(Fluoroorgano)fluoroboranes and -borates. 12. Reactions of (Trifluorovinyl)lithium with Chloro-, Chloromethoxy-, and (Trifluorovinyl)methoxyboranes, a Useful Route to (Trifluorovinyl)fluoroborate Salts

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Reactions of $LiCF{=}CF_2$ with the boron electrophiles $BCl(OMe)_2$, $BCl_2(OMe)$, BCl_3, and $CF_2{=}CFB(OMe)_2$ were studied. The nucleophilic addition of $LiCF{=}CF_2$ to $BCl(OMe)_2$ (2:1) and $BCl_2(OMe)$ (3:1) resulted in formation of a mixture of $Li[(CF_2{=}CF)_nB(OMe)_{4-n}]$ salts, which were converted to $K[(CF_2{=}CF)_nBF_{4-n}]$ ($n = 1-4$) using aqueous $K[HF_2]$. The salt $K[(CF_2{=}CF)_4B]$ was prepared from BCl_3 and $LiCF{=}CF_2$ (excess) and subsequent treatment with aqueous KF in 76% yield. The salt $K[(CF_2{=}CF)_2BF_2]$ was synthesized by reacting (trifluorovinyl)dimethoxyborane with $LiCF{=}CF_2$ and subsequent substitution of methoxy by fluorine. $K[(CF_2{=}CF)_3BF]$ was obtained by the reaction of $(CF_2{=}CF)_3B$ with KF.

Introduction

Alkenylhaloboranes R_nBX_{3-n} (X = F, Cl, Br, I) and alkenylfluoroborate salts $M[R_nBF_{4-n}]$ are well-established compounds, and their preparations and reactivities have been reviewed[1,2] and reported in original papers published in the past decade.[3] The replacement of all or the majority of the hydrogen atoms in the alkenyl group R by fluorine caused significant changes of their properties. The synthetic approaches to polyfluorinated organoboranes and -borate salts as well as the reactivity of these compounds show a number of peculiarities which derive from the combination of their specific properties as organofluorine and organoboron compounds. The recent advances in this field were reported in our review.[4]

The first trifluorovinylboranes, $(CF_2{=}CF)_nBX_{3-n}$ ($n = 1-3$; X = F, Cl, Br), were synthesized more than 40 years ago.[5] A few years ago, trifluorovinylboranes of the type $(CF_2{=}CF)_nBX_{3-n}$ (n = 1, 2; X = OAlk, Me) were prepared.[6] In recent years the $Cs[CF_2{=}CFB(CF_3)_2F]$ salt was characterized.[7] Quite recently we reported a convenient route to the potassium (1,2-difluoroalken-1-yl)trifluoroborates $K[RCF{=}CFBF_3]$ (R = F, Cl, CF_3, C_2F_5, C_6F_{13}, C_4F_9, C_4H_9, C_6H_5, Et_3Si)[8,9] and (2,2-difluoroalken-1-yl)trifluoroborates $K[CF_2{=}CRBF_3]$ (R = H, Cl, CF_3)[10] by the reaction of (polyfluoroalkenyl)lithium reagents with $B(OMe)_3$ and subsequent methoxy by fluorine substitution in the intermediate Li[(polyfluoroalkenyl)B-$(OMe)_3$] salts with $K[HF_2]$ in acidified aqueous solution. Similar reactions starting with $LiCF{=}CFOC_3F_7$ gave $K[C_3F_7OCF{=}CFBF_3]$ with an admixture (7 mol %) of $K[(C_3F_7OCF{=}CF)_2BF_2]$. The undesired disubstituted byproduct was a result of the not inconsiderable dissociation of the borate anion $[C_3F_7OCF{=}CFB(OMe)_3]^-$ into the methoxy anion and the corresponding alkenyldimethoxyborane, which is able to add rapidly the second nucleophile $LiCF{=}CFOC_3F_7$.[11] Quite recently we reported the first preparation of tetrakis(trifluorovinyl)borate salts $M[(CF_2{=}CF)_4B]$, which were obtained by reaction of $(CF_2{=}CF)_2SnBu\text{-}n_2$, BCl_3, and MCl.[12] Con-

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tinuing our systematic research on polyfluoroorganoboron compounds, we have investigated some promising routes to the new salts $\mathrm{M[(CF_2{=}CF)_nBF_{4-n}]}$ ($n = 2, 3$) based on the nucleophilic addition of (trifluorovinyl)lithium to chloro-, chloromethoxy-, and (trifluorovinyl)methoxyboranes.

