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FULL PAPER

Convenient Preparation and Structure Determination of Air- and Moisture-Tolerant Difluoromethylborates

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Dedication ((optional))

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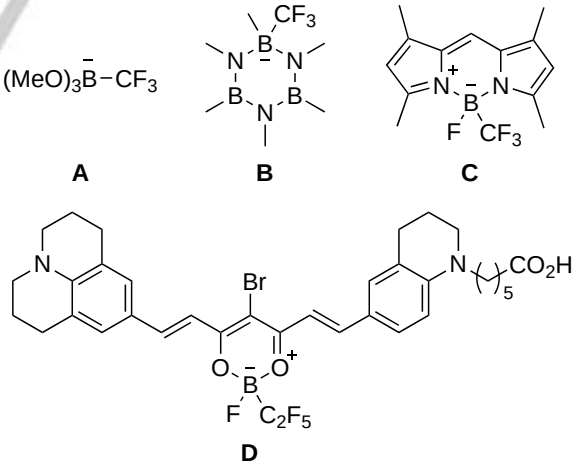
Abstract: Convenient and reliable synthetic methods for difluoromethylborates have been established. The intermediary generated difluoromethylsilicate species from $TMSCF_2H$ (TMS = trimethylsilyl) and potassium *tert*-butoxide were allowed to react with pinBPh ($Me_4C_2O_2BPh$) in the presence of 18-crown-6 to give the corresponding borate compound $[pinB(Ph)CF_2H]^-K^+$(18-crown-6) as an air- and moisture-tolerant solid. The unambiguously determined crystal structure of $[pinB(Ph)CF_2H]^-K^+$(18-crown-6) revealed that the difluoromethylborate unit partially coordinating on the potassium ion. Reaction of $[pinB(Ph)CF_2H]^-K^+$(18-crown-6) with potassium difluoride (KHF_2) in acetic acid enabled substitution of the pinacol unit and phenyl group with fluorides, and gave (difluoromethyl)trifluoroborate $[F_3BCF_2H]^-K^+$(18-crown-6) in a good yield. The crystal structure of air- and moisture-tolerant $[F_3BCF_2H]^-K^+$(18-crown-6), which would be a promising reagent for synthesis of various difluoromethylboron species, showed a polyrotaxane-like polymeric structure based on the K···F interactions between the K^+(18-crown-6), CF_2H, and BF_3 units.

Introduction

Developing synthetic methodologies for organofluorine compounds has been important because introduction of the fluorinated functional groups has been quite useful for medicinal, agrochemical, and materials researches. The introduction of fluoro-functional groups into the lead or seed organic compounds has been one of the required approaches to improve/express the desired properties.[1] For example, the C–F bond length of 1.39 Å is much smaller than that of the C–C bond of 1.54 Å, and is comparable with the C–O bond. Such structural property of the C–F bond has been utilized as an isosteric and isopolar replacement for the hydroxy (OH) group in biologically relevant molecules. Similarly, the difluoromethyl (CF_2H) group has been used as isosteric and isopolar replacement with respect to carbonyl group, and furthermore, bioisosteric and isopolar with respect to the hydroxy and thiohydroxy (SH) groups. In addition, the difluoromethyl-substituted compounds exhibit enhanced hydrophobicity and lipophilicity leading to unique physicochemical and biological properties.[2]

Also, chemistry of organoboron compounds has been of great interest from the views of organic synthesis[3] and materials science.[4] Recently, boron compounds bearing the fluoroalkyl group(s) are of interest and useful for novel synthetic methodologies and materials development. Figure 1 shows examples of perfluoroalkylborates. Trimethoxy(trifluoromethyl) borate **A**[5] can be utilized for copper-mediated trifluoromethylation of aryl iodides[5a,b] and nucleophilic trifluoromethylation.[5c] Besides CF_3, various perfluoroalkyl groups are available to construct the corresponding trimethoxy(perfluroalkyl)borates[5b] and the related boron compounds.[6] The CF_3-borazine derivative **B** can be prepared via activation of fluoroform (HCF_3) and is useful as a CF_3^- source.[7] The BODIPY derivative **C** would be useful as a fluorescent material.[8] The boron 1,3-diketonate **D** works as a biocompatible oxidation catalyst of amyloid peptide under near-infrared light irradiation.[9]



A B C D

Figure 1. Examples of perfluoroalkylated borates.

