyHCI}}$$



Fig. 1. A formula unit of $[Cu(bpy)_3][C_2F_5BF_3]_2$ in the crystal (displacement ellipsoids are depicted at the 50% probability level and H atoms are omitted for clarity). Selected interatomic distances [pm] and angles [*] of the $[C_2F_5BF_3]^-$ anion: B1-C1 163.0(4), C1-C2 152.2(3), B1-F1 138.6(3), B1-F2 140.3(3), B1-F3 139.0(3), C1-F4 137.9(2), C1-F5 137.9(3), C2-F6 133.0(3), C2-F7 134.1(3), C2-F8 132.5(3), B1-C1-C2 118.6(2) and the $[Cu(bpy)_3]^{2+}$ cation: Cu1…N1 202.6(2), Cu1…N2 229.3(2), Cu1…N3 204.7(2), N1…Cu1…N3' 165.56(7), N2…Cu1…N2' 179.56(6), N1…Cu1…N1' 80.13(7), N2…Cu1…N3 76.02(6).

dimethoxyethane (20 mL). Gaseous HCl was passed through the reaction mixture at room temperature within 15 min. All volatiles were removed in vacuum and the residue was extracted with acetonitrile (25 mL) and filtered. After evaporation of the acetonitrile in vacuum, the $K[C_2F_5BF_3]$ was dried in fine vacuum. Yield: 87% (150 mg, 0.66 mmol).

3.2.2.5. Method 5. Magnesium turnings (600 mg, 24.7 mmol) and trimethoxyborane B(OCH₃)₃ (2.7 mL, 24.4 mmol) were placed into a glass flask and dry THF (40 mL) was added. Pentafluoroethyl iodide C_2F_5I (4.00 g, 16.3 mmol) was added to this mixture at -78 °C. The reaction mixture was warmed up to room temperature in an Ar atmosphere and was stirred for 12 h. The resulting suspension was evaporated in vacuum and the residue was treated with a solution of KHF_2 (27.0 g, 346 mmol) in aqueous HCl (37%, 100 mL) at 0 °C. The reaction mixture was warmed up to room temperature and all volatiles were removed in vacuum. The solid remainder was extracted with acetonitrile (150 mL), neutralized with potassium carbonate (16 g) and filtered. The filtrate was evaporated in vacuum and the solid residue was washed with dichloromethane. The colorless K[C₂F₅BF₃] was dried in vacuum. Yield: 71% (2.60 g, 11.5 mmol; calculated based on C₂F₅I). Additional K[C₂F₅BF₃] precipitated from the CH₂Cl₂ solution upon standing. Yield of the second crop: 15% (0.55 g, 2.43 mmol).

3.2.2.6. Method 6. Magnesium turnings (1.0 g, 42 mmol) and trimethoxyborane B(OCH₃)₃ (4.6 mL, 40.9 mmol) were placed into a glass flask and suspended in dry THF (35 mL). Pentafluoroethyl iodide C₂F₅I (6.69 g, 27.3 mmol) was added to this mixture at -78 °C. The reaction mixture was slowly warmed up to room temperature overnight in an Ar atmosphere. The resulting suspension was evaporated in vacuum and the residue was treated with KHF₂ (14.5 g, 186 mmol) in 1,2-dimetoxyethane (100 mL) and cooled to 0 °C. Gaseous HCl was passed through the reaction mixture for 10 min. Then an additional quantity of KHF₂ (2.0 g, 26 mmol) was added and gaseous HCl was

