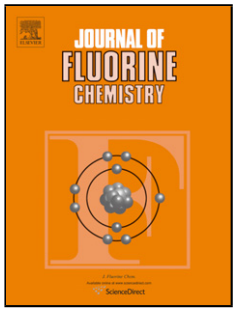

Title: Synthesis of potassium 4-(1-azol-1-yl)**-2,3,5,6-tetrafluorophenyltrifluoroborates from K[$C_6F_5BF_3$] and alkali metal azol-1-ides. The dramatic distinction in nucleophilicity of alkali metal azol-1-ides and dialkylamides**

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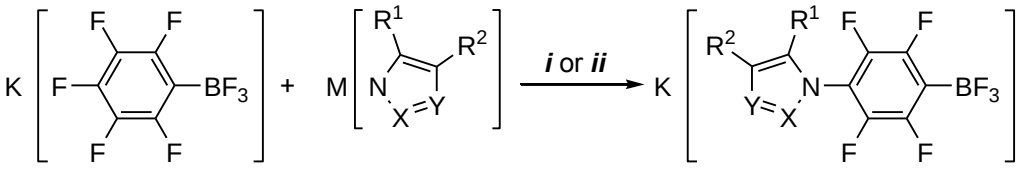
PII: S0022-1139(13)00266-2
DOI: http://dx.doi.org/doi:10.1016/j.jfluchem.2013.07.011
Reference: FLUOR 8160

To appear in: *FLUOR*

Received date: 27-5-2013
Revised date: 9-7-2013
Accepted date: 15-7-2013

Please cite this article as: A.Yu. Shabalin, N.Yu. Adonin, V.V. Bardin, O.P. Taran, A.B. Ayusheev, V.N. Parmon, Synthesis of potassium 4-(1-azol-1-yl)**-2,3,5,6-tetrafluorophenyltrifluoroborates from K[$C_6F_5BF_3$] and alkali metal azol-1-ides. The dramatic distinction in nucleophilicity of alkali metal azol-1-ides and dialkylamides,** *Journal of Fluorine Chemistry* **(2013), http://dx.doi.org/10.1016/j.jfluchem.2013.07.011**



M = Na, K; X, Y = CH, N; R^1, R^2 = H,

Conditions: ***i:*** (M = K) DMF, 80 °C.
ii: (M = Na) 1. Dipolar aprotic solvent, 80-130 °C; 2. KHF_2, 25 °C

Nucleophilic substitution of fluorine atom in $K[C_6F_5BF_3]$ with alkali metal azol-1-ides in polar aprotic solvent (DMF, DMSO) at 60–130 °C gives potassium 4-azolino-2,3,5,6-tetrafluorophenyltrifluoroborates, $K[4\text{-}AzC_6F_4BF_3]$ (AzH = pyrrol, pyrazol, imidazol, indol, and benzimidazol).

Diethylamine and morpholine as well as the corresponding sodium amides do not react with $K[C_6F_5BF_3]$ under the same conditions while at 150 °C pentafluorobenzene and $R_2NC_6F_4H$ forms.

In any cases the N-nucleophiles attack a carbon atom in the *para*-position to BF_3 group of $K[C_6F_5BF_3]$.

Synthesis of potassium 4-(1-azol-1-yl)-2,3,5,6-tetrafluorophenyltrifluoroborates from $K[C_6F_5BF_3]$ and alkali metal azol-1-ides. The dramatic distinction in nucleophilicity of alkali metal azol-1-ides and dialkylamides

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Abstract. Nucleophilic substitution of fluorine atom in $K[C_6F_5BF_3]$ with alkali metal azol-1-ides in polar aprotic solvent (DMF, DMSO) at 60–130 °C gives potassium 4-(azol-1-yl)-2,3,5,6-tetrafluorophenyltrifluoroborates, $K[4\text{-}AzC_6F_4BF_3]$ (AzH = pyrrole, pyrazole, imidazole, indole, and benzimidazole). Unexpectedly, diethylamine and morpholine do not react with $K[C_6F_5BF_3]$ under the same conditions while pentafluorobenzene and $R_2NC_6F_4H$ form at 150 °C. Reaction of $K[C_6F_5BF_3]$ with $Na[NR_2]$ in diglyme or DMSO proceeds similar way. The assumed reason is the relatively low nucleophilicity of both secondary amines and alkali metal dialkylamides which results in destructive by-reaction with $K[C_6F_5BF_3]$ rather than in its aminodefluorination. This is confirmed by the competitive nucleophilic aminodefluorination of a model substrate, C_6F_5Ph, with sodium indolide/sodium morpholinide.

Keywords. Pentafluorophenyltrifluoroborate, N-Nucleophile, Nucleophilic substitution, NMR spectroscopy

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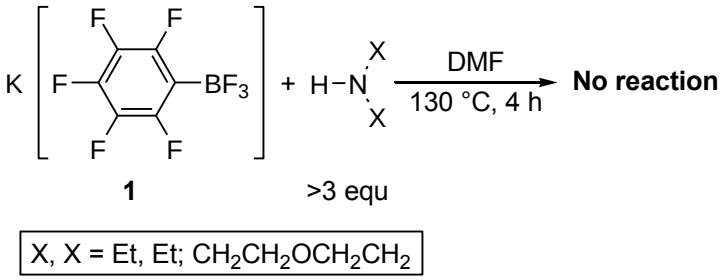
1. Introduction

Nucleophilic aminodefluorination of pentafluorobenzenes C_6F_5X with dialkylamine (excess) or dialkylamine in the presence of a base is the well-studied routine preparation of fluoro-containing dialkylaminobenzenes. Constitution of products is determined by many factors although the main of ones are the nature of substituent X and N-nucleophile [1-3]. When X is an organoelement substituent, it can behave as an alternative reactive centre. For instance, C_6F_5X (X = $SiMe_3$, $GeEt_3$) reacts with lithium piperidin-1-ide (THF, –20 °C) giving 4-$XC_6F_4NC_5H_{10}$ whereas the reaction with piperidine (2 equivalents) (THF, 20 °C) leads to 4-$XC_6F_4NC_5H_{10}$ and C_6F_5H (25:75) [4-6]. The formation of $(4\text{-}H_2NNHC_6F_4)_2Hg$ from bis(pentafluorophenyl)mercury and NH_2NH_2 is accompanied by partial hydrodemercuration, too [7]. The high electrophilicity of the silicon atom in $C_6F_5SiMe_2Y$ (Y = Cl, Br) [8-10] or $C_6F_5SiF_3$ [11] results in $C_6F_5SiMe_2NAlk_2$ (Alk = Me, Et) and $C_6F_5SiF_2NC_5H_{10}$, respectively, under the action of N-nucleophiles rather than substitution of aromatically bonded fluorine atom. Pentafluorophenylboranes $C_6F_5BX_2$ (X = F, Cl, C_6F_5) form adducts $C_6F_5BX_2$·N-base with amines and azoles (for more detail see reviews [12, 13]).

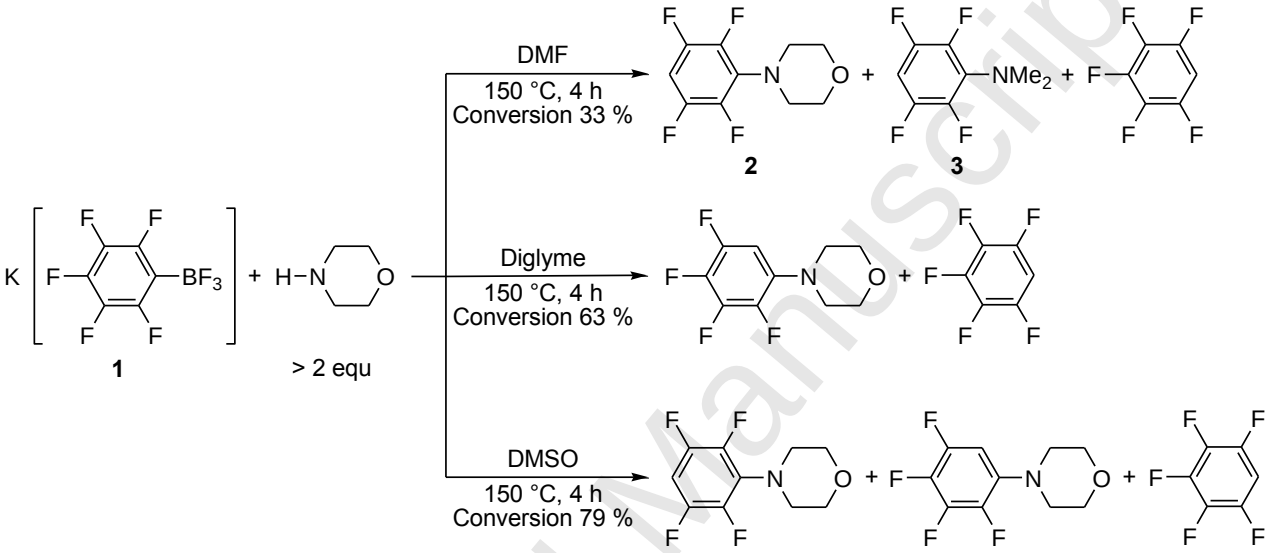
Recently we have reported the preparation of K[4-$ROC_6F_4BF_3$] (R = Me, Et, Pr, *i*-Pr, Bu, *t*-Bu, $PhCH_2$, $CH_2{=}CHCH_2$, Ph) by alkoxydefluorination of K[$C_6F_5BF_3$] with the corresponding O-nucleophiles MOR (M = Na, K) in polar aprotic solvents [14]. To continue the exploration of synthetic routes to polyfluoroorganyltrifluoroborates *via* modification of the organic moiety, we studied aminodefluorination of easily available salt K[$C_6F_5BF_3$] [15] with N-nucleophiles derived from either secondary amines and azoles [16].