On the other hand, examples of the difluoromethyl-substituted borate derivatives have been limited so far. Reaction of icosahedral dicarba-closo-dodecaborane with difluorocarbene was reported in 1987.[10] Recently, Szymczak and co-workers synthesized difluromethylborazine **E** and azaborinines **F** via activation of difluoromethane (Figure 2).[11] In contrast to **B**, **E** did

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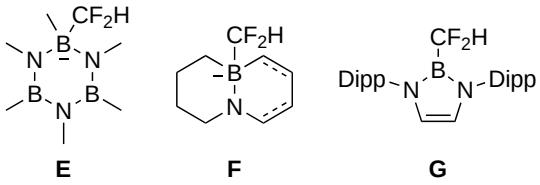
not work as the fluoroalkyl source well, and only the unsaturated version of **F** permitted transfer of CF_2H^- into the palladium(II) centre.



E **F** **G**

Figure 2. Difluromethylborates **E** and **F**, and difluoromethylborane **G**. Dipp = 2,6-*i*Pr$_2$C$_6$H$_3$.

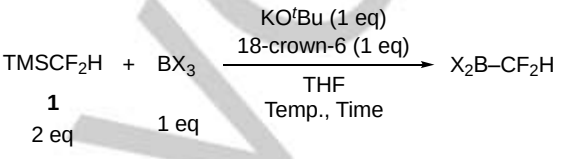
The limited examples of difluoromethylborates prompted us to synthesize novel CF_2H-substituted borates that are useful for synthesis of difluoromethyl-substituted compounds. In addition, the BCF_2H moiety would be useful for developing biologically relevant molecules. We previously reported synthesis of the difluoromethylboron compound **G** by using the borylanion for the C–F activation process,[12] but conversion of **G** into the corresponding borates have been difficult probably due to the sterically bulky N-containing unsaturated heterocyclic system protecting the B–CF_2H unit. Therefore, we decided to explore alternative and reliable synthetic methods for difluoromethylborates.

In this paper, we demonstrate efficient and convenient synthetic procedures for novel difluoromethylborates that are promising for developing novel difluromethylation and functional difluoromethylboron compounds. Crystal structures of the difluoromethylborate derivatives showing such as the polyrotaxane-like assembly are also discussed.

Results and Discussion

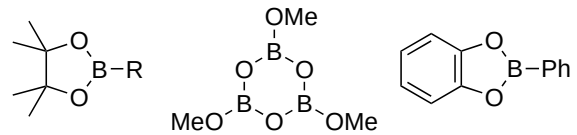
In the synthesis of **A**, trifluoromethyltrimethylsilane (Ruppert-Prakash reagent, $TMSCF_3$) has been utilized. Analogously, we commenced to examine reactions of difluoromethyltrimethylsilane (**1**) and $B(OMe)_3$ (**2a**) in the presence of potassium *tert*-butoxide (KO^tBu) and 18-crown-6[13] over the period of 2 h. In these conditions, the desired difluoromethylborate compound was not obtained, and the decomposition product (difluoromethane, CF_2H_2) was observed in the reaction mixture (Table 1, Entry 1). Screening the base reagents for reaction of **1** and **2a** resulted in fail (Table S1). Because **2a** was not suitable for synthesis of difluoromethylborates, we next employed several boron reagents in the presence of **1**, KO^tBu, and 18-crown-6. As shown in Table 1, pinBO^iPr (**2b**) methoxy boroxine (**2c**), $B(OPh)_3$ (**2d**), and catBPh (**2e**) did not give the corresponding difluoromethylborate compounds (Entries 2-5). On the other hand, to our delight, reaction of **1** with pinBPh (**2f**) gave the desired difluoromethylation product **3** in 80% yield (Entry 6). Screening the temperatures was successful (Entries 7,8) to improve the yield up to 86% (Entry 7), indicating that the temperatures between –40 °C to 0 °C were suitable for the interaction between **2f** and the difluoromethylsilicate species. Reduction of the amount of **1** reduced the yield (Entry 9), indicating that only the bis(difluoromethyl)silicate $[Me_3Si(CF_2H)_2]^-$ intermediate[13] might be responsible to provide the difluoromethylborate product. Subsequent screening of the reaction time (Entries 10-13) concluded that the reaction time of 1 h was optimal for the reaction of **2** and the $[Me_3Si(CF_2H)_2]^-$ intermediate, and **3** was generated almost quantitatively and isolated in 82% yield (Entry 11). Reduction of the reaction time decreased the yield of **3** (Entries 12, 13). The reaction in the absence of 18-crown-6 could not generate **3** probably due to the instability of $[Me_3Si(CF_2H)_2]^-$ (Entry 14). Attempted synthesis of **3** by using **E** and **2f** has been unsuccessful.