Magnesium turnings (260 mg, 10.7 mmol) and trimethoxyborane B (OCH₃)₃ (1.5 mL, 13.5 mmol) were placed into a glass flask and suspended in dry THF (20 mL). Heptafluoropropyl iodide C₃F₇I (1.0 mL, 2.0 g, 6.8 mmol) was added to this mixture at -78 °C in an Ar atmosphere. The reaction mixture was slowly warmed up to room temperature and was stirred overnight. The resulting suspension was evaporated in vacuum and the residue was treated with KHF₂ (4.0 g, 51 mmol) in aqueous HCl (25 mL, 37%). After 2 h, additional KHF₂ (0.85 g, 10.9 mmol) was added and the reaction mixture was stirred overnight. After neutralization with potassium carbonate the reaction mixture was extracted with acetonitrile (100 mL). Insoluble material was filtered off and the volume of the filtrate was reduced to a few milliliters by evaporation in vacuum. K[C₃F₇BF₃] was precipitated by addition of dichloromethane (100 mL), filtered off and dried in vacuum. Yield: 46% (850 mg, 3.08 mmol; calculated based on heptafluoropropyl iodide). ^{11}B NMR (64 MHz, acetone-d_6): δ -0.53 (m). ^{19}F NMR (188 MHz, acetone-d₆): δ -81.62 (tq, ${}^{5}J_{F,F}$ = 2.6 Hz, ${}^{4}J_{F,F}$ = 9.3 Hz, CF₃, 3F), -128.75 (q, ${}^{4}J_{F,F} = 5.2$ Hz, CF₂, 2F), -135.02 (m, CF₂, 2F), -154.00 (q, ${}^{1}J_{B,F} = 40.2$ Hz, BF₃, 3F).

3.2.4. Preparation of potassium nonafluorobutyltrifluoroborate K $[C_4F_9BF_3]$

Magnesium turnings (0.53 g, 21.7 mmol) and B(OCH₃)₃ (2.4 mL, 21.7 mmol) were placed into a glass flask and suspended in dry THF (50 mL). Nonafluorobutyl iodide C₄F₉I (2.5 mL, 5.0 g, 14.5 mmol) was added to this mixture at -78 °C under an inert atmosphere (Ar). The reaction mixture was slowly warmed up to room temperature and was stirred overnight. The resulting suspension was evaporated in vacuum and the residue was treated with KHF₂ (14.5 g, 186 mmol) in aqueous HCl (75 mL, 37%). The reaction mixture was stirred for 5 h and evaporated in vacuum. The residue was treated with K₂CO₃ (20 g) in acetone (100 mL) and stirred for 1-2 h. The suspension was filtered and the filtrate was evaporated at a rotary evaporator. The solid K[C₄F₉BF₃] was washed with CH₂Cl₂ and dried in vacuum. Yield: 43% (2.03 g, 6.23 mmol; calculated based on nonafluorobutyl iodide). ¹¹B NMR (64 MHz, acetone-d₆): $\delta - 0.68$ (m). ¹⁹F NMR (188 MHz, acetone-d₆): δ -82.02 (tt, ${}^{5}J_{F,F} = 3.85$ Hz, ${}^{4}J_{F,F} = 9.8$ Hz, CF₃, 3F), -125.01 (m, CF₂, 2F), -126.97 (m, CF₂, 2F), -134.39 (m, CF₂, 2F), -153.77 (q, ${}^{1}J_{B,F} = 40.6 \text{ Hz}, \text{ BF}_{3}, \text{ 3F}$).

3.2.5. One-pot synthesis of 1-ethyl-3-methylimidazolium pentafluoroethyltrifluoroborate $EMIM[C_2F_5BF_3]$

3.2.5.1. Method 1. $K[C_2F_5B(OCH_3)_3]$ (0.50 g, 1.90 mmol) and KHF_2 (0.75 g, 9.60 mmol) were placed into a glass flask and suspended in 1-ethyl-3-methylimidazolium hydrogensulfate EMIM[HSO₄] (3 mL). Concentrated H_2SO_4 (1 mL) was added to this suspension and the

