(Fluoroorgano)fluoroboranes and -borates. 14. Preparation of Potassium ((Perfluoroorgano)ethynyl)trifluoroborates $K[R_FC{\equiv}CBF_3]$

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The first representatives of an unknown family of organoboron compounds, the ((perfluoroorgano)ethynyl)trifluoroborate salts $K[R_FC{\equiv}CBF_3]$ (R_F = CF_3, C_3F_7, $(CF_3)_2CF$, C_6F_{13}, CF_3-$CF{=}CF$, $C_4F_9CF{=}CF$, C_6F_5), were prepared and characterized by multi-NMR spectroscopy (^{11}B, ^{13}C, and ^{19}F) and their vibrational spectra (IR and Raman).

Introduction

Despite the remarkable progress in organoboron chemistry, (alkynyl)fluoroborates remained unknown until 1999, when Darses et al. reported the preparation of the first two potassium (alkynyl)trifluoroborates, $K[RC{\equiv}CBF_3]$ (R = Bu, Et_3Si).[1] Later Molander et al. extended this series of salts with R = C_8H_{17}, C_6H_5, C_6H_5-CH_2CH_2, $CClH_2CH_2CH_2$, $CH_2{=}C(CH_3)$, Me_3Si, and t-$BuMe_2SiOCH_2CH_2$.[2] Both groups introduced (alkynyl)-trifluoroborates successfully into Pd-catalyzed cross-coupling reactions and demonstrated impressively the application potential of alkynyltrifluoroborate salts.

It is well-known that the replacement of all or the majority of hydrogen atoms by fluorine atoms in hydrocarbons or in their organoelement derivatives caused significant changes of their physical and chemical properties. [3] In this regard the chemistry of organoboron compounds is no exception. A recently published review presented a number of peculiarities which were derived from the combination of the specific properties of both roots, organofluorine and organoboron chemistry, and their co-action.[4]

We have continued our systematic studies in the field of polyfluorinated organofluoroborates and -boranes and investigated approaches to the synthesis of ((perfluoroorgano)ethynyl)trifluoroborate salts $K[R_FC{\equiv}CBF_3]$. We have included perfluorinated alkyl, alkenyl, and aryl groups R_F attached to C-2 of the ethynyl unit.[5]

Results and Discussion

Over the last few years we have reported a straightforward and widely applicable route to potassium (polyfluoroalkyl)trifluoroborates,[6−7] (polyfluoroalk-1-enyl)trifluoroborates,[8−11] and (polyfluoroaryl)trifluoroborates[7,12] which is based on the nucleophilic addition of (polyfluoroorganyl)lithium (or -magnesium halide) to tris(alkoxy)boranes and the subsequent replacement of the alkoxy groups by fluorine in the intermediate (polyfluoroorganyl)trialkoxyborates using aqueous solutions of $K[HF_2]$ or $K[HF_2]$ in hydrofluoric acid (Scheme 1).

Scheme 1

$$R'_FM \xrightarrow{B(OAlk)_3} M[R'_FB(OAlk)_3] \xrightarrow{K[HF_2]} K[R'_FBF_3]$$

$$M = Li, MgX$$

We applied this reaction strategy to the synthesis of potassium ((perfluoroorgano)ethynyl)trifluoroborates. In general, the reactive key nucleophiles $R_FC{\equiv}CM$ were obtained by metalation of perfluoroorganoethynes $R_FC{\equiv}$

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CH, or in some cases they were generated in situ from an appropriate precursor.

Synthesis of $R_FC{\equiv}CH$. Perfluorinated organoethynes $R_FC{\equiv}CH$ are in general not commercially available. This is in contrast to the fact that a considerable progress in their chemistry has been achieved.[13] We employed short and reliable procedures for the synthesis of $R_FC{\equiv}CH$ compounds. We applied methods which principally were described in the literature. Thus, (pentafluorophenyl)acetylene (**1**) was prepared from iodopentafluorobenzene in two steps (Scheme 2).[14,15] We should note that in our hands the formation of ((pentafluorophenyl)ethynyl)trimethylsilane (**2**) was always accompanied by a significant reduction of C_6F_5I to C_6F_5H, which was not mentioned in the original report.[15] This side reaction diminished the isolated yield of **2** to 45−48% under either the reported or modified reaction conditions (temperature, reaction time).

