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Polyfluoroorganotrifluoroborates and -difluoroboranes: interesting materials in fluoroorgano and fluoroorgano-element chemistry

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Abstract

The aimed introduction of the polyfluoroorgano groups (4-C_5F_4N), $C_6F_{13}C_2H_4$, and C_2F_5 into methoxy group-containing boron electrophiles is reported. The new compounds obtained after transformations K[(4-C_5F_4N)BF_3], (4-C_5F_4N)BF_2, K[$C_6F_{13}C_2H_4BF_3$], $C_6F_{13}C_2H_4BF_2$, K[$(C_2F_5)_2B(OMe)_2$], and K[$(C_2F_5)_2BF_2$] were isolated and characterised. Additionally some of their precursors as there are Li(4-C_5F_4N), Li[(4-C_5F_4N)$B(OMe)_3$], (4-C_5F_4N)$B(OH)_2$ and the by-products Li[$(4\text{-}C_5F_4N)_2B(OMe)_2$], $(4\text{-}C_5F_4N)_2BOH$, and K[$(4\text{-}C_5F_4N)_2BF_2$] are described. The usefulness of polyfluoroorganodifluoroboranes for introducing polyfluoroorgano groups into hypervalent F–E–F bonds is demonstrated by the synthesis of [C_6F_5(4-C_5F_4N)I][BF_4] and [*p*-FC_6H_4(*trans*-CF_3CF=CF)I][BF_4].

Keywords: Polyfluoroorgano groups; Methoxyborates; Fluoroborates; Aryl(heteroaryl)iodonium salts; Alkenyl(aryl)iodonium salts; NMR spectroscopy

1. Introduction

The aimed introduction of one perfluoroorgano group R_F into the Lewis acids BCl_3 [1] or BBr_3 establishes a preparative challenge. In contrast to the high electrophilic $BHal_3$ molecules the perfluoroorgano metal reagents R_FM are characterised by their weak carbon nucleophilicity. To realise the first step, the addition of R_F to the boron centre, highly electropositive metals bonded to R_F are indicated. The high nucleofugality of Cl^- and Br^- in the primary adduct $[R_FB(Hal)_3]^-$ caused the preferred formation of $R_FB(Ha)_2$ which, depending on the nature of R_F and its electron-withdrawing character, shows no significant reduction of the electrophilicity of the boron centre compared to $BHal_3$ itself and supports the introduction of a second or following R_F group (Scheme 1).

During the last years we have pursued a methodical approach, which can be widely applied for introducing perfluoro and polyfluoro as well as non-fluorinated organo groups. Trimethoxyborane in Et_2O shows a moderate reactivity compared to $B(Hal)_3$ caused by the better p_π–p_π-backbonding of the OMe group in comparison to the halogen atoms. For the introduction of a polyfluorophenyl group we have found that the reactivity of trialkoxyboranes decreased in the series Me > *n*-Pr > *i*-Pr [2]. The approach starting from $B(OMe)_3$ allowed the successful introduction of per- or/and polyfluoro alkynyl [3], alkenyl [4], aryl [2], and alkyl [5] groups. The process is characterised by the individual steps given in Scheme 2. The important influencing variables for the different reaction steps will be discussed together with new synthetic applications.

2. Results and discussion

2.1. The synthesis of potassium 2,3,5,6-tetrafluoropyrid-4-yltrifluoroborate and its conversion to the corresponding pyridyldifluoroborane (4-C_5F_4N)BF_2

In contrast to perfluorophenylboranes, which are intensively investigated, only little information is known about

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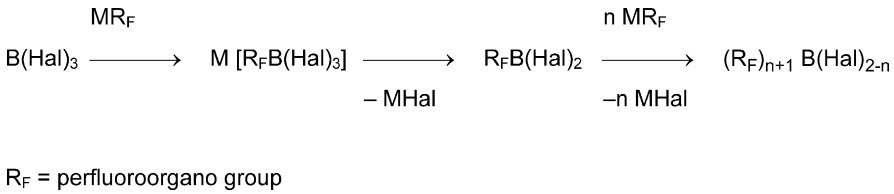


Scheme 1.

perfluoropyridylboranes from the literature. In 1992 Naumann described the synthesis of $B(4\text{-}C_5F_4N)_3$ and mentioned an admixture of $(4\text{-}C_5F_4N)_2BF$ and $(4\text{-}C_5F_4N)BF_2$, but gave no details of characterisation [6].

Our reaction sequence to $(4\text{-}C_5F_4N)BF_2$ includes the following individual steps: $C_5F_5N \rightarrow 2,3,5,6\text{-}C_5HF_4N \rightarrow Li(4\text{-}C_5F_4N) \rightarrow Li[(4\text{-}C_5F_4N)B(OMe)_3] \rightarrow K[(4\text{-}C_5F_4N)BF_3] \rightarrow (4\text{-}C_5F_4N)BF_2$.

The reduction of C-4 in C_5F_5N with Zn proceeded in aqueous ammonia (Eq. (1)) [7]. Lithiation of 2,3,5, 6-C_5HF_4N (**1**) was performed in hexane/Et_2O at −78 °C (Eq. (2)).

$$C_5F_5N + [NH_4]^+ + 3NH_3 + Zn \rightarrow \underset{\mathbf{1}}{2,3,5,6\text{-}C_5HF_4N} + F^- + [Zn(NH_3)_4]^{2+} \quad (1)$$

$$2,3,5,6\text{-}C_5HF_4N + n\text{-BuLi} \xrightarrow{-78\,^\circ C} Li(4\text{-}C_5F_4N) + n\text{-BuH} \quad (2)$$

$$Li(4\text{-}C_5F_4N) + B(OMe)_3 \rightarrow Li_{solv}[\underset{\mathbf{2}}{(4\text{-}C_5F_4N)B(OMe)_3}] \quad (3)$$

The low temperature addition of $Li(4\text{-}C_5F_4N)$ to a $B(OMe)_3$ solution in Et_2O was arranged under precise control of the temperature (Eq. (3)). ^{19}F NMR monitoring of this step revealed the formation of small quantities of $[(4\text{-}C_5F_4N)_2B(OMe)_2]^-$ as by-product beside $[(4\text{-}C_5F_4N)B(OMe)_3]^-$ (**2**). The following hydrolysis is a sensitive step (Eq. (4)). Principally hydrodeboration (Eq. (5)) is competing with the formation of the pyridylboronic acid (**3**), because the tetrafluoropyridyl group with the heteroatom nitrogen and the electron-withdrawing fluorine substituents is a good leaving group:

$$Li_{solv}[(4\text{-}C_5F_4N)B(OMe)_3] + HCl_{aq} + 2H_2O \rightarrow \underset{\mathbf{3}}{(4\text{-}C_5F_4N)B(OH)_2} + LiCl + 3MeOH \quad (4)$$

$$(4\text{-}C_5F_4N)B(OH)_2 + [H_3O]^+ \rightarrow 2,3,5,6\text{-}C_5HF_4N + B(OH)_3 + H^+ \quad (5)$$