Results and Discussion

Reactions of $\mathrm{LiCF{=}CF_2}$ with $\mathrm{BCl(OMe)_2}$, $\mathrm{BCl_2(OMe)}$, and $\mathrm{BCl_3}$. In an earlier study we showed that the reaction of equimolar amounts of $\mathrm{LiCF{=}CF_2}$ and $\mathrm{B(OMe)_3}$ in ether led to the formation of $\mathrm{Li[CF_2{=}CFB(OMe)_3]}$, which was identified in solution by ^{19}F NMR spectroscopy[8] and later isolated as a pure compound in 90% yield.[13] In contrast to the reactions of $\mathrm{LiC_6F_5}$[14] and $\mathrm{LiCF{=}CFOC_3F_7}$,[11] no bis- and tris(trifluorovinyl)boron compounds were formed. This can be ascribed to the poor nucleofugality of the methoxy anion in $\mathrm{[CF_2{=}CFB(OMe)_3]^-}$ due to the increased Lewis acidity of the borane $\mathrm{CF_2{=}CFB(OMe)_2}$ relative to that of $\mathrm{C_6F_5B(OMe)_2}$ and $\mathrm{C_3F_7OCF{=}CFB(OMe)_2}$.

The chloride anion was expected to be a better leaving anion than $\mathrm{[OMe]^-}$ in (trifluorovinyl)chloromethoxyborate anions. Therefore, we studied the nucleophilic trifluorovinylation of some chloromethoxyboranes $\mathrm{BCl_n(OMe)_{3-n}}$ ($n = 1-3$) with $\mathrm{LiCF{=}CF_2}$.

When $\mathrm{BCl(OMe)_2}$ (1 equiv) was added to a solution of (trifluorovinyl)lithium (~2 equiv) in ether at −78 °C and the reaction mixture was gradually warmed to 20 °C, the formation of mono-, bis-, tris-, and tetrakis(trifluorovinyl)borates was detected by ^{11}B and ^{19}F NMR spectroscopy (eq 1). Subsequent treatment of the (trifluorovinyl)methoxyborates with an aqueous solution of $\mathrm{K[HF_2]}$ resulted in substitution of methoxy by fluorine (eq 2).

$$2\mathrm{LiCF{=}CF_2} + \mathrm{BCl(OMe)_2} \rightarrow \mathrm{Li[(CF_2{=}CF)_nB(OMe)_{4-n}]} \quad (1)$$

$$n = 1\ (20\ \text{mol}\ \%),\ 2\ (56\ \text{mol}\ \%),\ 3\ (22\ \text{mol}\ \%),\ 4\ (1\ \text{mol}\ \%)$$

$$\mathrm{Li[(CF_2{=}CF)_nB(OMe)_{4-n}]} + \mathrm{K[HF_2]} \xrightarrow[-\mathrm{LiF},\ -\mathrm{MeOH}]{\mathrm{H_2O}} \mathrm{K[(CF_2{=}CF)_nBF_{4-n}]} \quad (2)$$

$$n = 1\ (34\ \text{mol}\ \%),\ 2\ (50\ \text{mol}\ \%),\ 3\ (14\ \text{mol}\ \%),\ 4\ (2\ \text{mol}\ \%)$$

When the opposite order of mixing was used, i.e., addition of (trifluorovinyl)lithium (~2 equiv) to a solution of $\mathrm{BCl(OMe)_2}$ (1 equiv) in ether under the same conditions, a somewhat different composition of the mixture of salts $\mathrm{Li[(CF_2{=}CF)_nB(OMe)_{4-n}]}$ was produced ($n = 1$ (40 mol %), 2 (34 mol %), 3 (21 mol %) and 4 (5 mol %)) and of salts $\mathrm{K[(CF_2{=}CF)_nBF_{4-n}]}$ after conversion to the potassium salts ($n = 1$ (46 mol %), 2 (38 mol %), 3 (14 mol %) and 4 (2 mol %)) (^{11}B, ^{19}F NMR). Our current attempts to separate the components of this $\mathrm{K[(CF_2{=}CF)_nBF_{4-n}]}$ mixture by anion exchange, crystallization, or selective extraction failed. Only $\mathrm{K[CF_2{=}CFBF_3]}$, which has a lower solubility in ether than the salts with $n > 1$, could be isolated from the mixture as a residual product in 28% yield by washing with ether.

The addition of $\mathrm{BCl_2(OMe)}$ (1 equiv) to a solution of $\mathrm{LiCF{=}CF_2}$ (~3 equiv) gave $\mathrm{Li[(CF_2{=}CF)_3BOMe]}$ (75%), as well as $\mathrm{Li[(CF_2{=}CF)_2B(OMe)_2]}$ and $\mathrm{Li[(CF_2{=}CF)_4B]}$ as minor products (eq 3).

$$3\mathrm{LiCF{=}CF_2} + \mathrm{BCl_2(OMe)} \rightarrow \mathrm{Li[(CF_2{=}CF)_nB(OMe)_{4-n}]} \quad (3)$$

$$n = 2\ (9\ \text{mol}\ \%),\ 3\ (75\ \text{mol}\ \%),\ 4\ (16\ \text{mol}\ \%)$$

Subsequent treatment with an aqueous solution of $\mathrm{K[HF_2]}$ resulted in the transformation of the lithium (trifluorovinyl)methoxyborates into the corresponding potassium salts (eq 4). However, this reaction was accompanied by a remarkable increase in potassium (trifluorovinyl)trifluoroborate and a corresponding diminution of the tris(trifluorovinyl)fluoroborate salt. A similar relative change of the fractions with different numbers of trifluorovinyl ligands ($n = 1, 3$) was observed in the aforementioned conversion (cf. eqs 1 and 2). A study of the nature of these phenomena was not within the scope of the present investigation.