Scheme 2

$$C_6F_5I + HC{\equiv}CSiMe_3 \xrightarrow[Et_3N,\ 48\ h,\ 30-35\ ^\circ C]{(Ph_3P)_2PdCl_2,\ CuI} \underset{\mathbf{2}}{C_6F_5C{\equiv}CSiMe_3}$$

$$C_6F_5C{\equiv}CSiMe_3 + KOH \xrightarrow{MeOH,\ 20\ ^\circ C} \underset{\mathbf{1}}{C_6F_5C{\equiv}CH}$$

The synthesis of 3,3,4,4,5,5,5-heptafluoropent-1-yne (**3**) and 3-(trifluoromethyl)-3,4,4,4-tetrafluorobut-1-yne (**4**) was performed by a coupling reaction which was offered for the preparation of $C_nF_{2n+1}C{\equiv}CH$ (n = 4, 6, 8)[16] and later modified (Scheme 3).[17−18]

Scheme 3

$$R_FI + HC{\equiv}CC(OH)(CH_3)_2 + Zn \xrightarrow{CF_3CO_2H,\ CH_2Cl_2} \underset{\mathbf{5},\ \mathbf{6}}{(E,Z)\text{-}R_FCH{=}ClC(OH)(CH_3)_2}$$

$$\mathbf{5},\ \mathbf{6} \xrightarrow[20\ ^\circ C]{KOH,\ aq\ EtOH} \underset{\mathbf{7},\ \mathbf{8}}{R_FC{\equiv}CC(OH)(CH_3)_2} \xrightarrow{NaOH} \underset{\mathbf{3},\ \mathbf{4}}{R_FC{\equiv}CH}$$

$R_F = C_3F_7$ (**5**, **7**, **3**), $(CF_3)_2CF$ (**6**, **8**, **4**)

It is worth mentioning that the elimination of HI from iodoalkene **6** ($R_F = (CF_3)_2CF$) with KOH in aqueous ethanol was accompanied by partial reduction to *trans*-$(CF_3)_2CFCH{=}CHC(OH)(CH_3)_2$ (**9**), while iodoalkene **5** did not undergo such a side reaction. However, alkyne **4** obtained in the next step was not contaminated with olefin **9** or products derived from **9**.

Perfluorinated alk-3-en-1-ynes $R_FCF{=}CFC{\equiv}CH$ were potential precursors for $K[R_FCF{=}CFC{\equiv}CBF_3]$ salts but unknown compounds. We elaborated an easy route of synthesis which consists of the nucleophilic substitution of one fluorine atom in perfluoroalk-1-ene by ((trimethylsilyl)ethynyl)lithium followed by protodesilylation of perfluorinated 1-(trimethylsilyl)alk-3-en-1-yne. For example, the reaction of hexafluoropropene with $Me_3SiC{\equiv}CLi$ yielded 1-(trimethylsilyl)pentafluoropent-3-en-1-yne (**10**; cis:trans = 1:2),[19] which was converted into pentafluoropent-3-en-1-yne (**11**) by treatment with KF in aqueous DMSO (Scheme 4).

Scheme 4

$$CF_3CF{=}CF_2 \xrightarrow[\geq -75\ ^\circ C]{Me_3SiC{\equiv}CLi} \underset{\mathbf{10}}{(E,Z)\text{-}CF_3CF{=}CFC{\equiv}CSiMe_3} \xrightarrow[\leq 50\ ^\circ C]{KF,\ aq\ DMSO} \underset{\mathbf{11}}{(E,Z)\text{-}CF_3CF{=}CFC{\equiv}CH}$$

Synthesis of $K[R_FC{\equiv}CBF_3]$ Salts from $R_FC{\equiv}CH$. The metalation of (perfluoroorgano)ethynes **11**, **3**, **4**, and **1** with BuLi or EtMgBr and sequential reactions with $B(OAlk)_3$ and $K[HF_2]$/aqueous HF resulted in potassium ((pentafluoroorgano)eth-1-ynyl)trifluoroborate **12** (cis:trans = 1:2) and **13**−**15**, respectively (Scheme 5).