Table 1. Reactions of difluoromethyltrimethylsilane (**1**) and boron reagents.



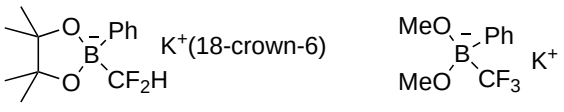
Entry[j]	BX_3	Temp.	Time	Result
1	$B(OMe)_3$ (**2a**)	–78 °C	2 h	decomp.
2	pinB-O^{i}Pr(**2b**)	–40 °C to r.t.	2 h	decomp.
3	**2c**	–40 °C to r.t.	2 h	decomp.
4	$B(OPh)_3$ (**2d**)	–40 °C to r.t.	2 h	decomp.
5	catB-Ph (**2e**)	–40 °C to r.t.	2 h	decomp.
6	pinB-Ph (**2f**)	–40 °C to r.t	2 h	**3** (80% yield)[a]
7	**2f**	–40 °C to 0 °C	2 h	**3** (86% yield)[a]
8	**2f**	–40 °C to –20 °C	2 h	**3** (68% yield)[a]
9	**2f**[b]	–40 °C to r.t	2 h	**3** (30% yield)[a]
10	**2f**	–40 °C to 0 °C	1.5 h	**3** (82% yield)[a]
11	**2f**	–40 °C to 0 °C	1 h	**3** (97 yield)[a,c]
12	**2f**	–40 °C to 0 °C	30 min	**3** (68% yield)[a]
13	**2f**	–40 °C to 0 °C	15 min	**3** (76% yield)[a]
14	**2f**[d]	–40 °C to r.t.	2 h	decomp.

[a] Determined by ^{19}F NMR. [b] 1 eq of **1** was used. [c] 82% isolated yield. [d] Without 18-crown-6.



2b: R = O^{i}Pr
2f: R = Ph

2c **2e**



3 **4**

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The difluoromethylborate-potassium salt **3** is a colorless crystalline compound, and can be handled in air and moisture. In contrast to **A**, **3** was not hygroscopic. The structure of **3** was characterized by the spectroscopic data. Furthermore, recrystallization from toluene and hexane was successful, and the crystal structure of **3** was confirmed by X-ray diffraction analysis (Figure 3). Whereas all the oxygen and fluorine atoms in **4** showed interactions with the potassium cations in the crystalline state,[14] only two heteroatoms in the pinBCF$_2$H unit of **3** coordinate on the K$^+$(18-crown-6) ion. One of the oxygen atoms in the 5-membered ring (O1) coordinates on the potassium ion, and correspondingly the B1–O1 distance is elongated compared with the B1–O2 bond. The C1–F1 distance is slightly larger than the C1–F2 length due to the F1···K1 interaction.

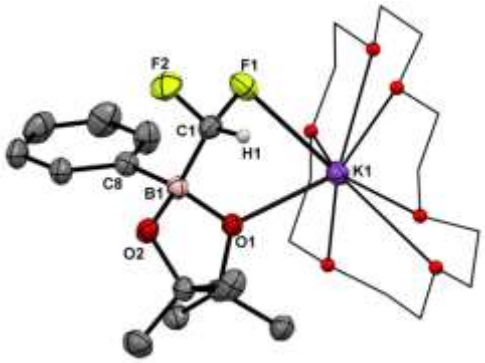
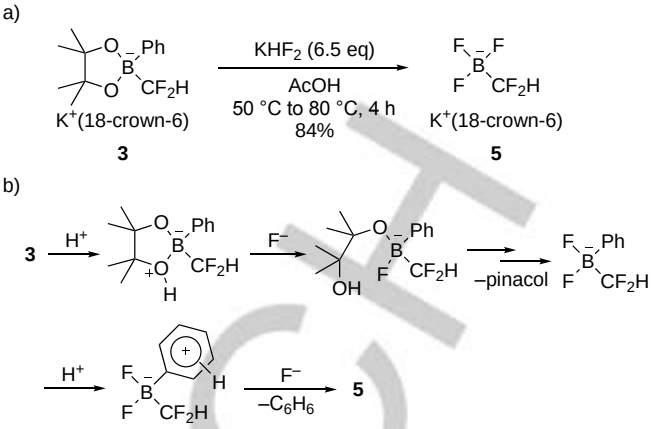


Figure 3. Molecular structure of **3** (40% probability level). Hydrogen atoms except for H1 are omitted for clarity. The oxygen atoms in the crown ether ring are displayed as reddish balls. Selected bond lengths (Å): B1–C1 1.619(7), B1–C8 1.624 (6), B1–O1 1.498(6), B1–O2 1.475(6), C1–F1 1.406(5), C1–F2 1.399(5), O1–K1 2.637(3), F1–K1 3.020(3).