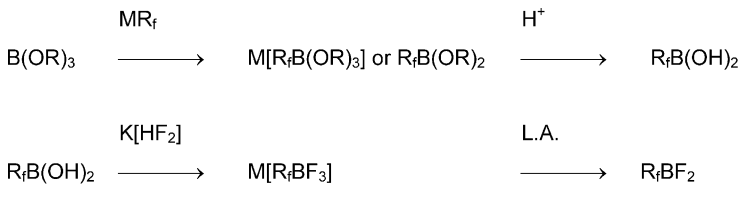
$$(4\text{-}C_5F_4N)B(OH)_2 + 2K[HF_2] \rightarrow \underset{\mathbf{4}}{K[(4\text{-}C_5F_4N)BF_3]} + KF + 2H_2O \quad (6)$$

An ether solution of **3** reacted with an aqueous solution of $K[HF_2]$ and formed $K[(4\text{-}C_5F_4N)BF_3]$ (Eq. (6)) with an admixture (9 mol%) of $K[(4\text{-}C_5F_4N)_2BF_2]$, which could be removed by crystallisation from boiling water and pure $K[(4\text{-}C_5F_4N)BF_3]$ (**4**) was isolated in 70% yield related to **1**. The final step, the removal of fluoride from **4**, revealed a distinct difference to the related salt $K[C_6F_5BF_3]$. Whereas the latter allowed the abstraction of a fluoride ion by BF_3 in a CH_2Cl_2 suspension at ca. −50 °C, salt **4** showed no reactivity under similar conditions. The stronger Lewis acid AsF_5 was necessary to abstract a fluoride ion from **4** and generate the new borane $(4\text{-}C_5F_4N)BF_2$ (**5**) in 62% yield (Eq. (7b)):

$$K[(4\text{-}C_5F_4N)BF_3](CH_2Cl_2 \text{ suspension}) + BF_3 \rightarrow \text{no reaction} \quad (7a)$$

$$K[(4\text{-}C_5F_4N)BF_3](CH_2Cl_2 \text{ suspension}) + AsF_5 \rightarrow \underset{\mathbf{5}}{(4\text{-}C_5F_4N)BF_2} + K[AsF_6]\downarrow \quad (7b)$$

Compound **5** is very volatile what makes the separation of the solvent difficult. With a significant loss in yield **5** could



Scheme 2.

be separated by low temperature crystallisation after concentration of the CH_2Cl_2 solution.

2.2. The synthesis of potassium 1H,1H,2H,2H-perfluoroctyltrifluoroborate and its conversion to 1H,1H,2H,2H-perfluoroctyldifluoroborane

In the literature we have found only one example of polyfluoroalkyldifluoroboranes R_fBF_2, namely $CF_3C_2H_4$-BF_2 [8], where the perfluoroalkyl part R_F of the polyfluoroalkyl group R_f was separated by an ethylene spacer. $CF_3C_2H_4BF_2$ was present in the product mixture of the gas phase reaction of $CF_3CH{=}CH_2$ and B_2F_4 in the molar ratio 4:1.

We were interested in a long-chain polyfluoroalkyldifluoroborane with the ''pony tail group'' $C_6F_{13}C_2H_4$ for practical applications. We have found that $BCl(OMe)_2$ is a suitable electrophile for introducing only one of such ''pony tail groups'' into the boron moiety when we used $C_6F_{13}C_2H_4MgBr$ (**6**) as a moderate carbon nucleophile. Compound **6** which was obtained in 57% yield is an alternative to $C_6F_{13}C_2H_4MgI$ [9,10]. In the Grignard reaction the main by-products were $(C_6F_{13}C_2H_4)_2$ from dimerisation and $C_6F_{13}C_2H_5$ from hydrogen abstraction. In 1962 Klebanskii and coworkers [11] reported the substitution of one *n*-butoxy group in $B(O\text{-}n\text{-}Bu)_3$ by a polyfluoroalkyl group using $CF_3C_2H_4MgCl$ as carbon nucleophile. Unfortunately, no experimental details and yields were given. We used a 1:>2 stoichiometry of **6** (without separation of the by-products) and $BCl(OMe)_2$ (Eq. (8)) and obtained an ether soluble product in the mixture which could not be unambiguously characterised as $C_6F_{13}C_2H_4B(OMe)_2$ (**7**), but the following transformation (Eq. (9)) to the salt $K[C_6F_{13}C_2H_4BF_3]$ (**8**) confirmed the presence of one polyfluoroalkyl group in **7**:

$$\underset{\mathbf{6}}{C_6F_{13}C_2H_4MgBr} + BCl(OMe)_2 \rightarrow \underset{\mathbf{7}}{C_6F_{13}C_2H_4B(OMe)_2} + Mg(Cl,Br)_2 \quad (8)$$

$$\underset{\mathbf{7}}{C_6F_{13}C_2H_4B(OMe)_2} + 2K[HF_2] + 2H_2O \rightarrow \underset{\mathbf{8}}{K[C_6F_{13}C_2H_4BF_3]} + KF + 2MeOH \quad (9)$$

The large quantity of by-products $(C_6F_{13}C_2H_4)_2$ and $C_6F_{13}C_2H_5$ as well as non-reacted starting material $C_6F_{13}C_2H_4Br$ were removed from **8** in high vacuum. The ^{19}F NMR spectrum of **8** showed the CF_3 group, the five CF_2 groups, and the BF_3 group in the correct integral ratio. The resolution of the CF_3 group allowed to determine $^4J(F^8, F^6) = 10$ Hz and $^5J(F^8, F^5) = 3$ Hz. The BF_3 group appeared broad and unresolved also in the ^{11}B mode. The ^{11}B shift value of 5.0 ppm appeared in the expected region and is comparable with that of $[C_8H_{17}BF_3]^-$ (5.3 ppm [12]) but significantly shielded in relation to $[C_6F_{13}BF_3]^-$ (0.5 ppm [5]). In the ^{19}F NMR the δ value of the BF_3 group shows the following sequence of deshielding: $[C_6F_{13}BF_3]^-$, −151.8 [5]; $[C_6F_{13}C_2H_4BF_3]^-$, −141.6; $[C_8H_{17}BF_3]^-$, −139.3 [12].