2. Results

Potassium pentafluorophenyltrifluoroborate (**1**) does not react with diethylamine or morpholine (>3 equivalents) in DMF at 130 °C over a period of 4 h (Scheme 1). Heating with morpholine at 150 °C for 4 h caused the incomplete consumption (33%) of **1** and formation of 4-(2,3,5,6-tetrafluorophenyl)morpholine (**2**), N,N-dimethyl-2,3,5,6-tetrafluoroaniline (**3**) and C_6F_5H instead of K[$R_2NC_6F_4BF_3$]. A higher conversion of K[$C_6F_5BF_3$] was achieved in diglyme or DMSO, but potassium 4-(morpholin-1-yl)-2,3,5,6-tetrafluorophenyltrifluoroborate was not found again (according to ^{19}F NMR data) (Scheme 2).

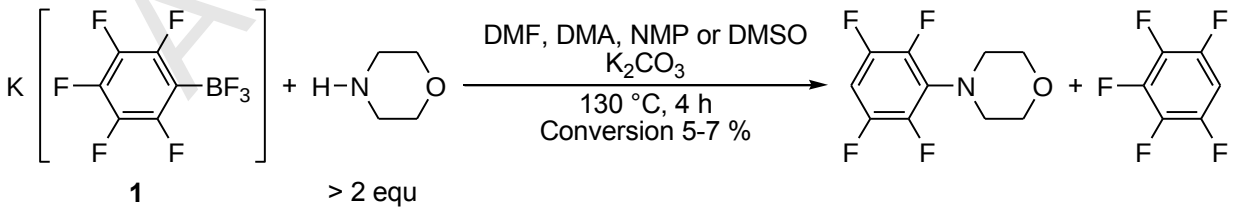


Scheme 1. Interaction of **1** with morpholine and diethylamine

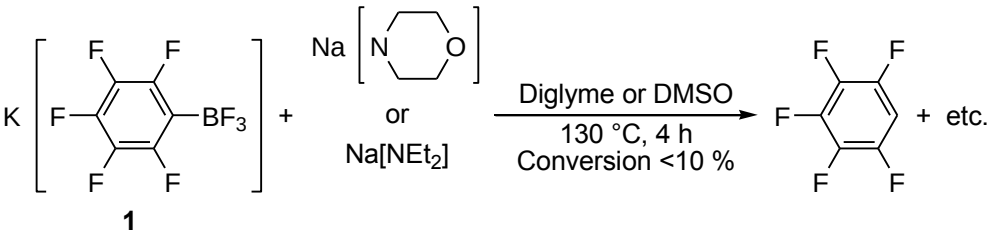


Scheme 2. Interaction of **1** with morpholine in different solvents

Attempted aminodefluorination of $K[C_6F_5BF_3]$ in the presence of other bases was unsuccessful, too. Stirring **1** with morpholine and K_2CO_3 in DMF as well in DMA, NMP or DMSO at 130 °C for 4 h results in C–B bond cleavage at a low conversion of starting salt **1** (Scheme 3). Moreover, the similar results were obtained using both sodium morpholinide and sodium diethylamide (Scheme 4).

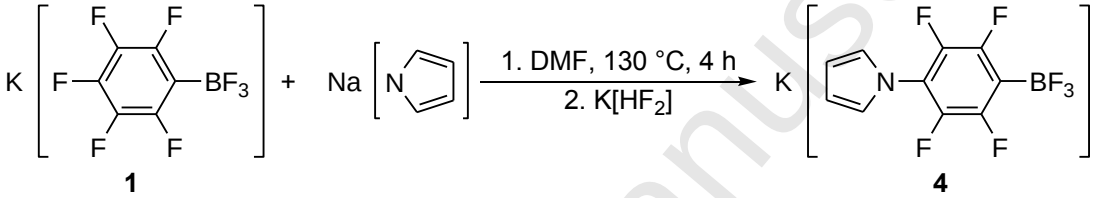


Scheme 3. Interaction of **1** with morpholine in different solvents



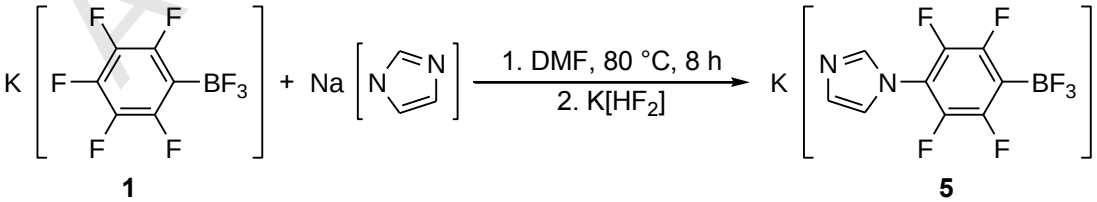
Scheme 4. Interaction of **1** with sodium morpholinide or sodium diethylamide

In contrast, heating of $K[C_6F_5BF_3]$ with sodium pyrrol-1-ide (1.4 equivalent) at 130 °C in DMF followed by treatment with $K[HF_2]$ gives potassium 4-(pyrrol-1-yl)-2,3,5,6-tetrafluorophenyltrifluoroborate (**4**) in 86% yield (Scheme 5).

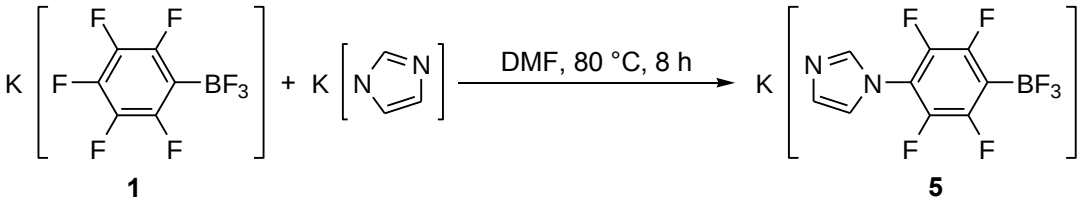


Scheme 5. Interaction of **1** with sodium pyrrol-1-ide

Treatment of $K[C_6F_5BF_3]$ with sodium imidazol-1-ide (generated *in situ* from imidazole and NaH) in DMF at 80 °C for 8 h gives potassium 4-(imidazol-1-yl)-2,3,5,6-tetrafluorophenyl-trifluoroborate (**5**) and admixture of potassium 3,4-bis(imidazol-1-yl)trifluorophenyltrifluoroborate (**6**) (after work up with $K[HF_2]$) (Scheme 6). Using individually prepared potassium imidazol-1-ide instead of sodium salt in DMF, NMP or DMSO has no noticeable effect (93% yield of **5**) (Scheme 7). Aminodefluorination in DMF at 60 °C over a period of 4 h allowed to avoid the formation of **6** but reduced conversion of **1** from 93 to 60%. In methanol, acetonitrile and DME conversion of **1** was 60, 23 and 0%, respectively (60 °C, 4 h).



Scheme 6. Interaction of **1** with sodium imidazol-1-ide



1 **5**

Scheme 7. Interaction of **1** with potassium imidazol-1-ide

Potassium 4-(pyrazol-1-yl)-2,3,5,6-tetrafluorophenyltrifluoroborate (**7**) was prepared from **1** and K[$C_6F_5BF_3$] at 80 °C in 64% yield. Like **5**, product contained small admixture of potassium 3,4-bis(pyrazol-1-yl)-2,5,6-trifluorophenyltrifluoroborate (**8**) (Scheme 8).