reaction mixture was stirred for 48 h at room temperature. After that, the reaction mixture was extracted with CH₂Cl₂ (2 × 3 mL). The combined organic phases were evaporated and the ionic liquid EMIM[C₂F₅BF₃] obtained was dried in vacuum. Yield: 70% (402 mg, 1.34 mmol). ¹H NMR (200 MHz, acetone-d₆): δ 8.88 (dd, ⁴J_{H,H} \approx ⁴J_{H,H} \approx 1.7 Hz, CH, 1H), 7.70 (dd, ³J_{H,H} \approx ⁴J_{H,H} \approx 1.8 Hz, CH, 1H), 7.62 (dd, ³J_{H,H} \approx ⁴J_{H,H} \approx 1.7 Hz, CH, 1H), 4.42 (q, ³J_{H,H} = 7.36 Hz, CH₂, 2H), 4.00 (s, CH₃, 3H), 1.54 (t, J_{H,H} = 7.36 Hz, CH₃, 3H). ¹¹B NMR (64 MHz, acetone-d₆): δ -0.51 (m). ¹⁹F NMR (188 MHz, acetone-d₆): δ -84.22 (q, ⁴J_{F,F} = 4.8 Hz, CF₃, 3F), -137.04 (q, ²J_{B,F} = 19.46 Hz, CF₂, 2F), -153.66 (qq, ¹J_{B,F} = 40.8 Hz, ⁴J_{F,F} = 4.9 Hz, BF₃, 3F).

3.2.5.2. Method 2. Li[C₂F₅B(OCH₃)₃] (1.00 g, 4.35 mmol) and KHF₂ (700 mg, 8.96 mmol) were suspended in CF₃COOH (10 mL). The reaction mixture was stirred at room temperature for one hour and then all volatiles were removed under reduced pressure. The remainder was dried in fine vacuum and then dissolved in water (25 mL). EMIM Cl (700 mg, 4.77 mmol) was added and the mixture was extracted with CH₂Cl₂ (2 × 25 mL). The combined organic layers were washed with water (2 × 2.5 mL). All volatiles were removed under reduced pressure. The obtained ionic liquid EMIM[C₂F₅BF₃] was dried in fine vacuum. Yield: 76% (0.99 g, 3.32 mmol).

3.2.6. Fluorination with $[Bu_3NH]H_3F_4$

 $\rm K[C_2F_5B(OCH_3)_3]$ (1.0 g, 3.8 mmol) and $\rm [Bu_3NH]H_3F_4$ (30.6 g, 115 mmol) were mixed at -78 °C. The suspension was warmed up to room temperature and was stirred for 12 h. Then, water (10 mL) was added and the mixture was extracted with chloroform (3 \times 10 mL). The combined organic phases were treated with water (10 mL) and the pH of the aqueous layer was adjusted to approximately pH 8–9 by addition of K₂CO₃. The aqueous phase was separated and washed with CH₂Cl₂ (10 mL). The water was distilled off at a rotary evaporator and the solid residue was extracted with K₂CO₃ (5 g), filtered, and evaporated to dryness to yield solid K[C₂F₅BF₃] that was dried in fine vacuum. Yield: 46% (401 mg, 1.77 mmol). The NMR spectroscopic data are consistent with those described above.

3.2.7. Synthesis of 1-ethyl-3-methylimidazolium

pentafluoroethyltrifluoroborate $EMIM[C_2F_5BF_3]$ using Olah reagent

Li[C₂F₅B(OCH₃)₃] (1.0 g, 4.4 mmol) was suspended in CH₂Cl₂ (15 mL) and Olah reagent (~70% HF/ ~ 30% pyridine, 4.0 mL) was added dropwise at room temperature via a plastic syringe (exothermic reaction). The reaction mixture was stirred for 1 hour at room temperature and diluted with water (15 mL). 1-Ethyl-3-methylimidazolium chloride EMIM Cl (750 mg, 5.12 mmol) was added and the reaction mixture was stirred for 10 min. The organic phase was separated and washed with water (2 × 3 mL). All volatiles of the organic phase were removed under reduced pressure. The obtained liquid EMIM[C₂F₅BF₃] (ionic liquid) was dried in fine vacuum. Yield: 84% (1.1 g, 3.7 mmol).