$$\mathrm{Li[(CF_2{=}CF)_nB(OMe)_{4-n}]} + \mathrm{K[HF_2]} \xrightarrow[-\mathrm{LiF},\ -\mathrm{MeOH}]{\mathrm{H_2O}} \mathrm{K[(CF_2{=}CF)_nBF_{4-n}]} \quad (4)$$

$$n = 1\ (17\ \text{mol}\ \%),\ 2\ (10\ \text{mol}\ \%),\ 3\ (58\ \text{mol}\ \%),\ 4\ (15\ \text{mol}\ \%)$$

Mixing the reagents described in eq 3 in reverse order gave a mixture of the same lithium (trifluorovinyl)methoxyborates $\mathrm{Li[(CF_2{=}CF)_nB(OMe)_{4-n}]}$ (eq 5), but the mole fractions of lithium tetrakis(trifluorovinyl)borate and lithium bis(trifluorovinyl)dimethoxyborate were increased while that of $\mathrm{Li[(CF_2{=}CF)_3B(OMe)]}$ was diminished. The subsequent reaction of $\mathrm{Li[(CF_2{=}CF)_nB(OMe)_{4-n}]}$ with $\mathrm{K[HF_2]}$ gave a mixture of potassium vinylfluoroborates $\mathrm{K[(CF_2{=}CF)_nBF_{4-n}]}$ ($n = 1$ (20 mol %), 2 (27 mol %), 3 (33 mol %), 4 (20 mol %)).

$$3\mathrm{LiCF{=}CF_2} + \mathrm{BCl_2(OMe)} \rightarrow \mathrm{Li[(CF_2{=}CF)_nB(OMe)_{4-n}]} \quad (5)$$

$$n = 2\ (30\ \text{mol}\ \%),\ 3\ (50\ \text{mol}\ \%),\ 4\ (20\ \text{mol}\ \%)$$

All $\mathrm{Li[(CF_2{=}CF)_nB(OMe)_{4-n}]}$ and $\mathrm{K[(CF_2{=}CF)_nBF_{4-n}]}$ ($n = 2, 3$) salts were identified by multinuclear NMR spectroscopy (Table 1; salts with $n = 1$[8,13] and $n = 4$[12] have been described previously).

The absence of $\mathrm{Li\ [(CF_2{=}CF)_nBCl_m(OMe)_{4-n-m}]}$ salts confirmed the assumed high leaving ability of $\mathrm{Cl^-}$ vis-à-vis $\mathrm{[OMe]^-}$ in these borate anions. This suggested the successful synthesis of the tetrakis(trifluorovinyl)borate salt by direct nucleophilic alkenylation of boron trichloride. The addition of $\mathrm{BCl_3}$ in hexane to a solution of $\mathrm{LiCF{=}CF_2}$ (in slight excess) in ether at −60 to −50 °C followed by warming to 20 °C did indeed give $\mathrm{Li[(CF_2{=}CF)_4B]}$, which was converted to the potassium salt (Scheme 1).

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Table 1. ^{19}F and ^{11}B NMR Spectra[a] of $M[(CF_2{=}CF)_nBX_{4-n}]$ (M = Li, K; X = OMe, F; n = 1−4)