1 **7**

Scheme 8. Preparation of potassium 4-(pyrazol-1-yl)-2,3,5,6-tetrafluorophenyltrifluoroborate (**7**)

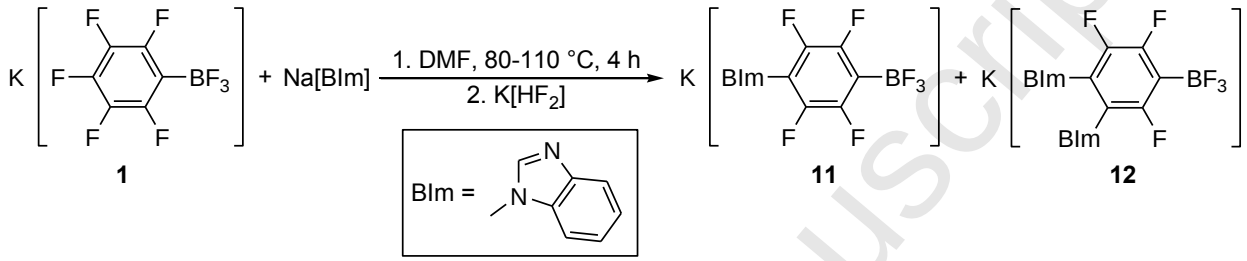
Substitution of fluorine atom in **1** with more spatially hindered N-nucleophiles, such as sodium indol-1-ide and sodium benzimidazol-1-ide, proceeds like substitution with alkali metal azolides but complicated by subsequent reaction with the second equivalent of the nucleophilic reagent. Thus, heating of K[$C_6F_5BF_3$] with sodium indol-1-ide in DMF at 130 °C forms 4-(indol-1-yl)-2,3,5,6-tetrafluorophenyltrifluoroborate (**9**) contaminated with residual borate **1** and 3,4-bis(indol-1-yl)-2,5,6-trifluorophenyltrifluoroborate (**10**) (ratio **9**:**1**:**10** = 88:6:6) (^{19}F NMR). After cation metathesis with excess K[HF_2], borate **9** was isolated at 74% yield (Scheme 9). Decreasing temperature from 130 to 100 °C and usage of stoichiometric ratio K[$C_6F_5BF_3$]: N-nucleophile results in the absence of **10**, but conversion of **1** diminishes, too.

1 **9**

Scheme 9. Interaction of **1** with sodium indol-1-ide

Reaction of K[$C_6F_5BF_3$] with sodium benzimidazol-1-ide (1.4 equivalent) in DMF at 130 °C for 4 h gives 4-(benzimidazol-1-yl)-2,3,5,6-tetrafluorophenyltrifluoroborate (**11**), 3,4-

bis(benzimidazol-1-yl)-2,5,6-trifluorophenyltrifluoroborate (**12**) and by-products (C_6F_5H and 1-(2,3,5,6-tetrafluorophenyl)benzimidazole (**13**)) (Table 1, run 1). These by-products disappeared when the reaction was performed at 100 and 80 °C but, instead, unreacted borate **1** remained (Table 1, runs 2, 3) in a significant quantity. Lengthening the reaction period from 4 to 8 h does not affect on the composition of products (Table 1, run 4). Practically total conversion of **1** was achieved at 100 °C using 2.8-fold excess of nucleophile, although this lead to the further aminodefluorination of **11** (Table 1, run 5) (Scheme 10).



Scheme 10. Interaction of **1** with sodium benzimidazol-1-ide

<Here is place for Table 1>

3. Discussion

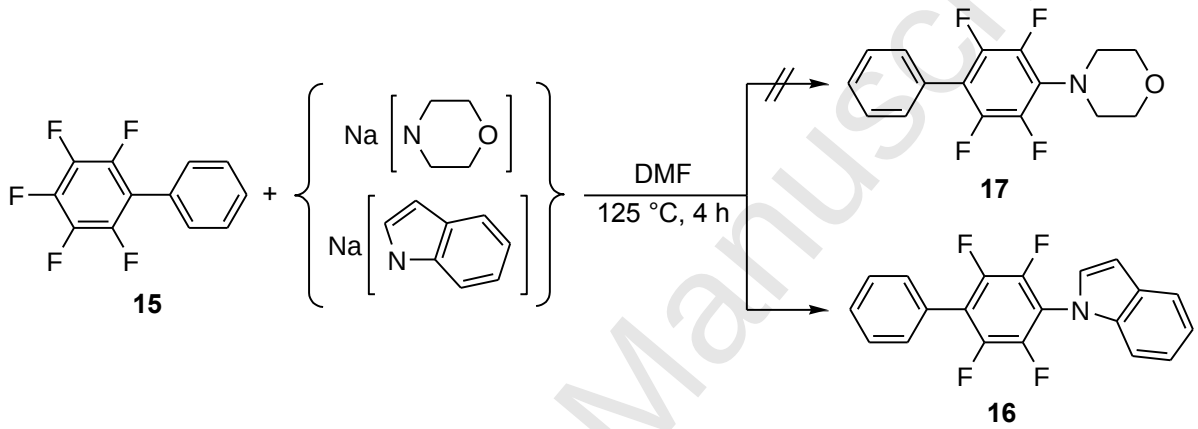
The obtained results show that aminodefluorination of $K[C_6F_5BF_3]$ with alkali metal azolides MAz in polar solvents occurs at 60–130 °C and leads to substitution of a fluorine atom at *para*-position to BF_3 group. The other isomers $K[AzC_6F_4BF_3]$ are not detected. When Az is pyrrol-1-yl, the subsequent replacement of fluorine atom in $K[4\text{-}AzC_6F_4BF_3]$ does not occur or negligible. This process becomes noticeable with other nucleophiles: pyrazol-1-ide, imidazol-1-ide, indol-1-ide, and in peculiar, benzimidazol-1-ide. Although these minor by-products were not isolated, the constitution of them in a mixture with the precursor, $K[4\text{-}AzC_6F_4BF_3]$ was deduced from ^{19}F NMR spectra. Thus, the reaction mixture derived from $K[C_6F_5BF_3]$ and sodium imidazol-1-ide produces resonances at –116.7, –125.9, –152.2 and –133.9 ppm in ratio 1:1:1:3 which were assigned to fluorine atoms F^2, F^6, F^5, and BF_3 of $K[3,4\text{-}Im_2C_6F_3BF_3]$ (Im = imidazol-1-yl), respectively. An incremental calculation of chemical shifts based on ^{19}F NMR spectra of $K[C_6F_5BF_3]$ [15] and 1-(pentafluorophenyl)imidazole C_6F_5Im [17] gives magnitudes $\delta(F)$ = –115 (F^2), –121 (F^6), and –146 (F^5) ppm, respectively, these are in agreement with experimentally observed ones. For comparison, the experimental/predicted chemical shifts of $K[4\text{-}ImC_6F_4BF_3]$ are –132.2/–131 ($F^{2,6}$) and –152.5/–149 ($F^{3,5}$) ppm. The predicted chemical shifts of fluorine atoms bonded to aryl moiety in alternative izomers are –121 (F^6), –142 (F^4), and –153 (F^5) ppm ($K[2,3\text{-}Im_2C_6F_3BF_3]$), –128 ($F^6$), –133 ($F^3$), and –139 ($F^5$) ppm ($K[2,4\text{-}Im_2C_6F_3BF_3]$), and –115 ($F^6$), –142 ($F^4$) and –146 ($F^3$) ppm

(K[2,5-$Im_2C_6F_3BF_3$]). This allows the presence of these borates to be rejected. The predicted ^{19}F NMR spectra of symmetric borates K[2,6-$Im_2C_6F_3BF_3$] and K[3,5-$Im_2C_6F_3BF_3$] consist of two groups of resonances in 2:1 ratio besides signal of BF_3 group which also were not found. The closely related picture is obtained for borate K[3,4-$Az_2C_6F_3BF_3$] (Az = pyrazin-1-yl) using spectrum of 1-(pentafluorophenyl)pyrazole [18].

Predicted chemical shifts for K[3,4-$Az_2C_6F_3BF_3$] (Az = indol-1-yl **10** and benzimidazol-1-yl **12**) are –115 (F^2), –127 (F^6), and –149 (F^5) ppm (from ^{19}F NMR spectra of K[$C_6F_5BF_3$] and 1-(pentafluorophenyl)indole (**14**)). However, despite similarity with ^{19}F NMR spectra of **6** and **8**, the spectra of borates **10** and **12** have remarkable peculiarity. Spectrum of **10** contains signals at –114.1, –114.4, –126.6, –149.6, –149.7 (1:1:2:1:1) and –135.0 (BF_3) ppm. Spectrum of **12** is characterized by signals at –114.6, –114.9, –124.3, –148.8, –149.5 (1:1:2:1:1) and –135.1 (BF_3) ppm. Resonances at ca. –114 ppm have identical fine structure (multiplet) as well as resonances at ca. –149 ppm (doublet of doublet). We assume that these groups of signals belong to two stereomers with different mutual arrangement of bulky neighbouring substituents Az. In one of them both phenyl moieties locate at one side of planar polyfluorinated aryl ring ("cis" arrangement). In the other stereomer phenyl moieties locate at opposite sides ("trans" arrangement).