Scheme 5

$$\underset{\mathbf{11},\ \mathbf{3},\ \mathbf{4}}{R_FC{\equiv}CH} \xrightarrow[(3)\ K[HF_2],\ aq\ HF]{(1)\ EtMgBr\ or\ BuLi;\ (2)\ B(OMe)_3;} \underset{\mathbf{12}\ (21\%),\ \mathbf{13}\ (45\%),\ \mathbf{14}\ (72\%)}{K[R_FC{\equiv}CBF_3]}$$

$R_F = CF_3CF{=}CF$ (**11**, **12**), C_3F_7 (**3**, **13**), $(CF_3)_2CF$ (**4**, **14**)

$$\underset{\mathbf{1}}{C_6F_5C{\equiv}CH} \xrightarrow[(3)\ K[HF_2],\ aq\ HF]{(1)\ EtMgBr;\ (2)\ B(O\text{-}i\text{-}Pr)_3;} \underset{\mathbf{15}\ (64\%)}{K[C_6F_5C{\equiv}CBF_3]}$$

Synthesis of $R_FC{\equiv}CLi$ without Direct Metalation of $R_FC{\equiv}CH$ and Its Conversion into $K[R_FC{\equiv}CBF_3]$ Salts. In some cases more convenient paths to the nucleophile $R_FC{\equiv}CLi$ are possible without the primary preparation of (perfluoroorgano)ethynes: for example, in the case of $CF_3C{\equiv}CLi$. Principally trifluoropropyne is commercially available as a starting material, but it is very expensive. Here the recent reports of Brisdon et al. opened a suitable route to (trifluoropropynyl)lithium by the reaction of 1,1,1,3,3-pentafluoropropane with 3 equiv of BuLi.[20,21] $CF_3C{\equiv}CLi$ generated by this route reacted with $B(OMe)_3$ to give lithium (trifluoroprop-1-ynyl)trimethoxyborate (major) and lithium bis(trifluoroprop-1-ynyl)dimethoxyborate (minor), which were both identified in solution by ^{11}B and ^{19}F NMR spectroscopy. After treatment of the reaction mixture with $K[HF_2]$ in aqueous HF, potassium (trifluoroprop-1-ynyl)trifluoroborate (**16**) was the only product and could be isolated. Probably, protodeboration

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of the $[(CF_3C{\equiv}C)_2B(OMe)_2]^-$ anion occurred more quickly than its fluorodemethoxylation (Scheme 6).

Scheme 6

$$CF_3CH_2CHF_2 \xrightarrow[(2)\ B(OMe)_3]{(1)\ 3BuLi} \underset{\text{major}}{Li[CF_3C{\equiv}CB(OMe_3)_3]} +$$

$$\underset{\text{minor}}{Li[(CF_3C{\equiv}C)_2B(OMe)_2]} \xrightarrow{K[HF_2]/HF_{aq}} \underset{\textbf{16}\ (53\%)}{K[CF_3C{\equiv}CBF_3]}$$

Principally potassium salts of long-chain ((perfluoroalkyl)ethynyl)trifluoroborates, e.g. potassium (perfluoropent-1-ynyl)trifluoroborate (**13**), can be prepared from 1-iodoperfluoropropane in accordance with Scheme 3. We decided to elaborate another route, which is demonstrated for (perfluorooct-1-ynyl)lithium as a key nucleophile. This route started with the easily available olefin $C_6F_{13}CBr{=}CH_2$ (**17**),[22] which was treated with LDA, and in situ generated $C_6F_{13}C{\equiv}CLi$ was finally converted into the salt **18** as previously described (Scheme 7).

Scheme 7

$$\underset{\textbf{17}}{C_6F_{13}CBr{=}CH_2} \xrightarrow{2LDA} C_6F_{13}C{\equiv}CLi \xrightarrow[(2)\ K[HF]_2,\ aq\ HF]{(1)\ B(O\text{-}i\text{-}Pr)_3} \underset{\textbf{18}\ (20\%)}{K[C_6F_{13}C{\equiv}CBF_3]}$$

This reaction route gave an interesting and unexpected result when, instead of LDA, butyllithium was used in the reaction sequence. The interaction of olefin **17** with 2 equiv of BuLi is described in Scheme 8 and led to potassium (perfluorooct-3-en-1-ynyl)trifluoroborate (**19**; cis:trans = 1:2) in 44% yield. When the molar ratio **17**:BuLi was applied equal to 1:3, the isolated yield of salt **19** increased to 66% and the ratio of cis to trans changed to 5:6. We assume that the primary reaction of olefin **17** and BuLi resulted in the 2-lithioalkene **A**, which quickly eliminated LiF to form the polyfluorinated octa-1,2-diene **B**. The abstraction of one proton from **B** followed by the elimination of one fluoride anion resulted in enyne **C**, whose lithiation gave the carbon nucleophile **D** (Scheme 8).