		^{19}F NMR chem shift, ppm[b]					
compd	solvent	F-2trans	F-2cis	F-1	B−*F*	^{11}B NMR chem shift, ppm	coupling const, Hz
$Li[B(CF{=}CF)_4]$	ether	−98.11	−122.33	−187.67		−20.74	^3J(F-1,F-2cis) = 105; ^2J(F-2cis,F-2trans) = 82; ^3J(F-1,F-2trans) = 25; ^2J(B,F-1) = 24
$Li[(CF_2{=}CF)_3BOMe]$	ether	−99.06	−122.82	−191.87		−7.59	^3J(F-1,F-2cis) = 108; ^2J(F-2cis,F-2trans) = 83; ^3J(F-1,F-2trans) = 24
$Li[(CF_2{=}CF)_2B(OMe)_2]$	ether	−99.56	−123.10	−192.75		1.24	^3J(F-1,F-2cis) = 109; ^2J(F-2cis,F-2trans) = 86; ^3J(F-1,F-2trans) = 26
$Li[CF_2{=}CFB(OMe)_3]$	ether	−100.03	−123.17	−194.04		2.46	^3J(F-1,F-2cis) = 108; ^2J(F-2cis,F-2trans) = 85; ^3J(F-1,F-2trans) = 25
$K[B(CF{=}CF_2)_4]$	ether	−100.00	−123.74	−183.49		−20.78	^3J(F-1,F-2cis) = 110; ^2J(F-2cis,F-2trans) = 90; ^3J(F-1,F-2trans) 27
$K[(CF_2{=}CF)_3BF]$	ether	−98.57	−122.30	−192.10	−211.55	−4.28	^3J(F-1,F-2cis) = 112; ^2J(F-2cis,F-2trans) = 91; ^3J(F-1,F-2trans) = 26; ^4J(F-2cis,B*F*) = 12; ^2J(F-1,B) = 23; ^1J(B,F) = 55
$K[(CF_2{=}CF)_2BF_2]$	ether	−99.03	−123.54	−197.43	−163.96	2.00	^3J(F-1,F-2cis) = 111; ^2J(F-2cis,F-2trans) = 87; ^3J(F-1,F-2trans) = 25; ^4J(F-2cis,B*F*) = 10; ^4J(F-2trans,B*F*) = 8
$K[CF_2{=}CFBF_3]$	ether[c]	−100.73	−124.10	−198.29	−143.61	2.50	^3J(F-1,F-2cis) = 111; ^2J(F-2cis,F-2trans) = 90; ^3J(F-1,F-2trans) = 25; ^4J(F-2cis,B*F*) = 10;
$K[B(CF{=}CF_2)_4]$	CD_3CN	−99.36	−123.66	−182.00		−20.68	^3J(F-1,F-2cis) = 110.2; ^2J(F-2cis,F-2trans) = 89.7; ^3J(F-1,F-2trans) = 26.5; ^2J(B,F-1) = 21.5, ^3J(B,F-2trans) = 3.2; ^3J(B,F-2cis) = 2.2
$K[(CF{=}CF_2)_3BF]$	CD_3CN	−99.59	−123.48	−189.43	−216.12	−4.83[d]	^3J(F-1,F-2cis) = 111.2; ^2J(F-2cis,F-2trans) = 91.0; ^3J(F-1,F-2trans) = 26.0; ^3J(F-2cis, B*F*) = 12.0; ^1J(B*F*) = 54.0
$K[(CF_2{=}CF)_2BF_2]$	CD_3CN	−99.44	−123.42	−195.42	−164.77	1.72	^3J(F-1,F-2cis) = 111.1; ^2J(F-2cis,F-2trans) = 91.0; ^3J(F-1,F-2trans) = 25.0; ^4J(F-2trans,B*F*) = 7.5; ^4J(F-2cis,B*F*) = 11.2
$K[CF_2{=}CFBF_3]$	CH_3CN	−101.29	−124.11	−195.60	−143.29	∼ 2.50	^3J(F-1,F-2cis) = 110; ^2J(F-2cis,F-2trans) = 92; ^3J(F-1,F-2trans) = 25; ^4J(F-2trans,B*F*) = 8; ^4J(F-2cis,B*F*) = 10 ^1J(B,F) = 41

[a] Measured at 24 °C. [b] The fluorine atoms F^2 at C-2 in vinylborates are specified by cis and trans relative to the position of the boron atom. [c] Water-saturated ether was used for sufficient solubility. [d] Measured in CH_3CN.

Scheme 1

$$4LiCF{=}CF_2 + BCl_3 \xrightarrow[-3LiCl]{} Li[(CF_2{=}CF)_4B] \xrightarrow[-LiF]{KF,\ H_2O} K[(CF_2{=}CF)_4B]$$

Reaction of $LiCF{=}CF_2$ with $CF_2{=}CFB(OMe)_2$. Due to the fact that the pure bis- and tris(trifluorovinyl)fluoroborates could not be isolated from the mixture of the reaction products obtained by the direct nucleophilic trifluorovinylation of $BCl_n(OMe)_{3-n}$ (n = 1, 2), we tried addition of $LiCF{=}CF_2$ to $CF_2{=}CFB(OMe)_2$. In this case, the above-mentioned stability of (trifluorovinyl)methoxyborates toward elimination of MeO^- should prevent the addition of the third trifluorovinyl group to the boron atom. The required (trifluorovinyl)dimethoxyborane was obtained by the abstraction of a methoxy anion from $Li[CF_2{=}CFB(OMe)_3]$ with chlorotrimethylsilane[8] in ether solution. Without isolation of the intermediate borane $CF_2{=}CFB(OMe)_2$, the reaction with $LiCF{=}CF_2$ was performed. The ^{11}B and ^{19}F NMR spectra of the product solution showed the presence of both of the borate anions $[(CF_2{=}CF)_2B(OMe)_2]^-$ and $[CF_2{=}CFB(OMe)_3]^-$ in the molar ratio 85:15. After the substitution of methoxy by fluorine with $K[HF_2]$, the target salt $K[(CF_2{=}CF)_2BF_2]$ was separated from its mixture with $K[CF_2{=}CFBF_3]$ by extraction with ether (Scheme 2).