In contrast to alkali metal azolides, secondary amines and their sodium salts do not react with K[$C_6F_5BF_3$] up to 130 °C whereas at higher temperature hydrodeboration of **1** produces C_6F_5H and by-products derived from it. Generally, nucleophilicity of secondary amines R_2NH is higher of the nucleophilicity of azoles AzH and alkali metal amides, MNR_2 and MAz, are more reactive than their parent amines [18-22]. To our knowledge, the relative reactivity of alkali metal dialkylamide and alkali metal azolides are not compared up to date, and reported results on nucleophilic aminodefluorination of polyfluoroarenes cannot be interpreted unambiguously without kinetic measurements. For instance, the reaction of C_6F_5I with morpholine or with 2-methylimidazole in DMSO in the presence of KOH (2.5 equivalent) (120 °C, 24 h) gives 4-(2,3,5,6-tetrafluorophenyl)morpholine (90%) and 1-(2,3,5,6-tetrafluorophenyl)-2-methylimidazole (85%), respectively [23] (the reductive hydrodeiodination and hydrodebromination of polyhalogenobenzenes in polar aprotic solvents is the result of the halogenophilic attack, see review [24]). Aminodefluorination of C_6F_6 with NaAz (AzH = pyrazole [22], pyrrole [25]) (DMF, rt, 2–10 h) and with $LiNR_2$ (R_2NH = Me_2NH, pyrrolidine, piperidine) (THF, rt, 24 h) [21] occurs similar way. Qualitatively, the closely related reactivity of both sorts of N-nucleophiles, MNR_2 and MAz, can be outlined from these experiments. To get more accurate data on the relative nucleophilicity of sodium azolide *vs* sodium dialkylamide, we explored the competitive nucleophilic aminodefluorination of 2,3,4,5,6-pentafluorobiphenyl (**15**) (model substrate) with

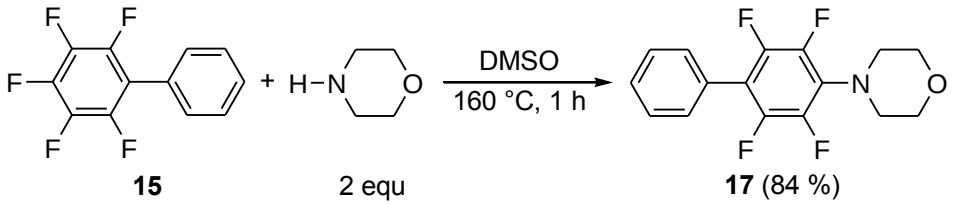
sodium indolide / sodium morpholinide. In the first experiment, indole and morpholine (1:1) were treated with NaH (1.5 equivalent) and the formed salts were introduced in the reaction with **15** in DMF at 130 °C for 4 h. The ^{19}F NMR spectrum of solution showed 1-(2,3,5,6-tetrafluoro-4-phenylphenyl)indole (**16**), the absence of **15** and 4-(2,3,5,6-tetrafluoro-4-phenylphenyl)morpholine (**17**). After work up, **16** was isolated at 88% yield. When biphenyl **15** (2 equivalents) reacts with N-nucleophiles prepared from morpholine (1 equivalent), indole (1 equivalent) and NaH (3 equivalents), only substituted indole **16** is formed again whereas the corresponding morpholine derivative is not produced (^{19}F NMR) (Scheme 11).



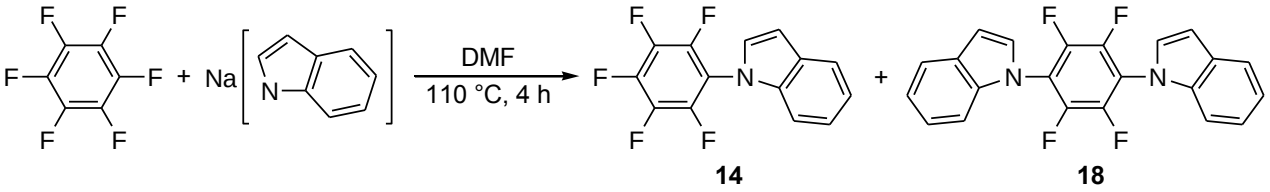
Scheme 11. Reaction of biphenyl **15** with a mixture of sodium morpholinide and sodium indolide

These results demonstrate a lower nucleophilicity of sodium morpholinide towards **15** with respect to the nucleophilicity of sodium indolide. So that, the conversion of **1** into K[4-Az$C_6F_4BF_3$] by the action of MAz and the failure of the related substitution with R_2NH and $NaNR_2$ can be explained by kinetic reasons: the rate of substitution by MNR_2 (M = H, Na) is too slow at ≤130 °C whereas at higher temperature by-reactions (hydrodeboration etc) proceed rather than substitution of aromatically bonded fluorine atom.

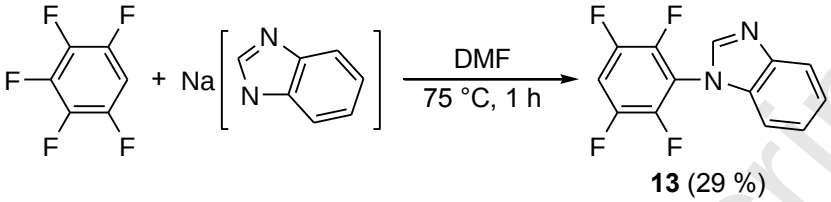
For reliable identification of some unknown polyfluoroarenes or those described without ^{1}H and ^{19}F NMR spectra, we prepared the required substances in compliance with Schemes 12-14.



Scheme 12. Preparation of biphenyl **17**



Scheme 13. Preparation of 1-(pentafluorophenyl)indole (**14**)



Scheme 14. Preparation of **13**

4. Conclusions

Aminodefluorination of $K[C_6F_5BF_3]$ with alkali metal azolides, AzM, in polar solvents at 60–130 °C gives borates $K[4\text{-}AzC_6F_4BF_3]$ at a high yield along with admixture of $K[3,4\text{-}Az_2C_6F_3BF_3]$. Isomers $K[2\text{-}AzC_6F_4BF_3]$ and $K[3\text{-}AzC_6F_4BF_3]$ are not found. Potassium 4-diethylamino-2,3,5,6-tetrafluorophenyltrifluoroborates and potassium 4-morpholino-2,3,5,6-tetrafluorophenyltrifluoroborate are not obtained this way because of the low substitution rate and competitive by-reactions. The lower nucleophilicity of R_2NNa vs AzNa was confirmed by the competitive reaction with C_6F_5Ph.

4. Experimental

4.1. General considerations

The NMR spectra were recorded using a Bruker AVANCE 300 spectrometer (^1H at 300.13 MHz, ^{19}F at 282.40 MHz, and ^{11}B at 96.29 MHz). The chemical shifts are referenced to TMS (^1H), CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)), and $BF_3{\cdot}OEt_2/CDCl_3$ (15% v/v) (^{11}B), respectively. IR spectra were measured on a Shimadzu FTIR-8300, Varian 640-IR and Tensor 27 spectrometers. GC-MS analysis was done using a Hewlett-Packard 1800A (with HP-5MS column) instrument. High resolution mass spectra were recorded using a Thermo Scientific DFS spectrometer in EI mode (70 eV). These analyses as well as elemental analysis were performed in the Collective Service Center of SB RAS (Novosibirsk).

DMF was distilled over P_4O_{10} at reduced pressure. Diglyme (Acros), 1,2-dimethoxyethane (Acros), N-methylpyrrolidone (Acros), dimethylacetamide (Acros), and dimethyl sulfoxide (Panreac) were stirred with CaH_2 and distilled. Methanol was refluxed with CaO and distilled. NaH (60% dispersion in oil) (Sigma-Aldrich), pyrrole (Fluka), pyrazole (Acros), imidazole (Acros),

indole (Acros) were used as supplied. K_2CO_3 was calcinated at 450 °C for 4 h before use. Morpholine and diethylamine were stirred with CaH_2 for 6–8 hs and distilled. Potassium pentafluorophenyltrifluoroborate [15], benzimidazole [26] and 2,3,4,5,6-pentafluorobiphenyl [27] were prepared as described.

All reactions with NaH were performed under an atmosphere of dry argon.

4.2. Reaction of $K[C_6F_5BF_3]$ with secondary amines

4.2.1. Solution of $K[C_6F_5BF_3]$ (137 mg, 0.50 mmol) with diethylamine (117 mg, 1.60 mmol) in DMF (1 mL) was kept in a sealed tube at 130 °C for 4 h. No reaction occurred (^{19}F NMR).

4.2.2. Reaction of $K[C_6F_5BF_3]$ (50 mg, 0.18 mmol) and morpholine (51 mg, 0.59 mmol) in DMF (0.8 mL) (130 °C, 4 h) gave the same result.

4.2.3. Solution of $K[C_6F_5BF_3]$ (50 mg, 0.18 mmol) and morpholine (51 mg, 0.59 mmol) in DMF (0.8 mL) was kept in a sealed tube at 150 °C for 4 h. After cooling, resonances of $K[C_6F_5BF_3]$ (0.12 mmol) (33% conversion), 4-(2,3,5,6-tetrafluorophenyl)morpholine (0.03 mmol), and N,N-dimethyl-2,3,5,6-tetrafluoroaniline [28] (0.04 mmol) besides $K[BF_4]$ (0.09 mmol) and C_6F_5H (trace) were detected (^{19}F NMR).

4.2.4. Solution of $K[C_6F_5BF_3]$ (44 mg, 0.16 mmol) and morpholine (82 mg, 0.94 mmol) in diglyme (0.8 mL) was kept in a sealed tube at 150 °C for 4 h to form C_6F_5H (0.10 mmol) and 4-(2,3,5,6-tetrafluorophenyl)morpholine (0.01 mmol) at 63% conversion of $K[C_6F_5BF_3]$ (residual 0.06 mmol) (^{19}F NMR).