Scheme 8

$$C_6F_{13}CBr{=}CH_2 \xrightarrow{BuLi} \underset{\textbf{A}}{C_6F_{13}CLi{=}CH_2} \xrightarrow[-LiF]{}$$

$$\underset{\textbf{B}}{C_5F_{11}CF{=}C{=}CH_2} \xrightarrow{BuLi} C_5F_{11}CF{=}C{=}CH^- \rightarrow$$

$$C_5F_{11}CF^-C{\equiv}CH \xrightarrow[-F^-]{}$$

$$\underset{\textbf{C}}{C_4F_9CF{=}CFC{\equiv}CH} \xrightarrow{BuLi}$$

$$\underset{\textbf{D}}{C_4F_9CF{=}CFC{\equiv}CLi} \xrightarrow[(2)\ K[HF_2],\ aq\ HF]{(1)\ B(O\text{-}i\text{-}Pr)_3} \underset{\textbf{19}\ (44-66\%)}{K[C_4F_9CF{=}CFC{\equiv}CBF_3]}$$

The fact that the final product consisted only of salt **19** means that the conversion of the primary intermediate **A** into the nucleophile **D** proceeded more quickly than its reaction with the electrophile $B(O\text{-}i\text{-}Pr)_3$. Indeed, the ^{19}F NMR spectrum of the reaction mixture from $C_6F_{13}CBr{=}CH_2$ (**17**), BuLi (2 equiv), and $B(O\text{-}i\text{-}Pr)_3$ still showed a significant amount of nonreacted substrate **17**.

NMR Spectra of $K[R_FC{\equiv}CBF_3]$. Signals in the ^{11}B NMR spectra of all ((perfluoroorgano)ethynyl)trifluoroborates are located between −2 and −3 ppm. This indicates a weak shielding of the boron atom in $[R_FC{\equiv}CBF_3]^-$ anions with respect to those in perfluorinated alkenyltrifluoroborates and alkyltrifluoroborates, whose ^{11}B NMR signals are located at −0.2 to −0.7 ppm.[4,23] Distinctions of the boron-bonded fluorine atoms in the ^{19}F NMR spectra of these classes of (perfluoroorganyl)trifluoroborates are more interesting. The spectra of ((perfluoroorgano)ethynyl)trifluoroborate salts $K[R_FC{\equiv}CBF_3]$ either in acetonitrile or in acetone contain the signal of the BF_3 group (quartet 1:1:1:1, $^1J_{FB}$ = 31−34 Hz) at −134 to −137 ppm, which shifts to low frequencies (ca. 2 ppm) in the highly polar solvents DMSO and D_2O. Similar shifts from −142 to −144 ppm or from −140 to −142 ppm are observed in the spectra of potassium (perfluoroalkenyl)trifluoroborates $K[R_FCF{=}CFBF_3]$ on going from solutions in MeCN to DMSO. The ^{19}F chemical shifts of the BF_3 group in potassium (perfluoroalkyl)trifluoroborates $K[R_FCF_2CF_2BF_3]$ are located at −152 to −153 ppm, and they are practically unaffected by the change of solvent.[4,23] This picture of increasing shielding of the B*F*$_3$ nucleus in the series $[R_FC{\equiv}CBF_3]^- < R_FCF{=}CFBF_3]^- < [R_FCF_2CF_2BF_3]^-$ follows the increasing number of fluorine atoms at carbon atom C-1 and reflects the diminishing of negative charge on the fluorine atoms bonded to boron from perfluorinated alkynyltrifluoroborates to alkyltrifluoroborates. It is worth noting that the $^1J_{FB}$ coupling constants in spectra of nonfluorinated organyltrifluoroborate anions always exceed those of their perfluorinated analogues, and both increase from alkynyl- to alkyltrifluoroborates.[4,23]

The ^{13}C NMR data concerning the chemical shifts δ(C-1) and δ(C-2) and the $^nJ_{CB}$ coupling constants (n = 1, 2) of alkynylboron compounds are very limited.[24] In addition, reported spectra of the recently prepared potassium alkynyltrifluoroborates $K[RC{\equiv}CBF_3]$ did not contain these data.[2] The chemical shift δ(C-2) (broad multiplet at 89 ppm) was reported only for the salt $K[C_4H_9C{\equiv}CBF_3]$.[1] We have carried out a ^{13}C and $^{13}C\{^{19}F\}$ NMR characterization on representative members of the new ((perfluoroorgano)ethynyl)trifluoroborate salts **16**, **12**, **14**, and **15**.