Scheme 2

$$Li[CF_2{=}CFB(OMe)_3] \xrightarrow[-LiCl,\ -Me_3SiOMe]{ClSiMe_3} CF_2{=}CFB(OMe)_2 \xrightarrow{LiCF{=}CF_2} Li[(CF_2{=}CF)_2B(OMe)_2] \xrightarrow[-LiF,\ -MeOH]{K[HF_2],\ H_2O} K[(CF_2{=}CF)_2BF_2]$$

Reaction of $B(CF{=}CF_2)_3$ with KF. Potassium tris(trifluorovinyl)fluoroborate was prepared by the reaction of fluoride anion with tris(trifluorovinyl)borane (eq 7). The latter was synthesized by reaction of bis(trifluorovinyl)di-*n*-butyltin with boron trichloride[12] and used without isolation (eq 6).

$$3(CF_2{=}CF)_2SnBu\text{-}n_2 + 2BCl_3 \xrightarrow{CH_2Cl_2} 2B(CF{=}CF_2)_3 + 3n\text{-}Bu_2SnCl_2 \quad (6)$$

$$2B(CF{=}CF_2)_3 + 3n\text{-}Bu_2SnCl_2 + 4KF \rightarrow 2K[(CF_2{=}CF)_3BF] + 3n\text{-}Bu_2SnF_2 + 2KCl \quad (7)$$

Conclusion

The stepwise introduction of the electron-withdrawing $CF_2{=}CF$ group into a boron electrophile with $LiCF{=}CF_2$ cannot be controlled simply by the stoichiometry of the reactants. Using the differences in nucleofugality of the chloride and methoxide anions, it is possible to find suitable conditions for preparing $Li[(CF_2{=}CF)_nB(OMe)_{4-n}]$ salts with n = 1, 2, 4. The low tendency of $Li[CF_2{=}CFB(OMe)_3]$ to eliminate a $[OMe]^-$ anion allowed the specific formation of the monoalkenylation product. The aimed abstraction of one of its $[OMe]^-$ anions followed by the addition of $LiCF{=}CF_2$ opened an access to $Li[(CF_2{=}CF)_2B(OMe)_2]$. On the other hand, the high nucleofugality of chloride allowed the introduction of four $CF_2{=}CF$ groups into BCl_3 in the reaction with a slight excess of $LiCF{=}CF_2$, but with $(CF_2{=}CF)_2SnBu\text{-}n_2$ and BCl_3 only $B(CF{=}CF_2)_3$ was achieved. The lithium (trifluorovinyl)methoxyborate salts $Li[(CF_2{=}CF)_nB(OMe)_{4-n}]$ could be converted to the corresponding potassium (trifluorovinyl)fluoroborate salts $K[(CF_2{=}CF)_nBF_{4-n}]$ using an excess of $K[HF_2]$. Finally, salts with the tris(trifluorovinyl)borate anion $[(CF_2{=}CF)_3BX]^-$ which were not accessible by the direct introduction of $CF_2{=}CF$

groups were available by addition of X^- to the Lewis acid $(CF_2{=}CF)_3B$: e.g., with KF the salt $K[(CF_2{=}CF)_3BF]$ was prepared.

Experimental Section

Materials and Methods. 1,1,1,2-Tetrafluoroethane (HFC-134a; ABCR), 2.5 M *n*-BuLi in hexanes (Aldrich), di-*n*-butyltin dichloride (Fluka), boron trichloride (Merck), 1.0 M BCl_3 in hexanes (Aldrich), 1.0 M BCl_3 in CH_2Cl_2 (Aldrich), KF (spray dried; Aldrich), and anhydrous diethyl ether (Baker) were used as supplied. $B(OMe)_3$ (Fluka) was distilled over sodium before use. Chloromethoxyboranes $BCl(OMe)_2$ (bp 72.5−73 °C, lit.[15] bp 74.7 °C) and $BCl_2(OMe)$ (bp 56.5−57 °C, lit.[16] bp 58−61 °C) were prepared by reaction of stoichiometric amounts of BCl_3 and $B(OMe)_3$.

NMR Spectroscopic Measurements. NMR spectra were recorded on a Bruker AVANCE 300 (FT 300.13 MHz, ^1H; 96.29 MHz,^{11}B; 75.47 MHz,^{13}C; 282.40 MHz,^{19}F) spectrometer. The chemical shifts are referenced to TMS (^1H, ^{13}C), $BF_3{\cdot}OEt_3$/$CDCl_3$ 15% v/v (^{11}B), and CCl_3F (^{19}F, with C_6F_6 as secondary reference (−162.9 ppm)), respectively.

The assignment of the ^{19}F spectra of the $[(CF_2{=}CF)_nBF_{4-n}]^-$ anions is based on the known spectra of $K[CF_2{=}CFBF_3]$[8] and $[Me_4N][(CF_2{=}CF)_4B]$,[12] which were prepared by independent methods and were fully characterized by their ^{11}B and ^{19}F spectra; the latter was additionally characterized by X-ray and elemental analysis. The ratio of the three types of vinylic fluorine atoms to the boron-bonded ones confirms the constitution of the $[(CF_2{=}CF)_nBF_{4-n}]^-$ anions. $\delta(F^1)$ and $\delta(BF)$ fit in a systematic trend: $\delta(F^1)$ shifts to higher frequency with increasing *n*, whereas the B*F* resonance shows the opposite behavior.