4.2.5. Solution of $K[C_6F_5BF_3]$ (123 mg, 0.45 mmol) and morpholine (93 mg, 0.107 mmol) in DMSO (1 mL) was kept in a sealed tube at 150 °C for 4 h to form C_6F_5H (0.01 mmol), 4-(2,3,5,6-tetrafluorophenyl)morpholine (0.30 mmol) and 4-(2,3,4,5-tetrafluorophenyl)morpholine **19** (0.05 mmol) at 79% conversion of $K[C_6F_5BF_3]$ (residual 0.09 mmol) (^{19}F NMR). The solution was diluted with water (15 mL), and the products were steam distilled. The distillate was acidified with 5% HCl, extracted with $CHCl_3$, and the extract was dried with $MgSO_4$. The solvent was removed under reduced pressure to give a mixture of tetrafluorophenylmorpholines **2** and **19** (white solid) (53 mg) (96:4).

4-(2,3,5,6-Tetrafluorophenyl)morpholine (**2**) (mixture with **19**). ^{1}H NMR (CH_2Cl_2): δ 6.66 (tt, $^4J(H^4, F^{2,6})$ = 7 Hz, $^3J(H^4, F^{3,5})$ = 10 Hz, 1H, H^4), 3.69 (m, 4H, H^β), 3.17 (m, 4H, H^α). ^{19}F NMR (CH_2Cl_2): δ –141.9 (ddd, $^3J(F^3, F^2)$ = 20 Hz, $^5J(F^3, F^6)$ = 10 Hz, $^3J(F^3, H^4)$ = 10 Hz, 2F, $F^{3,5}$), –151.8 (ddd, $^3J(F^2, F^3)$ = 20 Hz, $^5J(F^2, F^5)$ = 10 Hz, $^4J(F^2, H^4)$ = 8 Hz, 2F, $F^{2,6}$) (lit. [23]: ^{1}H NMR ($CDCl_3$): δ 6.71 (tt, ^3J(H, F) = 7.2 Hz, ^2J(H, F) = 9.8 Hz, 1H), 3.82 (m, 4H), 3.27-3.29 (m, 4H). ^{19}F NMR ($CDCl_3$): δ –140.7 (m, 2F), –151.6 (m, 2F)).

4-(2,3,4,5-Tetrafluorophenyl)morpholine (**19**) (mixture with **2**). ^{1}H NMR (CH_2Cl_2): δ 6.50 (dddd, $^{3}J(H^{6}, F^{5})$ = 12 Hz, $^{4}J(H^{6}, F^{4})$ = 8 Hz, $^{4}J(H^{6}, F^{2})$ = 8 Hz, $^{5}J(H^{6}, F^{3})$ = 3 Hz, 1H, H^{6}), 3.73 (m, 4H, H^{β}), 2.94 (m, 4H, H^{α}). ^{19}F NMR (CH_2Cl_2): δ –141.2 (ddd, $^{3}J(F^{5}, F^{4})$ = 22 Hz, $^{5}J(F^{5}, F^{2})$ = 11 Hz, $^{3}J(F^{5}, H^{6})$ = 11 Hz, 1F, F^{5}), –150.9 (ddd, $^{3}J(F^{2}, F^{3})$ = 19 Hz, $^{5}J(F^{2}, F^{5})$ = 11 Hz, $^{4}J(F^{2}, H^{6})$ = 8 Hz, 1F, F^{2}), –157.9 (dd, $^{3}J(F^{3}, F^{2})$ = 19 Hz, $^{3}J(F^{3}, F^{4})$ = 20 Hz, 1F, F^{3}), –167.6 (ddd, $^{3}J(F^{4}, F^{5})$ = 22 Hz, $^{3}J(F^{4}, F^{3})$ = 20 Hz, $^{4}J(F^{4}, H^{6})$ = 8 Hz, 1F, F^{4}). HRMS (ESI), *m/z*: calcd. for $C_{10}H_9F_4NO$ 235,0620; found 235.0614 (isomer mixture).

4.2.6. $K[C_6F_5BF_3]$ (137 mg, 0.50 mmol), morpholine (104 mg, 1.2 mmol) and K_2CO_3 (138 mg, 1.0 mmol) were kept in DMF (1 mL) at 150 °C for 4 h. The ^{19}F NMR spectrum showed signals of $K[C_6F_5BF_3]$ and **2** (93:7) besides C_6F_5H (trace). Similar results were obtained in DMAc, NMP and DMSO.

4.3. Reaction of $K[C_6F_5BF_3]$ with sodium diethylamide

Diethylamine (58 mg, 0.80 mmol), NaH (28 mg, 0.70 mmol) and DMSO (1 mL) were stirred at 25 °C for 1 h. $K[C_6F_5BF_3]$ (137 mg, 0.50 mmol) and C_6H_5F (48 mg, 0.50 mmol) (quantitative internal reference) were added, the suspension was stirred at 130 °C for 4 h in a sealed tube, cooled to 25 °C and filtered. The solution contained $K[C_6F_5BF_3]$ besides minor unknown products (^{19}F NMR).

4.4. Reaction of $K[C_6F_5BF_3]$ with sodium morpholinide

4.4.1. Morpholine (38 mg, 0.44 mmol) and NaH (15 mg, 0.37 mmol) in diglyme (0.4 mL) were stirred at 25 °C for 1.5 h, diluted with diglyme (2 mL), and $K[C_6F_5BF_3]$ (107 mg, 0.39 mmol) and C_6H_5F (48 mg, 0.50 mmol) (quantitative internal reference) were added. The suspension was stirred at 130 °C for 4 h in a sealed tube, cooled to 25 °C and filtered. The solution contained $K[C_6F_5BF_3]$ (>0.35 mmol) besides minor unknown products (^{19}F NMR).

4.4.2. The reaction of sodium morpholinide [from morpholine (70 mg, 0.8 mmol) and NaH (28 mg, 0.7 mmol)] with $K[C_6F_5BF_3]$ (137 mg, 0.5 mmol) in DMSO (1 mL) was performed similar way. The ^{19}F NMR spectrum showed signals of $K[C_6F_5BF_3]$, C_6F_5H and $K[BF_4]$ (90:5:5).

*4.5. Preparation of potassium 4-(pyrrol-1-yl)-*2,3,5,6*-tetrafluorophenyltrifluoroborate (**4**)*

A 10 mL flask was charged with NaH (56 mg, 1.4 mmol), DMF (2 mL), and pyrrole (115 mg, 1.6 mmol). The reaction mixture was stirred at 25 °C for 30 min in the atmosphere of dry argon and $K[C_6F_5BF_3]$ (274 mg, 1.0 mmol) was added. The flask was closed with a stopper and the reaction mixture was magnetically stirred at 130 °C for 4 h. After cooling to 25 °C, the solvent was

evaporated at reduced pressure. The residue was stirred at 25 °C for 8 h with water (0.2 mL) and $K[HF_2]$ (780 mg, 10 mmol), diluted with MeCN (5 mL) and stirred with K_2CO_3 (50 mg) for 1–2 h. The suspension was filtered through silica gel (60 μm), which was washed additionally with acetonitrile (10 mL). The combined solution was evaporated at reduced pressure to yield **4** (white solid) (276 mg, 86%).

$K[4\text{-}C_4H_4NC_6F_4BF_3]$ (**4**). ^{1}H NMR (CH_3CN): δ 6.92 (m, 2H), 6.32 (m, 2H). ^{1}H NMR (acetone): δ 7.11 (m, 2H), 6.45 (m, 2H). ^{11}B NMR (acetone): δ 1.82 (q, ^1J(B, F) = 41 Hz, BF_3). ^{19}F NMR (CD_3CN): δ –133.7 (ddq, $^3J(F^2, F^3)$ = 23 Hz, $^5J(F^2, F^5)$ = 12 Hz, $^4J(F^2, BF_3)$ = 12 Hz, 2F, $F^{2,6}$), –135.0 (q (1:1:1:1), ^1J(F, B) = 42 Hz, 3F, BF_3), –152.9 (dd, $^3J(F^3, F^2)$ = 23 Hz, $^5J(F^3, F^6)$ = 12 Hz, 2F, $F^{3,5}$). ^{19}F NMR (acetone): δ –134.3 (m, 2F, $F^{2,6}$), –133.4 (m, 3F, BF_3), –153.5 (m, 2F, $F^{3, 5}$). ^{19}F NMR (DMF): δ –133.2 (q (1:1:1:1), ^1J(F, B) = 45 Hz, 3F, BF_3), –133.9 (ddq, $^3J(F^2, F^3)$ = 23 Hz, $^5J(F^2, F^5)$ = 12 Hz, $^4J(F^2, BF_3)$ = 12 Hz, 2F, $F^{2,6}$), –153.0 (dd, $^3J(F^3, F^2)$ = 24 Hz, $^5J(F^3, F^6)$ = 11 Hz, 2F, $F^{3, 5}$). IR (KBr): 3147 (w), 1656 (m), 1529 (m), 1454 (vs), 1397 (w), 1380 (w), 1332 (w), 1302 (w), 1251 (m), 1231 (s), 1112 (m), 1069 (m), 1038 (m), 1003 (m), 974 (s), 950 (vs), 852 (w), 778 (m), 760 (w), 726 (m), 712 (m), 637 (w), 597 (w), 446 (w) cm^{-1}.