$$\underset{\mathbf{8}}{K[C_6F_{13}C_2H_4BF_3]}(CH_2Cl_2\ \text{suspension}) + BF_3 \rightarrow \underset{\mathbf{9}}{C_6F_{13}C_2H_4BF_2} + K[BF_4]\downarrow \quad (10)$$

The abstraction of a fluoride ion from **8** proceeded in a CH_2Cl_2 suspension at −50 °C with an excess of BF_3 (Eq. (10)). $C_6F_{13}C_2H_4BF_2$ (**9**) is a volatile and low boiling compound (b.p. 24 °C/2 × 10^{-2} hPa). The volatility is responsible for the remarkable loss of yield during the separation. The ^{19}F resonance of the BF_2 group of **9** at −73.8 ppm is similar to that of $C_8H_{17}BF_2$ (−73.2 [13]) and deshielded relative to $C_6F_{13}BF_2$ (−78.3 ppm [5]). Even in the ^{11}B mode **9** ($\delta = 27.5$) behaves like $C_8H_{17}BF_2$ ($\delta = 28.4$) and different to $C_6F_{13}BF_2$ (δ = 19.2 ppm). A remarkable difference in the ^{19}F NMR spectrum of the ''pony tail'' part of **9** and **8** was found for the CF_2 group in direct neighbourhood to the C_2H_4 spacer: $\delta(F^3)$ −116.6 (**9**) versus −114.0 ppm (**8**).

2.3. The synthesis of potassium bis(pentafluoroethyl)dimethoxyborate and potassium bis(pentafluoroethyl)difluoroborate

The aimed introduction of two perfluoroorgano groups into a boron electrophile comprises a two-step reaction with the additional demand that a further introduction of R_F nucleophiles must be avoided. After the first addition of R_F to BXY_2 under formation of $[R_FBXY_2]^-$ we have to discuss two circumstances: (a) the adduct represents a stable entity or (b) the adduct is labile and looses spontaneously X^-. In case (a) X^- must be eliminated in a separate and specific reaction. We present here an example of option (b). We used $BCl(OMe)_2$ as electrophile and LiC_2F_5 as nucleophile with the highest reactivity available and counted on the experience that the chloride ion is a good nucleofuge. In agreement with Eq. (11b) we assumed the fast elimination of Cl^- from adduct **10** followed by a further addition of a C_2F_5 nucleophile under the formation of **11a**:

$$LiC_2F_5 + BCl(OMe)_2 \rightarrow \underset{\mathbf{10}}{Li_{solv}[C_2F_5BCl(OMe)_2]} \quad (11a)$$

$$Li_{solv}[C_2F_5BCl(OMe)_2] \rightarrow C_2F_5B(OMe)_2 + LiCl \quad (11b)$$

$$LiC_2F_5 + C_2F_5B(OMe)_2 \rightarrow \underset{\mathbf{11a}}{Li_{solv}[(C_2F_5)_2B(OMe)_2]} \quad (11c)$$

To avoid a negative influence of Et_2O, coordinated at Li^+ in **11a**, and to get a well-defined salt we carried out a metathesis reaction of **11a** with KF in the presence of water

and isolated the salt $K[(C_2F_5)_2B(OMe)_2]$ (**11b**) (Eq. (12)):

$$Li_{solv}[(C_2F_5)_2B(OMe)_2] + KF \xrightarrow{Et_2O,H_2O} \underset{\mathbf{11b}}{K[(C_2F_5)_2B(OMe)_2]} + LiF\downarrow \quad (12)$$

Compound **11b** was characterised by ^{19}F and ^{11}B NMR and its elemental analysis. The quintet of the ^{11}B, F^1 coupling and the shift value in the ^{11}B resonance are indicative for the presence of two C_2F_5 groups at boron and the anionic nature of the species. The substitution of both OMe groups by fluorine could not be achieved by 52% HF_{aq} within 4 days at ambient temperature (Eq. (13a)). Subsequent treatment with aHF at 20 °C over 24 h resulted in the desired salt $K[(C_2F_5)_2BF_2]$ (**12**) with 56.8% yield related to $BCl(OMe)_2$ (Eq. (13b)):

$$K[(C_2F_5)_2B(OMe)_2] + HF_{aq}\,(52\%) \rightarrow K[(C_2F_5)_2B(OMe)F] + MeOH \quad (13a)$$

$$K[(C_2F_5)_2B(OMe)F] + HF\,(aHF) \rightarrow \underset{\mathbf{12}}{K[(C_2F_5)_2BF_2]} + MeOH \quad (13b)$$

The purification of **12** for electrochemical measurements proceeded on an aqueous solution with charcoal. Compound **12** is soluble in H_2O, MeOH, Et_2O, and MeCN. The observed coupling constants ($^1J(B, F)$ = 64 Hz and $^2J(B, F^1)$ = 22 Hz) in the ^{11}B NMR signal at 0.1 ppm are in agreement with the constitution of the anion of **12**.

2.4. The introduction of the 2,3,5,6-tetrafluoropyrid-4-yl group into the hypervalent IF_2 triad of pentafluorophenyliodinedifluoride

Recently we have reported a convenient access to the class of fluorophenyl(pentafluorophenyl)iodonium tetrafluoroborate salts [14]. The salts $[C_6H_{5-n}F_n(C_6F_5)I][BF_4]$ with n = 0, 1, 2, 3, and 5 were obtained in good yields and high purity by the reaction of $C_6F_5IF_2$ with the boranes $C_6H_{5-n}F_nBF_2$ (Eq. (14)).