The difluoromethylborate-potassium salt **3** is a promising reagent for the difluoromethylation reactions. Also, **3** would be useful for synthesis of organoboron compounds bearing the BCF$_2$H unit(s). In this study, we attempted conversion of the pinBPh unit in **3** affording the BF$_3$ moiety. To our delight, treatment of **3** with potassium bifluoride (KHF$_2$) in acetic acid afforded the desired product **5** in a good yield (Scheme 1a). In this reaction, even the phenyl group was eliminated as benzene probably due to the proton, and the substitution reaction with fluorides proceeded to give the trifluoroborate unit (Scheme 1b). The (difluoromethyl)trifluoroborate-potassium salt **5** is an air- and moisture-tolerant solid, and no decomposition of crystalline **5** was observed under 1 week exposure to air and moisture.



Scheme 1. A) Preparation of (difluoromethyl)trfluoroborate **5** from **3**. b) Possible reaction mechanisms for the substitution process providing **5** under the acidic conditions.

The structure of **5** was characterized by the spectroscopic data. Table 2 indicates that the experimentally determined NMR parameters of **5** are comparable with the GIAO chemical shifts of [F$_3$BCF$_2$H]$^-$. Thus, **5** would provide the (difluoromethyl)trifluoromethyl anion in the homogeneous solution. Furthermore, the crystal structure of **5** was confirmed by X-ray diffraction analysis. Figure 4a displays the principal unit for the one-dimensional polymeric structure of **5** in the crystalline state. Both the CF$_2$H and BF$_3$ groups interact with the potassium ions to generate the string, and the 18-crown-6 rings construct the polyrotaxane-like structure (Figure 4b). Two fluorine atoms in the BF$_3$ unit interact with the potassium ion. The potassium-coordinated fluorine atoms in the difluoromethyl groups are disordered, and the metric parameters should not be discussed in detail. Nevertheless, it is obvious that the one-dimensional coordination polymer structure is constructed by the F···K interactions. In addition, the crystal structure of **5** would be helpful not only to understand the physical and chemical properties but also to design novel functional materials based on the linearly assembled difluoromethylboron units accompanying the 18-crown-6 rings.

Table 2. Experimental NMR chemical shifts and GIAO results for **5**

	Experimental[a]	GIAO[b]
δ_F (CF$_2$H)	–141.2[c]	–149.8
δ_F (BF$_3$)	–156.7	–169.5
δ_B	–0.53[d]	–1.06
δ_H (CF$_2$H)	5.55	5.53

[a] In $CDCl_3$ at 298 K. [b] [BF$_3$CF$_2$H]$^-$: ωB97XD/6-311++G(2d,p)//ωB97XD/6-311+G(d), IEFPCM = chloroform. [c] Average of –141.9 - –142.5 (m). [d] Average of +0.76 - –1.29 (m).

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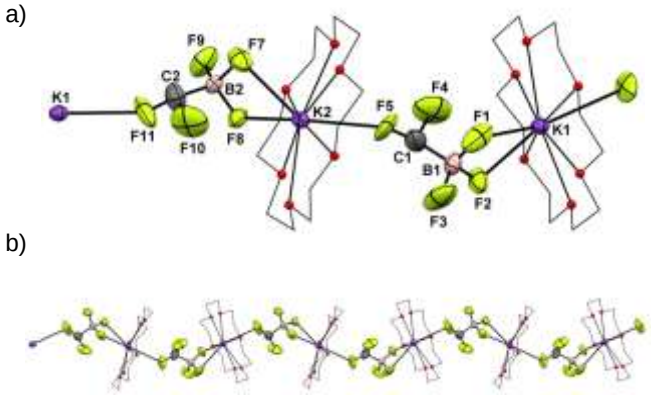

Figure 4. a) A drawing of the principal unit of **5** (40% probability level). Hydrogen atoms are omitted for clarity. The oxygen atoms in the crown ether ring are displayed as reddish balls. The potassium-coordinated fluorine atoms in the CF_2H groups are disordered, and one of the atoms are displayed. b) Coordination polymer structure along the *a* axis.