Anal. calcd for $C_{10}H_4BF_7KN$ (321.04): C, 37.41; H, 1.26; F, 41.42; found: C, 37.6; H, 1.50; F, 41.7.

4.6. Preparation of potassium 4-(indol-1-yl)-2,3,5,6-*tetrafluorophenyltrifluoroborate (**9**)*

4.6.1. A 10 mL flask was charged with DMF (5 mL), NaH (71 mg, 1.77 mmol) and indole (220 mg, 1.86 mmol), and the reaction mixture was stirred at 25 °C for 1 h at the atmosphere of dry argon to form yellowish solution. $K[C_6F_5BF_3]$ (423 mg, 1.54 mmol) was added, and the reaction mixture was magnetically stirred at 100 °C for 4 h. The ^{19}F NMR spectrum showed resonances of $[C_6F_5BF_3]^-$ and $[4\text{-}C_8H_6NC_6F_4BF_3]^-$ (2:8). $K[HF_2]$ (838 mg, 10.7 mmol) were added, and the mixture was stirred at 25 °C for 24 h. The suspension was filtered through a glass filter, the flask and the filter cake were washed with acetone (2x5 mL) and washings were combined with filtrate. The solvent was distilled off at reduced pressure. The residual solid was washed with ether (10 mL) and dried. The white solid (327 mg) consisted of **9** and **1** (9:1).

4.6.2. A 10 mL flask was charged with DMF (5 mL), NaH (54 mg, 1.35 mmol) and indole (163 mg, 1.39 mmol), and the reaction mixture was stirred at 25 °C for 1 h in the atmosphere of dry argon to form yellowish solution. Then $K[C_6F_5BF_3]$ (278 mg, 1.0 mmol) was added, and reaction mixture was magnetically stirred at 130 °C for 4 h. The ^{19}F NMR spectrum of the mother liquor contained resonances of $[C_6F_5BF_3]^-$, $[4\text{-}C_8H_6NC_6F_4BF_3]^-$, $[3,4\text{-}(C_8H_6N)_2C_6F_4BF_3]^-$ (6:88:6). $K[HF_2]$ (788 mg, 10 mmol) was added, and the mixture was stirred at 25 °C for 19 h. The

suspension was filtered through a glass filter, the flask and filter cake were washed with acetone (3x3 mL) and washings were combined with filtrate. The solvent was distilled off at reduced pressure, and the residue was washed with ether (3x4 mL). After recrystallization from MeOH the residual white solid was dried in air to yield **9** (273 mg, 74%).

K[4-$C_8H_6NC_6F_4BF_3$] (**9**). ^{1}H NMR (acetone): δ 7.65 (d, $^3J(H^4, H^5)$ = 7 Hz, 1H, H^4), 7.41 (d, $^3J(H^2, H^3)$ = 3 Hz, 1H, H^2), 7.20–7.14 (m, 3H, $H^{5,6,7}$), 6.74 (d, $^3J(H^3, H^2)$ = 3 Hz, 1H, H^3). ^{19}F NMR (acetone): δ –133.5 (m, 2F, $F^{2,6}$), –133.8 (q (1:1:1:1), ^1J(F, B) = 43 Hz, 3F, BF_3), –150.3 (dd, $^3J(F^3, F^2)$ = 21 Hz, $^5J(F^3, F^6)$ = 11 Hz, 2F, $F^{3,5}$). ^{19}F NMR (DMF): δ –133.1 (q (1:1:1:1), ^1J(F, B) = 43 Hz, 3F, BF_3), –133.5 (m, 2F, $F^{2,6}$), –150.4 (dd, $^3J(F^3, F^2)$ = 21 Hz, $^5J(F^3, F^6)$ = 11 Hz, 2F, $F^{3,5}$). IR (KBr): 3058 (vw), 1651 (m), 1533 (m), 1514 (w), 1450 (vs), 1369 (w), 1304 (w), 1251 (m), 1265 (m), 1198 (s), 1130 (w), 1103 (m), 1070 (m), 1024 (m), 953 (vs), 854 (w), 785 (w), 769 (w), 746 (m), 714 (m), 640 (w), 422 (vw) cm^{-1}.

Anal. calcd for $C_{14}H_6BF_7KN$ (371.11): C, 45.31; H, 1.63; F, 35.84, N, 3.77; found: C, 44.7; H, 1.90; F, 35.9, N, 3.75.

4.7. Preparation of potassium imidazol-1-ide

A 250 mL flask was charged with imidazole (68.1 g, 1 mol), KOH (56.1 g, 1 mol), and intensively shaken until all mixture liquidified. Then it was warmed for 30 min in a boiling water bath and volatiles were evaporated to dryness at 130–140 °C (bath) in high vacuum. Potassium imidazol-1-ide (104 g, 98%) was stored in dry argon atmosphere before use.

4.8. Reaction of K[$C_6F_5BF_3$] with alkali imidazol-1-ide

4.8.1. Preparation of potassium 4-(imidazol-1-yl)-2,3,5,6-tetrafluorophenyltrifluoroborate (**5**)

A 10 mL flask equipped with a magnetic stir bar was charged with potassium imidazol-1-ide (64 mg, 0.6 mmol), DMF (1 mL), and K[$C_6F_5BF_3$] (137 mg, 0.5 mmol) and mounted in a pre-heated oil bath (80 °C). The reaction mixture was stirred for 8 h, cooled to 25 °C, and the solvent was evaporated at reduced pressure. The residue was suspended in MeCN, filtered through silica gel (60 μm) and the filtrate was evaporated to dryness in vacuum to give **5** (white solid) (153 mg, 93%).

K[4-$C_3H_3N_2C_6F_4BF_3$] (**5**). ^{1}H NMR (CH_3CN): δ 7.72 (s, 1H, H^2), 7.28 (s, 1H, H^5), 7.31 (s, 1H, H^4). ^{1}H NMR (acetone): δ 8.02 (s, 1H, H^2), 7.55 (s, 1H, H^5), 7.33 (s, 1H, H^4). ^{11}B NMR (acetone): δ 1.74 (q, ^1J(B, F) = 42 Hz, BF_3). ^{19}F NMR (CD_3CN): δ –133.7 (m, 2F, $F^{2,6}$), –133.9 (q (1:1:1:1), ^1J(F, B) = 42 Hz, 3F, BF_3), –152.1 (dd, $^3J(F^3, F^2)$ = 22 Hz, $^5J(F^3, F^6)$ = 11 Hz, 2F, $F^{3,5}$). ^{19}F NMR (acetone): δ –132.2 (m, 2F, $F^{2,6}$), –133.9 (q (1:1:1:1), ^1J(F, B) = 41 Hz, 3F, BF_3), –152.5

(dd, $^{3}J(F^{3}, F^{2})$ = 24 Hz, $^{5}J(F^{3}, F^{6})$ = 12 Hz, 2F, $F^{3,5}$). IR (KBr): 3139 (w), 2927 (w), 1655 (m), 1632 (m), 1522 (m), 1457 (vs), 1404 (w), 1350 (w), 1291 (w), 1256 (m), 1211 (s), 1111 (m), 1085 (m), 1059 (m), 1033 (m), 998 (s), 958 (vs), 907 (w), 880 (w), 863 (w), 817 (w), 784 (m), 760 (w), 745 (m), 654 (m), 636 (m), 613 (w) cm^{-1}.

Anal. calcd for $C_9H_3BF_7KN_2$ (322.03): C, 33.57; H, 0.94; F, 41.30; N, 8.70; found: C, 35.1; H, 1.33; F, 41.1; N, 9.24.

4.8.2. The reaction of potassium imidazol-1-ide (64 mg, 0.6 mmol) with $K[C_6F_5BF_3]$ (137 mg, 0.5 mmol) in NMP or DMSO (1 mL) was performed similar way at 80 °C for 8 h to give the same result (^{19}F NMR, quantitative internal standard $C_6H_5CF_3$ (10 μL, 0.082 mmol)). When the reaction was performed at 60 °C for 4 h in DMF, MeOH, MeCN or DME, the conversion of $K[C_6F_5BF_3]$ was 62, 60, 23 and 0 %, respectively.

4.8.3. A 10 mL flask was successively charged with DMF (2.5 mL), NaH (54 mg, 1.35 mmol) and imidazole (80 mg, 1.17 mmol). The suspension was stirred at 25 °C for 1 h in the atmosphere of dry argon to form a solution. $K[C_6F_5BF_3]$ (236 mg, 0.86 mmol) was added, and the reaction mixture was magnetically stirred at 80 °C for 8 h. After cooling to ambient temperature, $K[HF_2]$ (0.8 g, 10 mmol) was added. The suspension was stirred for 19 h and filtered through a glass filter. The solvent was evaporated at reduced pressure to give a 232 mg mixture of **5** (0.72 mmol), **1** (0.06 mmol) and **6** (0.06 mmol) (^{19}F NMR).