We used this method actually for the introduction of the 2,3,5,6-tetrafluoropyrid-4-yl group into the hypervalent IF_2 triad of $C_6F_5IF_2$. Here we have observed a principal deviation from Eq. (14). Despite of optimal local concentrations during the reaction (a very diluted (4-$C_5F_4N)BF_2$ solution in CH_2Cl_2 was added to ca. 15 times more concentrated $C_6F_5IF_2$ solution within 1 h under intensive stirring) and additionally a 45% stoichiometric excess of $C_6F_5IF_2$ we observed the fluoride acceptor product of **5** beside the transfer of the (4-C_5F_4N) group of **5** to I(III) under formation of the desired $[C_6F_5$(4-$C_5F_4N)I]^+$ cation. The mixture of $[BF_4]^-$ and [(4-$C_5F_4N)BF_3]^-$ anions (Eq. (15)) corresponded quantitatively to the new cation $[C_6F_5$(4-$C_5F_4N)I]^+$:

$$C_6F_5IF_2 + C_6H_{5-n}F_nBF_2 \xrightarrow{CH_2Cl_2} [C_6H_{5-n}F_n(C_6F_5)I][BF_4] \quad (14)$$

$$C_6F_5IF_2 + \underset{\mathbf{5}}{(4\text{-}C_5F_4N)BF_2} \xrightarrow{CH_2Cl_2} \underset{\mathbf{13a}\ (\text{main product})}{[C_6F_5(4\text{-}C_5F_4N)I][BF_4]} + \underset{\mathbf{13b}\ (\text{minor product})}{[C_6F_5(4\text{-}C_5F_4N)I][(4\text{-}C_5F_4N)BF_3]} \quad (15)$$

The formation of $[C_6F_5$(4-$C_5F_4N)I][$(4-$C_5F_4N)BF_3]$ (**13b**) beside $[C_6F_5$(4-$C_5F_4N)I][BF_4]$ (**13a**) indicates the strength of the Lewis acidity of **5**. This experimental result and the fact that BF_3 was not able to abstract fluoride from $[$(4-$C_5F_4N)BF_3]^-$ in comparison to the reactivity of $C_6F_5BF_2$ and $K[C_6F_5BF_3]$ allow the conclusion that (4-$C_5F_4N)BF_2$ is a stronger Lewis acid than $C_6F_5BF_2$. It is worthwhile to mention that until now we have no experimental hint for an intermolecular interaction of **5** in solutions by a N···B contact.

Principally, we were able to abstract a fluoride ion from the $[$(4-$C_5F_4N)BF_3]^-$ anion by interaction with AsF_5 in CH_2Cl_2 (Eq. (16a)).

$$\underset{\mathbf{13b}}{[C_6F_5(4\text{-}C_5F_4N)I][(4\text{-}C_5F_4N)BF_3]} + AsF_5 \xrightarrow{CH_2Cl_2} \underset{\mathbf{13c}}{[C_6F_5(4\text{-}C_5F_4N)I][AsF_6]} + (4\text{-}C_5F_4N)BF_2 \quad (16a)$$

$$(4\text{-}C_5F_4N)BF_2 + MeCN \xrightarrow{CH_2Cl_2} \underset{\mathbf{14}}{(4\text{-}C_5F_4N)BF_2 \cdot NCMe} \quad (16b)$$

2.5. The introduction of the trans-perfluoropropen-1-yl group into the hypervalent IF_2 triad of p-fluorophenyliodinedifluoride

Polyfluoroorganodifluoroboranes are unique reagents for the introduction of polyfluoroorgano groups (alkynyl, alkenyl, and aryl) into XeF_2 [15]. Under this acidic conditions the corresponding polyfluoroorganoxenonium tetrafluoroborates and in few cases polyfluoroorganoxenonium polyfluoroorganotrifluoroborates were obtained. *Trans*-2-X-CF=$CFBF_2$ showed a differentiated reactivity, depending on the nature of X. X = H, F, and Cl underwent xenodeboration whereas X = CF_3, C_4F_9, C_4H_9, and Et_3Si formed no Xe–C compounds. It should be mentioned that *cis*-X-CF=$CFBF_2$ (X = CF_3 and C_2F_5) underwent xenodeboration. The before summarised results cannot be rationalised by electronic effects. Instead of this we have discussed steric aspects in the transition state. We were interested to find out if the non-reactivity of *trans*-$R_FCF=CFBF_2$ towards XeF_2 could be generalised for other hypervalent F–E–F triads. Therefore we decided to investigate the reactivity of the related hypervalent triad

IF_2 in *p*-$FC_6H_4IF_2$ with *trans*-$CF_3CF{=}CFBF_2$. Equimolar amounts of *p*-$FC_6H_4IF_2$ and *trans*-$CF_3CF{=}CFBF_2$ reacted already at −78 °C and formed the new iodonium salt [*p*-FC_6H_4(*trans*-$CF_3CF{=}CF$)I][BF_4] (15) (Eq. (17)). The reaction temperature was ca. 20 °C lower than the known one for xenodeboration reactions with XeF_2. An obvious explanation for this phenomenon may be the lower partial charge on I(III) in *p*-$FC_6H_4IF_2$ compared with that of Xe^{II} in XeF_2 which makes the abstraction of F^- easier:

$$p\text{-}FC_6H_4IF_2 + trans\text{-}CF_3CF{=}CFBF_2 \xrightarrow[-78\,^\circ C]{CH_2Cl_2} [p\text{-}FC_6H_4\,(trans\text{-}\underset{\mathbf{15}}{CF_3CF{=}CF})\,I][BF_4] \quad (17)$$

The reaction (17) proceeded stereospecific under retention. In contrast to the majority of iodonium tetrafluoroborates salt **15** is soluble in the weakly coordinating solvent CH_2Cl_2. The significant high frequent ^{19}F NMR shift of $[BF_4]^-$ (δ = −142.5) of a CH_2Cl_2 solution of **15** indicates an intensive cation–anion interaction in solution. The application of such perfluoroalkyl containing iodonium salts for electrophilic alkenylation reactions are under investigation.

3. Conclusion

The aimed introduction of one or two polyfluoroorgano nucleophiles into a boron electrophile BX_3 cannot be achieved only by choosing the correct stoichiometry. In $B(OMe)_3$ the electrophilicity of the boron centre is sufficiently moderated and optimal conditions (local concentration, reaction temperature) for the individual polyfluoroorgano nucleophiles (LiR_f or R_fMgHal) suitable for mono(polyfluoroorgano) boron compounds can be elaborated. For bis(perfluoroorgano) boron compounds one good nucleofuge should be additionally present in the alkoxyborane, e.g. $BCl(OMe)_2$. Perfluoroorganodifluoroboranes are suitable reagents for introducing perfluoroorgano groups (2,3,5,6-tetrafluoropyridyl, *trans*-pentafluoropropen-1-yl) into the hypervalent triad F–I–F of aryliodinedifluorides RIF_2.

4. Experimental details

NMR spectra were recorded on the Bruker spectrometer AVANCE 300 (^1H at 300.13 MHz, ^{11}B at 96.29 MHz, ^{19}F at 282.40 MHz, ^{13}C at 75.47 MHz). The chemical shifts are referenced to TMS (^1H, ^{13}C), $BF_3{\cdot}OEt_2/CDCl_3$, 15% (v/v) (^{11}B), and CCl_3F (^{19}F) (C_6F_6 as a secondary reference, δ = −162.9). Apparent multiplicities are given in quotation marks. To describe couplings of complex structures unambiguously we have differentiated atoms of the aromatic group (F-4 means F bonded at C-4) from that of the alkyl or alkenyl group (F^1 means F bonded at C^1). *Cis*/*trans* is related to the position of the B-containing substituent in the parent compound. DSC measurements were made with a Netzsch 204/1/g Phoenix instrument. The samples were placed in aluminium pans with a pierced lid and measured under an atmosphere of N_2 in a temperature range of 20–120 °C. C, H elemental analysis was performed with a HEKAtech EA3000 analyzer.