Thermal analysis was carried out using a Netzsch DSC 204 instrument. C, H, N elemental analysis was performed with a HEKAtech EA3000 analyzer. Using the recommended standard procedure potassium (trifluorovinyl)fluoroborate salts consistently gave contents of carbon lower than the calculated ones because they were not fully oxidized. For fluorine analysis a Schöniger type of combustion was used followed by a photometric determination of the lanthanum alizarin−complexone fluoride complex.

Synthesis of $LiCF{=}CF_2$. (A modified procedure based on the initial[17] and latest[18] protocols was used.) A 250 mL three-necked round-bottomed flask supplied with a magnetic stirrer bar and a low-temperature thermometer was charged with 50 mL of dry ether under an atmosphere of dry argon and cooled to −78 °C before CF_3CH_2F (3 g, 29 mmol) was condensed into the solution. Within 15 min a 2.5 M *n*-BuLi solution in hexanes (20 mL, 50 mmol) was added dropwise to the cold solution using a syringe. Finally, the solution was stirred at −78 °C for 1 h and at −60 to −50 °C for 1 h. The fine suspension was cooled to −78 °C and used in the reactions described below.

Synthesis of Bis(trifluorovinyl)di-*n*-butyltin. A solution of $n\text{-}Bu_2SnCl_2$ (12.5 g, 41 mmol) in 40 mL of ether was added dropwise to a stirred suspension of $LiCF{=}CF_2$ (prepared from CF_3CH_2F (12 g, 118 mmol) and 2.5 M *n*-BuLi in hexanes (80 mL, 200 mmol) in ether (200 mL)) at −78 °C. The resulting suspension was stirred at ≤−75 °C for 30 min before being gradually warmed to 20 °C within 4 h. The solvents were evaporated under reduced pressure, and the residue was extracted with pentane (3 × 70 mL). Evaporation of the combined extracts under reduced pressure gave 16 g of a brown oil. Bis(trifluorovinyl)di-*n*-butyltin (15.4 g, 95% yield) was obtained by vacuum distillation (slightly yellow oil, bp 60−62 °C/2.7 × 10^{-2} hPa) (lit.[19] bp 60−63 °C/0.5 hPa).

Reactions of $LiCF{=}CF_2$ with $BCl(OMe)_2$. A. The borane $BCl(OMe)_2$ (1 mL, 1.08 g, 10 mmol) was added dropwise by syringe to a stirred suspension of $LiCF{=}CF_2$ (prepared from CF_3CH_2F (29 mmol) and *n*-BuLi (50 mmol) in ether (50 mL)) at −78 °C. The reaction mixture was stirred at −78 °C for 30 min and then warmed to 20 °C over 2 h. The solvents were evaporated under reduced pressure, leaving a slightly brown solid. This was stirred for 1 h with a solution of $K[HF_2]$ (7.8 g, 100 mmol) in water (20 mL) in the presence of charcoal (∼0.5 g). The mixture was filtered, and the solid residue was washed with water (20 mL). The combined aqueous filtrates were treated with K_2CO_3 (7.5 g) in small portions and then with KF (3 g). The solution was extracted with acetonitrile (5 × 10 mL), and the combined extracts were dried with $MgSO_4$. After evaporation of the solvents, a colorless oil (2.08 g) was obtained. According to its ^{19}F and ^{11}B NMR spectra, it was a mixture of salts $K[(CF_2{=}CF)_nBF_{4-n}]$, with *n* = 1 (34 mol %), 2 (50 mol %), 3 (14 mol %), and 4 (2 mol %). After repeated washing with ether the pure salt $K[CF_2{=}CFBF_3]$[8] (540 mg, 2.8 mmol, 28% yield) remained.

B. A cold (−78 °C) solution of $LiCF{=}CF_2$ (prepared from CF_3CH_2F (29 mmol) and *n*-BuLi (50 mmol) in ether (50 mL)) was added to a cold (−78 °C) solution of the borane $BCl(OMe)_2$ (1 mL, 1.08 g, 10 mmol) in ether (10 mL) in five portions within 30 min. The resulting mixture was stirred at −78 °C for an additional 30 min before being warmed to 20 °C within 2 h. The ^{19}F and ^{11}B NMR spectra showed the formation of $Li[(CF_2{=}CF)_nB(OMe)_{4-n}]$, with *n* = 1 (40 mol %), 2 (34 mol %), 3 (21 mol %), and 4 (5 mol %). The solvent was removed under reduced pressure, and the residue was treated with $K[HF_2]$ (7.8 g, 100 mmol) in water (20 mL) in the presence of charcoal (∼0.5 g) for 1 h. After filtration and washing (20 mL) the combined aqueous phase was neutralized with K_2CO_3 (7.5 g) and saturated with KF (3 g) before the solution was extracted with acetonitrile (5 × 10 mL). The combined extracts were dried with $MgSO_4$. Salts of the type $K[(CF_2{=}CF)_nBF_{4-n}]$ (n = 1 (46 mol %), 2 (38 mol %), 3 (14 mol %) and 4 (2 mol %)) were obtained (^{11}B and ^{19}F NMR, Table 1).