4.9. Reaction of $K[C_6F_5BF_3]$ with alkali benzimidazol-1-ide

4.9.1. A 10 mL flask was charged with DMF (1 mL), NaH (14 mg, 0.35 mmol) and benzimidazole (47 mg, 0.40 mmol). After stirring at 25 °C for 1 h in the atmosphere of dry argon, $K[C_6F_5BF_3]$ (69 mg, 0.25 mmol) was added in one portion, the flask was closed with a stopper, mounted in a pre-heated oil bath, and the reaction mixture was stirred at 80–130 °C over a period of 4–8 h (Table 1). The conversion of $K[C_6F_5BF_3]$ and the yield of **11** were determined from ^{19}F NMR spectra with $C_6H_5CF_3$ (10 μL, 0.082 mmol) as the quantitative internal standard after cooling to 25 °C. The reaction at 130 °C was performed with $K[C_6F_5BF_3]$ (137 mg, 0.50 mmol), NaH (28 mg, 0.70 mmol) and benzimidazole (95 mg, 0.80 mmol) in 1 mL of DMF, and gave $M[C_6F_5BF_3]$ (0.02 mmol) (96% conversion), $M[4\text{-}C_7H_5N_2C_6F_4BF_3]$ (0.15 mmol), C_6F_5H (0.03 mmol), 1-(2,3,5,6-tetrafluorophenyl)benzimidazole (0.12 mmol) and **12** (0.06 mmol).

4.9.2. A 30 mL flask was charged with DMSO (7 mL), benzimidazole (250 mg, 2.13 mmol) and NaH (124 mg, 3.10 mmol) was added in one portion. The reaction mixture was stirred at 25 °C for 1 h. $K[C_6F_5BF_3]$ (423 mg, 1.54 mmol) was added into the solution, and the reaction set was mounted into a pre-heated (100 °C) oil bath. The solution was magnetically stirred at 100 °C for 5

h. After cooling to 25 °C, $K[HF_2]$ (2 g) was added, and the suspension was stirred at 25 °C overnight. The suspension was filtered through a glass filter, and the filtrate was poured out onto $CHCl_3$ (15 mL). The precipitate was separated by centrifugation, washed with $CHCl_3$ (8 mL), and dried in a vacuum desiccator yielding white powder (410 mg) which consisted of **11** and **12** (91:9).

$K[4\text{-}C_7H_5N_2C_6F_4BF_3]$ (**11**). ^{1}H NMR (acetone): δ 8.29 (m, 1H, H^2), 7.75 (m, 1H), 7.37 (m, 1H), 7.29 (m, 2H). ^{11}B NMR (acetone): δ 1.75 (q, ^1J(B, F) = 42 Hz, BF_3). ^{19}F NMR (acetone): δ –132.8 (m, 2F, $F^{2,6}$), –133.9 (q (1:1:1:1), ^1J(F, B) = 40 Hz, 3F, BF_3), –150.4 (dd, $^3J(F^3, F^2)$ = 23 Hz, $^5J(F^3, F^6)$ = 11 Hz, 2F, $F^{3,5}$). IR (KBr): 3124 (w), 2924 (vw), 1651 (w), 1614 (m), 1587 (s), 1495 (s), 1468 (vs), 1305 (m), 1290 (m), 1261 (s), 1217 (s), 1196 (m), 1152 (w), 1128 (m), 1101 (m), 1026 (s), 964 (vs), 895 (w), 875 (w), 858 (w), 781 (m), 764 (m), 742 (s), 636 (w) cm^{-1}.

$K[3,4\text{-}(C_7H_5N_2)_2C_6F_3BF_3]$ (**12**) (mixture with **11**). ^{1}H NMR (acetone): δ 8.11 and 7.96 (s, 2H, H^2), 7.50–7.46 (m, 2H), 7.38–7.33 (m, 2H), 7.21–6.96 (m, 4H) (stereomer A); 8.07 and 7.94 (s, 2H, H^2), 7.50–7.46 (m, 2H), 7.38–7.33 (m, 2H), 7.21–6.96 (m, 4H) (stereomer B). ^{19}F NMR (acetone): δ –114.6 (m, 1F, F^2), –124.3 (m, 1F, F^6), –135.1 (m, 3F, BF_3), –148.8 (m, 1F, F^5) (stereomer A); –114.9 (m, 1F, F^2), –124.3 (m, 1F, F^6), –135.1 (m, 3F, BF_3), –149.5 (m, 1F, F^5) (stereomer B) (tentative assignment).

*4.10. Preparation of potassium 4-(pyrazol-1-yl)-2,3,5,6-tetrafluorophenyltrifluoroborate (**7**)*

A 100 mL two-necked flask was equipped with a magnetic stir bar and topped with a T-piece. The reactor was evacuated and filled with dry argon. It was charged with DMF (20 mL), NaH (327 mg, 8.2 mmol), and pyrazole (454 mg, 6.6 mmol) was added in portion with stirring. After 30–40 min a clear solution was formed. $K[C_6F_5BF_3]$ (1.515g, 5.5 mmol) was added In the atmosphere of dry argon. The flask was mounted into a hot oil bath and the reaction mixture was stirred at 80 °C for 7 h. $K[HF_2]$ (2.15 g, 27 mmol) was added, and the suspension was stirred at 25 °C overnight. The solvent was removed at 15–17 Torr and 55–65 °C (bath), the residual oil was washed with hexane (3x20 mL), dried at reduced pressure and extracted with acetone (4x10 mL). The solvent was removed from an evaporator, brownish oil was washed with CH_2Cl_2 (6x5 mL) and the formed white solid was dried on air. Yield of **7** was 1.14 g (64%) (contaminated with ≤8% of **8**).

$K[4\text{-}C_3H_3N_2C_6F_4BF_3]$ (**7**). ^{1}H NMR (acetone): δ 7.94 (d, $^3J(H^3, H^4)$ = 2.4 Hz, 1H, H^3), 7.73 (d, $^3J(H^5, H^4)$ = 2.0 Hz, 1H, H^5), 6.52 (dd, $^3J(H^4, H^3)$ = 2.4 Hz, $^3J(H^4, H^5)$ = 2.0 Hz, 1H, H^4). ^{11}B NMR (acetone-d_6): δ 1.76 (q, ^1J(B, F) = 40 Hz, BF_3). ^{19}F NMR (acetone): δ –134.0 (m, 5F, $F^{2,6}$ and BF_3), –151.9 (m, 2F, $F^{3,5}$). IR (KBr): 3132 (w), 1657 (m), 1537 (m), 1510 (m), 1464 (vs), 1416 (w), 1402 (m), 1327 (w), 1269 (m), 1211 (s), 1198 (m), 1097 (s), 1036 (s), 1024 (s), 995 (s), 961

(vs), 916 (w), 880 (w), 862 (w), 843 (w), 779 (s), 762 (m), 748 (m), 633 (m), 608 (w), 446 (w) cm^{-1}.

Anal. calcd for $C_9H_3BF_7KN_2$ (322.03): C, 33.57; H, 0.94; F, 41.30, N, 8.70; found: C, 33.1; H, 0.92; F, 41.2, N, 8.50.

K[3,4-$(C_3H_3N_2)_2C_6F_3BF_3$] (**8**) (mixture with **7**). ^{1}H NMR (acetone): δ 7.49 (md, $^3J(H^3, H^4)$ = 2.4 Hz, 1H, H^3), 7.46 (md, $^3J(H^5, H^4)$ = 2.0 Hz, 1H, H^5), 6.24 (dd, $^3J(H^4, H^3)$ = 2.4 Hz, $^3J(H^4, H^5)$ = 2.0 Hz, 1H, H^4) (pyrazolino group at position 3), 7.53 (md, $^3J(H^3, H^4)$ = 2.4 Hz, 1H, H^3), 7.50 (md, $^3J(H^5, H^4)$ = 2.0 Hz, 1H, H^5), 6.25 (dd, $^3J(H^4, H^3)$ = 2.4 Hz, $^3J(H^4, H^5)$ = 2.0 Hz, 1H, H^4) (pyrazolino group at position 4) (tentitive assignment). ^{19}F NMR (acetone): δ –116.6 (m, 1F, F^2), –125.9 (m, 1F, F^6), –134 (m, 3F, BF_3), –151.2 (m, 1F, F^5).

4.11. Competitive reaction of $C_6F_5C_6H_5$ with sodium morpholin-1-ide and sodium indol-1-ide

4.11.1. A 20 mL flask was charged with DMF (5 mL) and NaH (59 mg, 1.47 mmol). Solution of indole (122 mg, 1.04 mmol) and morpholine (103 mg, 1.18 mmol) in DMF (1 mL) was added in one portion, and the reaction mixture was stirred at 25 °C for 1 h in the atmosphere of dry argon. $C_6F_5C_6H_5$ (236 mg, 0.96 mmol) was added, and the reaction mixture was magnetically stirred at 130 °C for 4 h. After cooling to 25 °C, the solution was poured out onto water (20 mL), the precipitate was filtered off, washed with water and dried in a vacuum desiccator over Sicapent®. Yield of 1-(2,3,5,6-tetrafluoro-4-phenylphenyl)indole (**16**) was 291 mg (88%).