$B(OMe)_3$ (Fluka) was distilled over sodium. $BCl(OMe)_2$ was obtained by dismutation of BCl_3 and $B(OMe)_3$ [16]. Arsenic pentafluoride was prepared from AsF_3 and elemental fluorine. Hydrogen fluoride was dried by electrolysis (stainless steel cell, Ni-electrodes). All manipulations with organodifluoroboranes and anhydrous HF (aHF) were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) equipment under an atmosphere of dry argon.

4.1. The synthesis of 2,3,5,6-tetrafluoropyrid-4-yl-difluoroborane

4.1.1. Preparation of 2,3,5,6-tetrafluoropyridine

In a 250 ml flask C_5F_5N (10.85 g, 64.2 mmol) and Zn powder (15.00 g, 229 mmol) were suspended in $NH_{3(aq)}$ (75 ml, 25%) and stirred for 6 h at 0 °C. After water vapour distillation 2,3,5,6-C_5HF_4N was separated from the aqueous phase and dried by molecular sieve 3 Å. 2,3,5,6-C_5HF_4N (7.04 g, 46.6 mmol) was isolated as colourless liquid (b.p. 98 °C) in 73% yield [7].

^{19}F NMR (Et_2O, 24 °C), δ: −91.5 (2F, m, F-2, 6), −140.5 (2F, m, F-3, 5).

4.1.2. Preparation of 2,3,5,6-tetrafluoropyrid-4-yllithium

An *n*-BuLi solution (2.5 m, 52 mmol in 20 ml hexanes and 20 ml ether) was added slowly within 30 min to the −78 °C cold and stirred solution of 2,3,5,6-C_5HF_4N (6.565 g, 43.46 mmol) in 60 ml Et_2O. The salmon-coloured solution was stirred for 1.5 h at −70 to −65 °C. A cold ^{19}F NMR sample indicated the end of the reaction.

^{19}F NMR (Et_2O–hexane, −60 °C), δ: −100.4 (2F, m, F-2, 6), −113.6 (2F, m, F-3, 5).

4.1.3. Preparation of lithium 2,3,5,6-tetrafluoropyrid-4-yl-trimethoxyborate

The −78 °C cold Li(4-C_5F_4N) solution described before was added (without warm-up) within 15 min under intensive stirring to the cold $B(OMe)_3$ solution (5.342 g, 51.41 mmol) in Et_2O (30 ml). During the addition the internal temperature never raised above −60 °C. Spontaneously a beige-coloured precipitation resulted. After 1.5 h a NMR sample of the mother liquor was taken in order to control the reaction. The reaction suspension was stirred for further 0.5 h before hydrolysis proceeded.

^{19}F NMR (mother liquor, −60 °C), δ: [(4-C_5F_4N)$B(OMe)_3$]$^-$ −95.2 (2F, "t", F-2, 6), −137.9 (2F, s, br, $\tau_{1/2}$ = 117 Hz, F-3, 5), [(4-$C_5F_4N)_2B(OMe)_2$]$^-$ −99.0 (2F, "t", F-2, 6), −135.5 (2F, "s", F-3, 5), 2,3,5,6-C_5HF_4N −90.7 (2F, "s", F-2, 6), −139.1 (2F, m, F-3, 5); molar ratio

6:3:1; ^{11}B NMR (mother liquor, −60 °C), δ: −3.8 (s, [(4-C_5F_4N)$B(OMe)_3]^-$), −4.6 (s, [(4-$C_5F_4N)_2B(OMe)_2]^-$).

4.1.4. Preparation of 2,3,5,6-tetrafluoropyrid-4-ylboronic acid

The −60 °C cold suspension, described before, was added within 5 min to an intensively stirred −40 °C cold solution of aqueous HCl (10%, 30 ml) in CH_3OH (30 ml). The cold ether phase was separated and the aqueous one extracted once more with 30 ml of Et_2O. The combined Et_2O phases were characterised by NMR at −60 °C. The aqueous phase contained $B(OH)_3$: ^{11}B NMR, δ: 19.0.

^{19}F NMR (ether, −60 °C), δ: (4-$C_5F_4N)B(OH)_2$ −93.2 (2F, m, F-2, 6), −134.2 (2F, m, F-3, 5), (4-$C_5F_4N)_2BOH$ −95.8 (2F, m, F-2, 6), −135.9 (2F, m, F-3, 5), 2,3,5,6-C_5HF_4N −91.1 (2F, "s", F-2, 6), −139.1 (2F, m, F-3, 5); molar ratio 96.8:3.1:0.1; ^{11}B NMR, δ: 26.0 (s, br, (4-$C_5F_4N)B(OH)_2$), 19.7 (s, br, (4-$C_5F_4N)_2BOH$).

4.1.5. Preparation of potassium 2,3,5,6-tetrafluoropyrid-4-yltrifluoroborate

The combined Et_2O phases (described above, −20 to 0 °C) were added to an intensively stirred 0 °C cold solution of K[HF_2] (11.00 g, 141 mmol) in H_2O (50 ml). A white solid precipitated. The mixture was slowly warmed to 20 °C and after 15 h the solid product was separated by vacuum filtration and dried in vacuum. After washing with water-saturated Et_2O (three times with 2 ml) the residue was dried in vacuum. The yield of K[(4-$C_5F_4N)BF_3$] with an admixture (9 mol%) of K[(4-$C_5F_4N)_2BF_2$] was 8.959 g.

^{19}F NMR (MeCN, 24 °C), δ: [(4-$C_5F_4N)BF_3]^-$ −97.3 (2F, m, F-2, 6), −135.2 (3F, qt, ^1J(B*F*, ^{11}B) = 42 Hz, ^4J(B*F*, F-2, 6) = 11 Hz, BF_3), −137.3 (2F, m, F-3, 5), [(4-$C_5F_4N)_2BF_2]^-$ −97.5 (4F, m, F-2, 6), −132.3 (2F, qquin, ^1J(B*F*, ^{11}B) = 50 Hz, ^4J(B*F*, F-2, 6) = 11 Hz, BF_2), −137.4 (4F, m, F-3, 5), $[BF_4]^-$ −150.37 (4F, s, ^{10}B*F*), −150.42 (4F, s, ^{11}B*F*), molar ratio 90.1:8.9:0.2; ^{11}B NMR (MeCN, 24 °C), δ: [(4-$C_5F_4N)BF_3]^-$ 1.2 (q, ^1J(*B*F) = 42 Hz, *B*F_3), [(4-$C_5F_4N)_2BF_2]^-$ 2.3 (t, ^1J(*B*F) = 50 Hz, *B*F_2), $[BF_4]^-$ −1.3 (s, *B*F_4).