Conclusion

In conclusion, we have developed convenient and reliable synthetic methods for difluoromethylborates. Using $TMSCF_2H$ (**1**) and pinBPh (**2f**) as the difluoromethyl and borate source, respectively, reaction in the presence of potassium *tert*-butoxide and 18-crown-6 provided the air- and moisture-tolerant crystalline difluoromethylborate-potassium salt $[pinB(Ph)CF_2H]^-K^+$(18-crown-6) (**3**). The structure of **3** was unambiguously determined. Reaction of **3** with potassium difluoride under the acidic conditions provided the (difluoromethyl)trifluoroborate-potassium salt $[F_3BCF_2H]^-K^+$(18-crown-6) (**5**). The X-ray diffraction data of **5** revealed the polyrotaxane-like pone-dimensional polymer structure via the K···F interactions accompanying the 18-crown-6 rings. Attempted difluoromethylation and synthesis of difluoromethylboron compounds starting from **3** and **5** are in progress.

Experimental Section

All experiments were carried out under inert atmosphere (argon) unless otherwise noted. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{11}B NMR spectra were measured on a Bruker Avance 300 spectrometer. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from $CHCl_3$ as an internal standard (δ = 7.26) in $CDCl_3$, C_6H_6 as an internal standard (δ = 7.16) in C_6D_6. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard (δ = 77.16) in $CDCl_3$, C_6D_6 as an internal standard (δ = 128.4). Chemical shifts of ^{19}F NMR were expressed in parts per million downfield from benzotrifluoride as an internal standard (δ = –63.24) in $CDCl_3$. Chemical shifts of ^{11}B NMR were expressed in parts per million downfield from BF_3/OEt_2 as an external standard (δ = 0) in $CDCl_3$. Mass spectra were measured on a JEOL JMS-T100LC spectrometer. $TMSCF_2H$ (**1**) was prepared from $TMSCF_3$ according to the literature.[15] X-ray diffraction data were measured on a Rigaku RAXIS-RAPID diffractometer. The structures were solved by a direct method (SHELXL-2014).[16] The X-ray structure solution and refinement were carried out using the Yadokari-XG software.[17] Density Functional Theory (DFT) calculations were carried out using Gaussian 09 (B.01) package.[18]

Preparation of **3**: (Difluoromethyl)trimethylsilane (**1**, 280 µL, 2.0 mmol) and 18-crown-6 (264 mg, 1.0 mmol) were dissolved in 1 mL THF and cooled to –60 °C. Potassium *tert*-butoxide (112 mg, 1.0 mmol) was added in one portion, and the mixture rapidly stirred for 20 min. 4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (**2f**, 204 mg, 1.0 mmol) was added and the solution stirred at 0 °C for 1 h. The solution was poured into 20 mL hexane and stirred at room temperature for 5 min. The suspension was filtered and washed with hexane (20 mL x 2) twice. After the residue was dried *in vacuo,* recrystallization from toluene to afford the title compound as colorless needles (452 mg, 82%). Single crystals for X-ray crystallography were obtained by recrystallization from toluene/hexane (1:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.98 (s, 6H), 1.19 (s, 6H), 3.55 (s, 24H), 5.68 (t, $^2J_{HF}$ = 50.6 Hz, 1H), 6.97–7.13 (m, 3H), 7.67–7.69 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –132.1 (d, $^2J_{FH}$ = 50.0 Hz); ^{11}B{^{1}H} NMR ($CDCl_3$, 96 MHz) δ 2.92 (brs); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 26.5, 26.6, 70.0, 78.3, 123.8, 125.9, 132.7 (CF_2H and C_{ipso} were not determined). HRMS (ESI) calcd for $C_{37}H_{66}BO_{14}F_2K_2$ $[M+K(C_{12}H_{24}O_6)]^+$ 861.3788, found 861.3927.