Reactions of $LiCF{=}CF_2$ with $BCl_2(OMe)$. A. The borane $BCl_2(OMe)$ (0.65 mL, 0.79 g, 7 mmol) was added dropwise by syringe to a cold (−78 °C) suspension of $LiCF{=}CF_2$ (prepared from CF_3CH_2F (29 mmol) and *n*-BuLi (50 mmol) in ether (50 mL)). The resulting mixture was stirred at −78 °C for 30 min and then gradually warmed to 20 °C within 2 h. The solvents were removed under reduced pressure. The residue was treated with $K[HF_2]$ (5.5 g, 70 mmol) in 20 mL of water and charcoal (0.5 g). After filtration the filter cake was washed with water (20 mL). The combined aqueous solution was neutralized and finally saturated with KF (3 g) and then extracted with acetonitrile (5 × 10 mL). The combined extracts were dried with $MgSO_4$. The salts $K[(CF_2{=}CF)_nBF_{4-n}]$ (*n* = 1 (17 mol %), 2 (10 mol %), 3 (58 mol %), 4 (15 mol %)) were obtained (^{11}B, ^{19}F NMR).

B. A cold (−78 °C) solution of $LiCF{=}CF_2$ (prepared from CF_3CH_2F (29 mmol) and *n*-BuLi (50 mmol) in ether (50 mL)) was added in five portions to a cold (−78 °C) solution of $BCl_2(OMe)$ (0.65 mL, 0.79 g, 7 mmol) in ether (10 mL) within 30 min. The resulting mixture was stirred at −78 °C for 30 min and then gradually warmed to 20 °C within 2 h. After the reaction

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with K[HF$_2$] as mentioned before, the ^{19}F and ^{11}B NMR spectra of the resulting solution showed the presence of the mixture of salts K[(CF$_2$═CF)$_n$BF$_{4-n}$] (n = 1 (20 mol %), 2 (27 mol %), 3 (33 mol %), 4 (20 mol %)).

Synthesis of Potassium (Trifluorovinyl)trifluoroborate and Potassium Bis(trifluorovinyl)difluoroborate. A cold (−78 °C) suspension of LiCF═CF$_2$ (prepared from CF$_3$CH$_2$F (29 mmol) and n-BuLi (50 mmol) in ether (50 mL)) was slowly added to a cold (−70 °C) solution of B(OMe)$_3$ (2.24 mL, 2.08 g, 20 mmol) in ether (20 mL). The resulting mixture was stirred at −78 °C for 30 min and then warmed to 20 °C within 3 h. The brown mixture was cooled to 0 °C before Me$_3$SiCl (2.54 mL, 2.17 g, 20 mmol) was added. While the mixture was stirred at 20 °C for 1 h, a white precipitate formed. The mixture was cooled to −78 °C, and a second portion of a cold (−8 °C) LiCF═CF$_2$ solution in ether (∼25 mmol) was added. The mixture was stirred at −70 °C for 30 min and finally warmed to 20 °C within 3 h. The ^{19}F and ^{11}B NMR spectra of the resulting solution showed the presence of Li[(CF$_2$═CF)$_2$B(OMe)$_2$] and Li[CF$_2$═CFB(OMe)$_3$][13] (see Table 1) in the molar ratio 85:15. The solvents were removed under reduced pressure, and the sticky solid was treated with K[HF$_2$] (15.6 g, 200 mmol) in water (40 mL) and charcoal (1.5 g) at 20 °C for 1.5 h. The suspension was filtered, and the filter cake was washed with water (40 mL). The combined aqueous filtrates were treated with potassium carbonate (15 g) before the solution was extracted with ether (5 × 10 mL). The combined ether extracts were dried with anhydrous K$_2$CO$_3$ and KF overnight. After decantation ether was distilled off and the colorless oil was dried (3 h) under vacuum (20 °C at 2.7 × 10^{-2} hPa). K[(CF$_2$═CF)$_2$BF$_2$] (3.0 g) was obtained.

This product contained approximately 5 mol % of K[CF$_2$═CFBF$_3$]. To remove this byproduct, 1.0 g of the product was dissolved in ether (50 mL) and the solution was treated with three portions (each 10 mL) of 10% aqueous KF. After this solution was dried with K$_2$CO$_3$, ether was removed and the residue was dried under high vacuum (5 h, 20 °C at 2 × 10^{-2} hPa). A 0.5 g amount of the product was obtained. Anal. Calcd for C$_4$BF$_8$K (251.14): F, 60.52. Found: F, 59.40. ^{13}C NMR (CD$_3$CN): δ 136.25 (br, C-1), 160.19 (ddd, $^1J_{\mathrm{CF}}$ = 295.6 Hz; $^1J_{\mathrm{CF}}$ = 272.0 Hz; $^2J_{\mathrm{CF}}$ = 42.5 Hz, C-2) ppm.

The aqueous solution remaining after the extraction with ether was additionally extracted with acetonitrile (5 × mL). After evaporation of the extract pure K[CF$_2$═CFBF$_3$] (1.10 g, 5.9 mmol, 29%) was isolated.