Recrystallisation from boiling water and drying in vacuum afforded pure K[(4-$C_5F_4N)BF_3$] 7.8 g, 30.35 mmol, 70% related to 2,3,5,6-C_5HF_4N.

^{19}F NMR (MeCN, 24 °C), δ: [(4-$C_5F_4N)BF_3]^-$ −97.3 (2F, m, F-2, 6), −135.2 (3F, qt, ^1J(B*F*, ^{11}B) = 42 Hz, ^4J(B*F*, F-2, 6) = 11 Hz, BF_3), −137.3 (2F, m, F-3, 5); ^{11}B NMR (MeCN, 24 °C), δ: [(4-$C_5F_4N)BF_3]^-$ 1.2 (q, ^1J(*B*F) = 42 Hz, *B*F_3).

4.1.6. Preparation of 2,3,5,6-tetrafluoropyrid-4-yldifluoroborane

A sample of the before described product (0.565 g, 2.2 mmol) was suspended in CH_2Cl_2 (6 ml, −78 °C, FEP trap). At −78 °C AsF_5 (0.23 ml, 3.3 mmol) was condensed to the suspension which was then warmed to −60 to −55 °C and stirred for 3.5 h. Afterwards the suspension was degassed at −78 °C (two times under static and once under dynamic vacuum). The mother liquor was separated and the solid residue extracted with CH_2Cl_2 (three times with 5 ml) at 20 °C. The combined CH_2Cl_2 phases were stored at −78 °C in a FEP trap, well protected against moisture, before being used for further reactions. The yield was 1.4 mmol, 62% (determined with $C_6H_5CF_3$ as internal standard, ^{19}F NMR). Attempts to concentrate the CH_2Cl_2 solution at −60 to −40 °C in vacuum and crystallise (4-$C_5F_4N)BF_2$ at −78 °C were connected with a large loss of the volatile product.

^{19}F NMR (CH_2Cl_2, 24 °C), δ: −70.9 (2F, s, br, $\tau_{1/2}$ = 80 Hz, BF_2) −89.9 (2F, m, F-2, 6), −130.6 (2F, m, F-3, 5); ^{11}B (CH_2Cl_2, 24 °C), δ: 21.7 (s, br, $\tau_{1/2}$ = 78 Hz, *B*F_2).

4.2. The synthesis of 1H,1H,2H,2H-perfluoroctyldifluoroborane

4.2.1. Preparation of K[$C_6F_{13}C_2H_4BF_3$]

In a two-necked flask provided with a magnetic stirring bar, a reflux condenser and a P_4O_{10} drying tube on top one third of a $C_6F_{13}C_2H_4Br$ solution (5.21 g, 12.447 mmol) in Et_2O (10 ml) was dropped to Mg turnings (0.46 g, 18.93 mmol) under a dry argon atmosphere and warmed gently till the reaction started. The remaining two third of the $C_6F_{13}C_2H_4Br$ solution was diluted with 45 ml Et_2O and added to the Mg turnings. After 2 h of reflux the rate of reaction was monitored by ^{19}F NMR (57% of $C_6F_{13}C_2H_4Br$ was converted to $C_6F_{13}C_2H_4MgBr$ and 5% to $C_6F_{13}C_2H_5$). $(C_6F_{13}C_2H_4)_2$ as a further by-product was overlapping with $C_6F_{13}C_2H_4Br$.

In a 250 ml two-necked flask equipped with a magnetic stirring bar, an internal thermometer and a drying tube the cold (0 °C) mother liquor of the above described Grignard reagent was added slowly to a 0 °C cold solution of $BCl(OMe)_2$ (1.72 g, 15.86 mmol) and Et_2O (50 ml). The temperature did not exceed 5 °C. The resulting slightly yellow suspension was stirred for 1 h at 0 °C before being hydrolysed with 5% HCl_{aq} (35 ml). Two liquid phases resulted. The Et_2O phase was separated, the aqueous phase was extracted three times with 30 ml Et_2O. The combined Et_2O phases were dried over $MgSO_4$ before Et_2O was distilled off. The solid residue was suspended in MeOH (3 ml) and added to a solution of K[HF_2] (3.2 g, 40.75 mmol) in water (9.4 ml). Immediately a colourless waxy solid precipitated. After 15 min this solid was extracted with 8 ml Et_2O. Separation of the Et_2O phase was followed by three further extractions with 3 ml of Et_2O. Et_2O was removed from the combined ether extracts and a solid residue remained. The $C_6F_{13}C_2H_4X$ (X = H and $C_6F_{13}C_2H_4$) containing by-products were removed from the salt by sublimation at 50 °C in vacuum. The residue of the sublimation contained only K[$C_6F_{13}C_2H_4BF_3$] (^{19}F, ^{11}B, and ^{1}H NMR).

^{19}F NMR (CD_3NO_2, 24 °C), δ: −79.8 (3F, tt, ^4J(F^8, F^6) = 10 Hz, ^5J(F^8, F^5) = 3 Hz, F^8), −114.0 (2F, m, F^3), −120.5

(2F, m, F^5), −121.4 (2F, m, F^6). −122.1 (2F, m, F^4), −124.8 (2F, m, F^7, −141.5 (3F, br, $\tau_{1/2}$ = 144 Hz, BF_3); ^{1}H NMR (CD_3NO_2, 24 °C), δ: 2.0 (2H, m, H^1), 0.3 (2H, m, H^2); ^{11}B NMR (CD_3NO_2, 24 °C), δ: 7.9 (s, br, $\tau_{1/2}$ = 211 Hz, *B*F_3); ^{11}B NMR (acetone-d_6, 24 °C), δ: 5.0 (s, br, $\tau_{1/2}$ = 200 Hz, *B*F_3).