3.2.8. Synthesis of tris(2,2'-bipyridine)copper(II)

pentafluoroethyltrifluoroborate [*Cu*(*bpy*)₃][*C*₂*F*₅*BF*₃]₂ 2,2'-Bipyridine (469 mg, 3.00 mmol) and CuNO₃'3H₂O (121 mg, 1.00 mmol) were dissolved in water (30 mL) and stirred at room temperature for one hour. A solution of K[C₂F₅BF₃] (497 mg, 2.20 mmol) in water (5 mL) was added dropwise, which resulted in the precipitation of a pale blue solid. The solid was filtered off and washed with water (2 × 20 mL) and Et₂O (2 x 20 mL). The solid residue was dried in fine vacuum. [Cu(bpy)₃][C₂F₅BF₃]₂ was obtained as a pale blue powder. Yield: 88% (792 mg, 0.88 mmol). ¹H NMR (400 MHz, CD₃CN): δ 12.1 (s vbr, 24H). ¹¹B NMR (128 MHz, CD₃CN): δ -0.7 (qt, ¹*J*_{B,F} = 40.3 Hz, ²*J*_{B,F} = 20.3 Hz, 2B). ¹⁹F NMR (377 MHz, CD₃CN): δ -84.4 (q br, CF₃, 6F), -137.2 (q, ²*J*_{B,F} = 19.5 Hz, CF₂, 4F), -154.3 (q, ¹*J*_{B,F} = 40.7 Hz, BF₃, 6F). Elem. anal. calcd. for C₃₄H₂₄B₂CuF₁₆N₆: C, 45.09; H, 2.67; N, 9.28. Found: C, 45.28; H, 2.64; N, 9.28. Crystals of $[Cu(bpy)_3]$ $[C_2F_5BF_3]_2$ suitable for a X-ray diffraction study were obtained from acetonitrile by slow evaporation of the solvent.

3.3. X-ray diffraction analysis of $[Cu(bpy)_3][C_2F_5BF_3]_2$

A single crystal of [Cu(bpy)₃][C₂F₅BF₃]₂ suitable for X-ray diffraction was investigated on a Bruker X8-Apex II diffractometer with a CCD area detector and a multi-layer mirror using Mo- K_{α} radiation $(\lambda = 0.71073 \text{ Å})$ at 100 K. The complex copper(II) salt crystallizes in the monoclinic space group I2/a (no. 15) with Z = 4 and unit cell parameters of a = 17.783(3), b = 10.984(2), c = 18.747(4)Å, $\hat{\beta} = 102.822(4)^{\circ}$, and V = 3570.3(11) Å³; $\rho_{calcd.} = 1.658$ Mg m⁻³, μ (Mo- K_{α}) = 0.733 mm⁻¹, F(000) = 1812. A total of 15883 reflections were collected (2.16 $\,<\,\theta_{\rm max}\,_<$ 26.11°). The structure was solved by intrinsic phasing methods [69,70], and refinements are based on fullmatrix least-squares calculations on F^2 with 3540 independent reflections [2940 independent reflections with $I > 2\sigma(I)$] and 367 variables [69,71]. The positions of all H atoms were located from ΔF synthesis. For CH idealized bond lengths and angles were used. The isotropic displacement parameters of the aromatic H atoms were kept equal to 120% of the equivalent isotropic displacement parameters of the respective parent C atom. All non-hydrogen atoms were refined anisotropically. The final refinement resulted in $R_1[F_0^2 > 2\sigma(F_0^2)] = 0.033$, $wR_2 = 0.082$ (all data), $w = 1/[\sigma^2(F_0^2) + (0.0316P) + 4.0609P]$, $\Delta \rho_{\text{max}} / \Delta \rho_{\text{min}} = + 0.363$ and -0.402 e Å⁻³.

All calculations were performed with the ShelXle graphical interface [72]. Molecular structure diagrams were drawn with the program Diamond 4.4.1 [73]. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1585537. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

3.4. Summary

Perfluoroalkyltrifluoroborates were prepared in good yields by the reaction of perfluoroalkyltrimethoxyborates with potassium bifluoride in acidic media, i.e. in 37% HCl(aq), acetic and trifluoroacetic acid or in acidic ionic liquids. These new and low-cost syntheses enable the preparation of perfluoroalkyltrifluoroborates in standard glassware avoiding the use of toxic and corrosive hydrofluoric acid and aHF.

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