Synthesis of Potassium Tris(trifluorovinyl)fluoroborate. A solution of 1.0 M BCl$_3$ in CH$_2$Cl$_2$ (1 mL, 1.0 mmol) was added dropwise to a solution of (CF$_2$═CF)$_2$SnBu-n_2 (592 mg, 1.5 mmol) in CH$_2$Cl$_2$ (2.5 mL). After it was stirred at 20 °C for 20 min, the mixture was transferred into a flask with KF (300 mg; spray dried). The suspension was stirred at 20 °C for 12 h under an atmosphere of dry argon and then evaporated to dryness under reduced pressure. The white solid was washed with water (2 × 5 mL) and filtered. The aqueous filtrate was extracted with ether. After the ether was removed, K[(CF$_2$═CF)$_3$BF] (160 mg) was obtained.

The product contained 92 mol % of K[(CF$_2$═CF)$_3$BF], 4 mol % of K[(CF$_2$═CF)$_4$B], and 4 mol % of K[(CF$_2$═CF)$_3$B(OH)]. For purification 160 mg of the product was dissolved in ether (20 mL) and was treated with three portions (each 2 mL) of a saturated aqueous solution of K[HF$_2$]. The ether phase was dried with K$_2$CO$_3$, ether was removed under vacuum, and the solid residue was crystallized from CH$_2$Cl$_2$−ether (89 mg), forming colorless crystals. T(dec) = 84.9 °C (DSC). Anal. Calcd for C$_6$BF$_{10}$K (313.16): C, 23.10; F, 60.90. Found: C, 21.89; F, 60.89. ^{13}C NMR (CD$_3$CN): δ 137.46 (br, C-1), 160.47 (ddd, $^1J_{\mathrm{CF}}$ = 294.8 Hz; $^1J_{\mathrm{CF}}$ = 274.2 Hz; $^2J_{\mathrm{CF}}$ = 44.5 Hz, C-2) ppm.

Synthesis of Potassium Tetrakis(trifluorovinyl)borate. A 1.0 M BCl$_3$ solution in hexanes (10 mL, 10 mmol) was added to a suspension of LiCF═CF$_2$ (prepared from CF$_3$CH$_2$F (58 mmol) and n-BuLi (100 mmol) in ether (100 mL)) at −78 °C. The reaction mixture was stirred at −60 to −50 °C for 2 h before being warmed to 20 °C within 2 h. The ^{19}F and ^{11}B NMR spectra showed the formation of the [B(CF═CF$_2$)$_4$]$^-$ anion.[12] The solvent was removed under reduced pressure. The sticky brown solid was stirred with KF (15 g) in 40 mL of water at 20 °C for 1 h in the presence of charcoal (2 g). After filtration the filter cake was washed with water (2 × 80 mL). The resulting colorless aqueous solution was extracted with ether (5 × 15 mL). The combined extracts were dried with anhydrous K$_2$CO$_3$ and KF for 24 h. After the ether was removed, K[B(CF═CF$_2$)$_4$] (2.84 g, 76%) was obtained (purity 95%). For analysis the product was recrystallized from CH$_2$Cl$_2$−ether and formed colorless crystals. T(dec) = 106.7 °C (DSC). Anal. Calcd for C$_8$BF$_{12}$K (373.98): C, 25.69; F, 60.96. Found: C, 24.13; F, 60.13 (For (NMe$_4$)[B(CF═CF$_2$)$_4$]: Anal. Calcd for C$_{12}$H$_{12}$BF$_{12}$N (409.02): C, 35.24; H, 2.96; N, 3.42; F, 55.74%. Found: C, 35.09; H, 2.90; N, 3.42; F, 55.65.) ^{13}C NMR (CD$_3$CN): δ 137.05 (dddq $^1J_{\mathrm{CF}}$ = 186.0 Hz; $^2J_{\mathrm{CF}}$ = 62.5 Hz; $^2J_{\mathrm{CF}}$ = 55.5 Hz; $^1J_{\mathrm{CB}}$ = 61.8 Hz, C-1), 160.77 (dddq, $^1J_{\mathrm{CF}}$ = 291.5 Hz; $^1J_{\mathrm{CF}}$ = 272.6 Hz; $^2J_{\mathrm{CF}}$ = 46.5 Hz; $^2J_{\mathrm{CB}}$ = 7.8 Hz, C-2) ppm.

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Supporting Information Available: Figures S1−S3 (^{19}F NMR of K[(CF$_2$═CF)$_n$BF$_{4-n}$], n = 2−4), Figures S4−S6 (^{11}B NMR of K[(CF$_2$═CF)$_n$BF$_{4-n}$], n = 2−4), Figures S7−S14 (^{19}F NMR of reaction mixtures containing Li[(CF$_2$═CF)$_n$B(OMe)$_{4-n}$] or K[(CF$_2$═CF)$_n$BF$_{4-n}$]) salts, and Comment S15 (considerations of the course of the reactions mentioned in eqs 1, 3, and 5). This material is available free of charge via the Internet at http://pubs.acs.org.

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