4.2.2. Preparation of $C_6F_{13}C_2H_4BF_2$

K[$C_6F_{13}C_2H_4BF_3$] (177 mg, 0.39 mmol) was suspended in CH_2Cl_2 (0.7 ml) at −50 °C in a FEP trap. BF_3 gas (8.3 mmol) was supplied under intensive stirring within 25 min. The appearance of the solid changed during the treatment with BF_3. After 1 h of stirring at 20 °C the excess of BF_3 was removed at −78 °C three times in static and once in dynamic vacuum. The mother liquor was separated after centrifugation. The solid residue was extracted three times with 0.5 ml of CH_2Cl_2. The content of $C_6F_{13}C_2H_4BF_2$ in the combined CH_2Cl_2 phase was determined with $C_6H_5CF_3$ as internal standard (^{19}F NMR): 0.20 mmol (52%). Removal of the solvent at ca. −50 °C in vacuum was connected with a larger loss of product. The boiling point of $C_6F_{13}C_2H_4BF_2$ was determined to 24 °C/2 × 10^{-2} hPa.

^{19}F NMR (CH_2Cl_2, 24 °C), δ: −73.8 (2F, s, br, $\tau_{1/2}$ = 218 Hz, BF_2), −81.6 (3F, tt, ^4J(F^8, F^6) = 10 Hz, ^5J(F^8, F^5) = 3 Hz, F^8), −116.6 (2F, m, F^3, −122.5 (2F, m, F^5), −123.5 (2F, m, F^6), −124.2 (2F, m, F^4), −126.8 (2F, m, F^7); ^{1}H NMR (CH_2Cl_2, 24 °C), δ: 1.5 (2H, m, H^1), 0.5 (2H, m, H^2); ^{11}B (CH_2Cl_2, 24 °C), δ: 27.5 (s, br, $\tau_{1/2}$ = 210 Hz, *B*F_2).

4.3. The synthesis of potassium bis(pentafluoroethyl)dimethoxyborate and potassium bis(pentafluoroethyl)difluoroborate

4.3.1. Preparation of K[$(C_2F_5)_2B(OMe)_2$]

A three-necked flask with a dry Ar-atmosphere equipped with an internal thermometer, and a magnetic stirring bar was charged with ether (120 ml) at −95 to −90 °C (acetone bath cooled with liquid N_2) before C_2F_5I (24 g, 38 mmol) was condensed. A MeLi solution in ether (20 ml, 1.6 m, 32 mmol) was added using a syringe within 15 min and keeping the temperature below −90 °C. After 30 min a $BCl(OMe)_2$ solution in hexane (1.5 g, 14 mmol, in 3.5 ml) was added in one portion to the white suspension using a syringe. The internal temperature increased up to a maximum of −85 °C. After 40 min at <−90 °C the bath was warmed to −78 °C for 3 h. Following the solution was warmed to 20 °C within 1 h and formed a suspension. KF (8 g, 138 mmol) and H_2O (20 ml) were added and stirring was continued for a further hour. The ether mother liquor was separated, the residue extracted with ether (three times 10 ml), the ether phases were combined and finally ether was removed under reduced pressure. A crystalline product (3.37 g, 69% yield of K[$(C_2F_5)_2B(OMe)_2$]) remained which was soluble in water and MeOH.

$C_6H_6BF_{10}KO_2$ (350.00): calculated (%): C 20.59, H 1.73; found (%) C 20.02, H 1.55.

^{19}F NMR (ether, 24 °C), δ: −82.5 (3F, s, br, CF_3), −125.6 (2F, q(unresolved), CF_2); ^{11}B NMR (ether, 24 °C), δ: −2.1 (quin, ^2J(B, F^1) = 15 Hz).

4.3.2. Preparation of K[$(C_2F_5)_2BF_2$]

K[$(C_2F_5)_2B(OMe)_2$] was treated with 52% HF_{aq} (40 ml) at 20 °C for 4 days. The solution was neutralised with KOH and saturated with KF before being extracted with ether. After removal of the ether an oily product (2.73 g) remained which was stirred with 7 ml aHF in a plugged FEP trap at 20 °C for 24 h. HF and volatile by-products were removed under reduced pressure and the solid residue was dissolved in 10 ml water and treated with charcoal (0.5 g). After filtration the residue was washed with water (10 ml) and the combined aqueous phases which showed an acidic reaction were neutralised with KOH and saturated with KF and finally extracted with ether (five times 10 ml). After removing of ether 2.59 g (7.95 mmol, 56.8%) of solid K[$(C_2F_5)_2BF_2$] were isolated. K[$(C_2F_5)_2BF_2$] is soluble in H_2O, MeOH, Et_2O, and MeCN.

Purification of K[$(C_2F_5)_2BF_2$] proceeded by dissolution in water and treatment with charcoal. Water was distilled off from the aqueous filtrate and the white solid residue was dried in a vacuum desiccator over P_4O_{10} for 2 days.

^{19}F NMR (ether, 24 °C), δ: −82.9 (6F, tm, ^3J(F^2, F^1) = 6 Hz, CF_3), −134.8 (4F, m (unresolved), CF_2), −175.0 (2F, m, ^1J(B*F*, ^{11}B) = 64 Hz, BF_2); ^{11}B (ether, 24 °C), δ: 0.1 (tquin, ^1J(B, F) = 64 Hz, ^2J(B, F^1) = 22 Hz; ^{13}C (D_2O, 24 °C), δ: 122.6 (qt, ^1J(C^2, F^2) = 285 Hz, ^2J(C^2, F^1) = 32 Hz, C^2), 120.5 (s, br, $\tau_{1/2}$ = 440 Hz, C^1).

4.4. The introduction of the 2,3,5,6-tetrafluoropyrid-4-yl group into the hypervalent IF_2 triad of pentafluorophenyliodinedifluoride

4.4.1. Pentafluorophenyl(2,3,5,6-tetrafluoropyrid-4-yl)iodonium tetrafluoroborate

A solution of (4-C_5F_4N)BF_2 (43 mg, 0.22 mmol) in CH_2Cl_2 (0 °C, 20 ml) was added within 1 h to a CH_2Cl_2 solution (0 °C, 2 ml) of $C_6F_5IF_2$ (107 mg, 0.32 mmol). Spontaneously a greenish solid was formed. After 1.5 h of stirring at 0 °C the mother liquor was separated and the solid residue was washed with CH_2Cl_2 (0 °C, 5 ml) and dried in vacuum and finally at 20 °C for 0.5 h. During this procedure the colour of the solid became white. The dissolution of the solid product in MeCN revealed a mixture (^{19}F NMR).