Preparation of **5**: A solution of KHF_2 (240 mg, 3.1 mmol) and **3** (279 mg, 0.50 mmol) in glacial acetic acid (3 mL) was stirred at 50 °C for 1 h and then for 3 h at 80 °C. All volatiles were removed *in vacuo*. The solution was poured into 20 mL hexane and stirred at room temperature for 5 min to remove residual AcOH. The suspension was filtered and washed with hexane. After the residue was dried *in vacuo,* to the residue was added CH_2Cl_2 (10 mL). The resulting suspension was filtered through a pad of Celite. After the solvent was removed *in vacuo*, **5** was obtained as colorless powder (177 mg, 84%). Single crystals of **5** were obtained by adding hexane to diffuse into a saturated solution of **5** in CH_2Cl_2. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.55 (t, $^2J_{HF}$ = 48.9 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ –141.9 - –142.5 (m, 2F), –156.7 (q, $^1J_{FB}$ = 47.4 Hz, 3F); ^{11}B{^{1}H} NMR ($CDCl_3$, 96 MHz) δ 0.76 - –1.29 (m); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 70.2 (CF_2H was not determined); HRMS (ESI) calcd for $C_{25}H_{49}BO_{12}F_5K_2$ $[M+K(C_{12}H_{24}O_6)]^+$ 725.2511, found 725.2478.

X-ray crystallographic data of **3**: $C_{25}H_{42}BF_2KO_8$ M_W = 558.49, crystal dimensions = 0.240 x 0.190 x 0.180 mm^3, orthorhombic, *P*na2$_1$ (#33), *a* = 25.3335(13), *b* = 11.0549(5), *c* = 10.5058(5) Å, *V* = 2942.2(2) Å^3, *Z* = 4, *T* = 166 K, λ = 0.71075 Å, ρ_{calc} = 1.261 g m^{-3}, $\mu_{MoK\alpha}$ = 0.236 mm^{-1}, F_{000} = 1192, –32≤*h*≤32, –14≤*k*≤14, –13≤*l*≤13, 46413 total reflections ($2\theta_{max}$ = 54.97°), 6652 unique (R_{int} = 0.1068), *R* = 0.0552 (σ>2σ(*I*)), 0.0847 (all data), w*R*2 = 0.1379 (σ>2σ(*I*)), 0.1513 (all data), *S* = 0.788 (338 parameters). CCDC-2017876.

X-ray crystallographic data of **5**: $C_{13}H_{25}BF_5KO_6$ M_W = 422.24, crystal dimensions = 0.230 x 0.210 x 0.090 mm^3, monoclinic, *P*2$_1$/c (#14), *a* = 15,6623(11), *b* = 16.2557(11), *c* = 17.1082(18) Å, β = 117.174(2)°, *V* = 3875.0(6) Å^3, *Z* = 8, *T* = 172 K, λ = 0.71075 Å, ρ_{calc} = 1.448 g m^{-3}, $\mu_{MoK\alpha}$ = 0.346mm^{-1}, F_{000} = 1760, –18≤*h*≤20, –21≤*k*≤20, –22≤*l*≤22, 60325 total reflections ($2\theta_{max}$ = 54.97°), 8615 unique (R_{int} = 0.0474), *R* = 0.0666 (σ>2σ(*I*)), 0.1041 (all data), w*R*2 = 0.1608 (σ>2σ(*I*)), 0.1890 (all data), *S* = 1.053 (489 parameters). CCDC-2017877.

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Keywords: difluoromethyl compounds • borates • substitution reactions • crystal structures • coordination polymers

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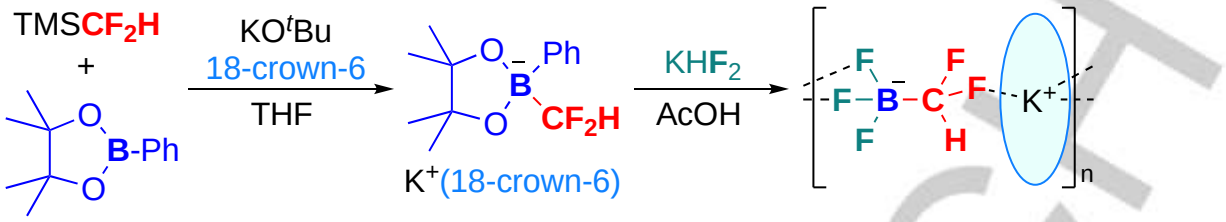

The difluoromethylsilicate species, generated from $TMSCF_2H$ and KO^tBu, reacts with pinB-Ph in the presence of 18-crown-6 to give $[pinB(Ph)CF_2H]^-K^+$(18-crown-6) as an air- and moisture-tolerant solid. Reaction of $[pinB(Ph)CF_2H]^-K^+$(18-crown-6) with KHF_2 in acetic acid gave the difluoromethylated trifluoroborate $[F_3BCF_2H]^-K^+$(18-crown-6) showing the polyrotaxane-like linear structure.

Institute and/or researcher Twitter usernames: ((optional))