1-(2,3,5,6-Tetrafluoro-4-phenylphenyl)indole (**16**). ^{1}H NMR (acetone): δ 7.71 (d, $^3J(H^4, H^5)$ = 8 Hz, 1H, H^4), 7.61 (d, $^3J(H^2, H^3)$ = 3 Hz, 1H, H^2), 7.62–7.52 (5H), 7.34–7.17 (3H), 6.83 (d, $^3J(H^3, H^2)$ = 3 Hz, 1H, H^3). ^{19}F NMR (acetone): δ –143.1 (dd, $^3J(F^{3'}, F^{2'})$ = 22 Hz, $^5J(F^{3'}, F^{6'})$ = 10 Hz, 2F, $F^{3',5'}$), –147.2 (dd, $^3J(F^{2'}, F^{3'})$ = 22 Hz, $^5J(F^{2'}, F^{5'})$ = 10 Hz, 2F, $F^{2',6'}$). IR (KBr): 3054 (w), 2924 (w), 2854 (w), 1651 (w), 1614 (w), 1529 (s), 1491 (vs), 1456 (m), 1438 (s), 1303 (w), 1279 (m), 1215 (m), 1151 (m), 978 (s), 791 (w), 766 (m), 744 (m), 725 (m), 696 (m), 648 (w) cm^{-1}. HRMS (ESI), *m/z*: calcd. for $C_{20}H_{11}F_4N$ 341.0827; found 341.0821.

4.11.2. A 20 mL flask was charged with DMF (5 mL) and NaH (130 mg, 3.25 mmol). The solution of indole (113 mg, 0.96 mmol) and morpholine (87 mg, 1.00 mmol) in DMF (1 mL) was added in one portion, and the reaction mixture was stirred at 25 °C for 1 h in the atmosphere of dry argon. $C_6F_5C_6H_5$ (508 mg, 2.08 mmol) was added, and the reaction mixture was magnetically stirred at 125 °C for 4 h. The solution contained tetrafluorophenylindole **16** (1.0 mmol) while 4-(2,3,5,6-tetrafluoro-4-phenylphenyl)morpholine was not detected (^{19}F NMR).

*4.12. Preparation of 4-(2,3,5,6-tetrafluoro-4-phenylphenyl)morpholine (**17**)*

$C_6F_5C_6H_5$ (190 mg, 0.77 mmol), morpholine (159 mmol, 1.82 mmol) and DMSO (1.5 mL) were heated at 160 °C for 1 h in a sealed tube. The semi-solid reaction mixture was poured out onto water, the precipitate was filtered off, washed with water and dried in a vacuum desiccator over Sicapent® to yield **17** (202 mg, 84%).

4-(2,3,5,6-Tetrafluoro-4-phenylphenyl)morpholine (**17**). ^{1}H NMR (acetone): δ 7.44 (m, 5H, C_6H_5), 3.72 (m, 4H, $H^{3,5}$), 3.26 (m, 4H, $H^{2,6}$). ^{19}F NMR (acetone): δ –145.6 (dd, $^3J(F^{3'}, F^{2'})$ = 21 Hz, $^5J(F^{3'}, F^{6'})$ = 9 Hz, 2F, $F^{3',5'}$), –150.9 (dd, $^3J(F^{2'}, F^{3'})$ = 21 Hz, $^5J(F^{2'}, F^{5'})$ = 9 Hz, 2F, $F^{2',6'}$). ^{19}F NMR (DMF): δ –145.7 (dd, $^3J(F^{3'}, F^{2'})$ = 21 Hz, $^5J(F^{3'}, F^{6'})$ = 9 Hz, 2F, $F^{3',5'}$), –151.0 (dd, $^3J(F^{2'}, F^{3'})$ = 21 Hz, $^5J(F^{2'}, F^{5'})$ = 9 Hz, 2F, $F^{2',6'}$). IR (KBr): 3057 (w), 2964 (m), 2912 (w), 2895 (w), 2855 (m), 1652 (w), 1516 (w), 1483 (vs), 1438 (s), 1400 (w), 1377 (w), 1363 (w), 1336 (w), 1285 (w), 1271 (m), 1256 (m), 1203 (w), 1178 (w), 1113 (s), 1072 (w), 1034 (w), 1011 (m), 974 (vs), 914 (m), 887 (m), 802 (w), 789 (w), 752 (m), 729 (m), 694 (m), 673 (w), 650 (w), 548 (w), 505 (w) cm^{-1}. HRMS (ESI), *m/z*: calcd. for $C_{16}H_{13}F_4NO$ 311,0933; found 311.0928.

*4.13. Preparation of 1-(2,3,5,6-tetrafluorophenyl)benzimidazole (**13**)*

NaH (117 mg, 2.92 mmol) was added to a solution of benzimidazole (252 mg, 2.15 mmol) in DMF (5 mL) under stirring. The reaction mixture was stirred at 25 °C for 1 h in the atmosphere of dry argon. Pentafluorobenzene (313 mg, 1.86 mmol) was injected with a syringe. After stirring at 25 °C for 20 min, the flask was mounted in a pre-heated bath (70–75 °C) for 1 h. The solution was cooled to 25 °C, poured into 5% HCl (20 mL), extracted with ether (2x15 mL), the extract was washed with water, and dried with $MgSO_4$. The solvent was evaporated at reduced pressure and the residue was dried in a vacuum desiccator over Sicapent® to yield **13** (white solid) (142 mg, 29%).

1-(2,3,5,6-Tetrafluorophenyl)benzimidazole (**13**). ^{1}H NMR (acetone): δ 8.33 (m, 1H, H^2), 7.77 (m, 2H), 7.34 (m, 2H), 7.42 (m, 1H, $H^{4'}$). ^{19}F NMR (acetone): δ –137.8 (m, 2F, $F^{3',5'}$), –146.5 (m, 2F, $F^{2',6'}$). HRMS (ESI), *m/z*: calcd. for $C_{13}H_6F_4N_2$ 266.0467; found 266.0463.

4.14. Reaction of C_6F_6 with sodium indol-1-ide

An ampoule was flushed with dry argon, charged successively with DMF (5 mL), indole (198 mg, 1.69 mmol) and NaH (70 mg, 1.75 mmol). In 1 h, hexafluorobenzene (1.11 g, 6 mmol) was added, the ampoule was sealed and heated at 110 °C for 4 h. The reaction mixture was poured into 5% HCl (50 mL) and extracted with ether (2x15 mL). The extract was washed with brine, dried with $MgSO_4$, and the solvent was evaporated at reduced pressure to yield 1-(pentafluorophenyl)indole (**14**) and 1,4-bis(indol-1-yl)tetrafluorobenzene (**18**) (1:1) (330 mg).

1-(Pentafluorophenyl)indole (**14**) (mixture with **18**). ^{1}H NMR (acetone): δ 7.62 (d 8 Hz, 1H), 7.41 (m, 1H), 7.15–7.05 (3H), 6.67 (d, $^{3}J(H^{3}, H^{2})$ = 3 Hz, 1H, H^{3}). ^{19}F NMR (acetone): δ –146.4 (m, 2F, $F^{2',6'}$), –156.0 (t, $^{3}J(F^{4'}, F^{3',5'})$ = 21 Hz, 1F, $F^{4'}$), –162.3 (m, 2F, $F^{3',5'}$).

1,4-Bis(indol-1-yl)tetrafluorobenzene (**18**) (mixture with **14**). ^{1}H NMR (acetone): δ 7.54 (d 8 Hz, 1H), 7.41 (m, 1H), 7.15–7.05 (3H), 6.73 (d, $^{3}J(H^{3}, H^{2})$ = 3 Hz, 1H, H^{3}). ^{19}F NMR (acetone): δ –146.2 (s, 4F, $F^{2',3',5',6'}$). HRMS (ESI), *m/z*: (mixture of **14** and **18**). calcd. for $C_{14}H_6F_5N$ **14** 283.0420; found 283.0421; calcd. for $C_{22}H_{12}F_4N_2$ **18** 380.0936; found 380.0946.

Acknowledgements

The study was supported by The Ministry of Education and Science of Russian Federation, project 2012-1.2.1-12-000-1004-038.

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Table 1. Reaction of $K[C_6F_5BF_3]$ **1** with sodium benzimidazolide (1.4 equiv) in DMF

Run	Temperature, °C	Time, h	Conversion of **1**, %	Ratio **11** : **12**
1	130	4	96	71 : 29[a]
2	100	4	84	75 : 25
3	80	4	60	88 : 12
4	100	8	86	78 : 22
5[b]	100	4	96	66 : 34

[a] Besides C_6F_5H and 1-(2,3,5,6-tetrafluorophenyl)benzimidazole.

[b] 2.8 equivalent of sodium benzimidazolide.