^{19}F NMR (MeCN, 24 °C), δ: [C_6F_5(4-C_5F_4N)I]$^+$ −84.3 (2F, m, F-2, 6, (4-C_5F_4N)), −119.7 (2F, m, F-2, 6, C_6F_5), −123.1 (2F, m, F-3, 5, (4-C_5F_4N)), −140.6 (1F, tt, ^3J(F-4, F-3, 5) = 20 Hz, ^4J(F-4, F-2, 6) = 7 Hz, F-4, C_6F_5), −155.1 (2F, m, F-3, 5, C_6F_5), [(4-C_5F_4N)BF_3]$^-$ −97.3 (2F, m, F-2, 6), −134.2 (3F, qt, ^1J(B*F*, ^{11}B) = 42 Hz, ^4J(B*F*, F-2, 6) = 12 Hz, B*F*), −137.3 (2F, m, F-3, 5), [BF_4]$^-$ −148.5 (s, br, B*F*), C_6F_5I −120.1 (2F, m, F-2, 6, C_6F_5), −153.4 (1F, t, ^3J(F-4, F-3, 5) = 19 Hz, F-4, C_6F_5), −160.1 (2F, m, F-3, 5, C_6F_5); molar ratio 98:21:77:2.

4.4.2. Pentafluorophenyl(2,3,5,6-tetrafluoropyrid-4-yl)iodonium hexafluoroarsenate

MeCN of the above-described solution was removed in vacuum and the resulting white solid was suspended in CH_2Cl_2 (−78 °C, 1 ml). Following AsF_5 (ca. 0.04 ml, 0.6 mmol) was condensed into the cold suspension. After 3 h of stirring finally at −60 °C the mixture was degassed at −78 °C (three times under static and 10 min under dynamic vacuum). After centrifugation the mother liquid was decanted and the solid residue was dissolved in MeCN.

^{19}F NMR (CH_3CN, 24 °C), δ: $[C_6F_5(4\text{-}C_5F_4N)I]^+$ −84.2 (2F, m, F-2, 6, (4-C_5F_4N)), −119.8 (2F, m, F-2, 6, C_6F_5), −123.2 (2F, m, F-3, 5, (4-C_5F_4N)), −140.5 (1F, tt, ^3J(F-4, F-3, 5) = 20 Hz, ^4J(F-4, F-2, 6) = 7 Hz, F-4, C_6F_5), −155.0 (2F, m, F-3, 5 C_6F_5), $[AsF_6]^-$ −64.5 ((1:1:1:1)q, ^1J(F, ^{75}As) = 930 Hz), $[BF_4]^-$ −148.8 (s, br, B*F*), (4-C_5F_4N)BF_2·CH_3CN −96.1 (2F, m, F-2, 6, (4-C_5F_4N)), −137.4 (2F, m, F-3, 5, (4-C_5F_4N)), −142 (2F, s, br, B*F*); molar ratio 85:82:3:15.

4.5. The introduction of the trans-perfluoropropen-1-yl group into the hypervalent IF_2 triad of p-fluorophenyliodinedifluoride: synthesis of p-fluorophenyl(trans-1,2,3,3,3-pentafluoropropen-1-yl)iodonium tetrafluoroborate

p-$FC_6H_4IF_2$ (797 mg, 3.06 mmol) was dissolved in CH_2Cl_2 (15 ml) at −60 °C in a 23 mm FEP trap provided with a suitable stirring bar. Under strong stirring *trans*-$CF_3CF{=}CFBF_2$ (532 mg, 2.96 mmol) was added as cold CH_2Cl_2 solution (15 ml, −78 °C) in 8–10 equal portions within 30 min. The resulting suspension was stirred for further 0.5 h. The mother liquor was separated from the light yellowish solid. The solid was washed with CH_2Cl_2 (two times with 5 ml) at −50 °C to remove the slight excess of *p*-$FC_6H_4IF_2$. The iodonium salt was dried at −78 °C in high vacuum. The mother liquor and the CH_2Cl_2 solution from washing were combined, evaporated in vacuum (−60 to −50 °C), and the solid residue was washed with *n*-pentane (three times with 5 ml) to remove non-reacted *p*-$FC_6H_4IF_2$. Five hundred milligrams of the iodonium salt (1.14 mmol, 38.5%) was obtained from the primary precipitation and 602 mg (1.37 mmol, 46.3%) from the mother liquor. The overall yield was 1102 mg (2.51 mmol, 84.8%). The melting point was 90–91 °C. A DSC measurement showed an endothermic process with T_{onset} = 92.2 °C. The salt was stored under dry argon at 20 °C for more than 6 months without decomposition.

^{19}F NMR (CH_2Cl_2, 24 °C): δ: −68.6 (3F, dd, ^3J(F^3, F^2) = 19 Hz, ^4J(F^3, F^1) = 11 Hz, C*F*$_3$), −101.4 (1F, tt, ^3J(F-4, H-3, 5) = 8 Hz, ^4J(F-4, H-2, 6) = 4 Hz, F-4), −120.8 (1F, dq, ^3J(F^2, F^1) = 142 Hz, ^3J(F^2, F^3) = 19 Hz, F^2), −140.2 (1F, dq, ^3J(F^1, F^2) = 142 Hz, ^4J(F^1, F^3) = 11 Hz, F^1), −142.5 (4F, s, B*F*$_4$); ^{1}H NMR (CH_2Cl_2, 24 °C): δ: 8.4 (2H, td, ^3J(H-2, 6, H-3, 5) = 9 Hz, ^4J(H-2, 6, F-4) = 5 Hz, H-2, 6), 7.5 (2H, td, ^3J(H-3, 5, H-2, 6) = 9 Hz, ^3J(H-3, 5, F-4) = 8 Hz, H-3,5); ^{11}B NMR (CH_2Cl_2, 24 °C): δ: −2.2 (s, *B*F_4); ^{13}C{^{1}H} NMR (CH_2Cl_2, 24 °C): δ: 166.3 (d, ^1J(C-4, F-4) = 259 Hz, C-4), 144.2 (dqd, ^1J(C^2, F^2) = 266 Hz, ^2J(C^2, F^3) = 43 Hz, ^2J(C^2, F^1) = 31 Hz, C^2), 139.9 (d, ^3J(C-2, 6, F-4) = 10 Hz, C-2, 6), 125.0 (ddq, ^1J(C^1, F^1) = 350 Hz, ^2J(C^1, F^2) = 63 Hz, ^3J(C^1, F^3) = 3 Hz, C^1), 121.1 (d, ^2J(C-3, 5, F-4) = 23 Hz, C-3, 5), 116.0 (qdd, ^1J(C^3, F^3) = 277 Hz, ^2J(C^3, F^2) = 36 Hz, ^3J(C^3, F^1) = 5 Hz, *C*F_3), 104.4 (s, C-1).

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