The resonances of the carbon atom C-2 in the $^{13}C\{^{19}F\}$ NMR spectra of all $K[R_FC{\equiv}CBF_3]$ salts were unresolved multiplets located in the narrow range from 72 to 76 ppm (Table 1). The resonances of the carbon atom C-1 of **16** ($R_F = CF_3$) and **14** ($R_F = (CF_3)_2CF$) were found at 104 and 112 ppm, respectively. Replacement of the perfluoroalkyl moiety R_F by the unsaturated

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Table 1. ^{13}C and $^{13}C\{^{19}F\}$ NMR Spectra of $K[RBF_3]$ Salts

R	solvent	^{13}C NMR chem shift, ppm	coupling const, Hz
$CF_3C{\equiv}C^a$	DMSO-d_6	104.5 (q, C-1), 75.1 (C-2), 114.5 (C-3)	^1J(C-1,B) = 104
$CF_3CF(CF_3)C{\equiv}C^a$	DMSO-d_6	112.2 (q, C-1), 71.8 (C-2), 84.8 (C-3), 119.4 (C-4)	^1J(C-1,B) = 99
$CF_3CF(CF_3)C{\equiv}C$	DMSO-d_6	112.0 (C-1), 71.8 (C-2), 84.7 (dsept, C-3), 119.3 (dq, C-4)	^2J(C-4,F-3) = 30; ^1J(C-4,F-4) = 286; ^1J(C-3,F-3) = 198; ^2J(C-3,F-4) = 36
cis-$CF_3CF{=}CFC{\equiv}C^a$	DMSO-d_6	123.1 (q, C-1), 73.4 (C-2), 135.2 (C-3), 139.2 (C-4), 119.9 (C-5)	^1J(C-1,B) = 100
cis-$CF_3CF{=}CFC{\equiv}C$	DMSO-d_6	~124 (C-1), 73.3 (C-2), 135.2 (dd, C-3), 139.2 (dqd, C-4), 119.0 (qdd, C-5)	^2J(C-4,F-3) = 29; ^2J(C-4,F-5) = 39; ^1J(C-4,F-4) = 258; ^2J(C-3,F-4) = 21; ^1J(C-3,F-3) = 248; ^1J(C-5,F-5) = 271; ^2J(C-5,F-4) = 36; ^3J(C-5,F-3) = 6
trans-$CF_3CF{=}CFC{\equiv}C^a$	DMSO-d_6	125.0 (q, C-1), 74.3 (C-2), 137.8 (C-3), 141.8 (C-4), 119.5 (C-5)	^1J(C-1,B) = 102
trans-$CF_3CF{=}CFC{\equiv}C$	DMSO-d_6	~124 (C-1), 74.2 (C-2), 137.8 (dd, C-3), 141.8 (dqd, C-4), 119.2 (qdd, C-5)	^2J(C-4,F-3) = 53; ^2J(C-4,F-5) = 40; ^1J(C-4,F-4) = 245; ^2J(C-3,F-4) = 44; ^1J(C-3,F-3) = 243; ^1J(C-5,F-5) = 270; ^2J(C-5,F-4) = 35; ^3J(C-5,F-3) = 8
$C_6F_5C{\equiv}C^a$	acetone-d_6	118.2 (q, C-1), 72.3 (C-2), 102.4 (C-α), 147.8 (C-β), 137.9 (C-γ), 140.6 (C-δ)	^1J(C-1,B) = 106
$C_6F_5C{\equiv}C$	acetone-d_6	117.4 (C-1), 71.8 (C-2), 101.9 (t, C-α), 147.2 (dd, C-β), 137.9 (ddd, C-γ), 140.6 (td, C-δ)	^2J(C-β,F-γ) = 8; ^1J(C-β,F-β) = 251; ^2J(C-δ,F-γ) = 14; ^1J(C-δ,F-δ) = 252; ^2J(C-γ,F-β) = 15; ^2J(C-γ,F-δ) = 15; ^1J(C-γ,F-γ) = 248; ^2J(C-α,F-β) = 19
$C_3F_7{}^a$	D_2O	121.5 (q, C-1), 112.9 (q, C-2), 120.8 (q, C-3)	^1J(C-1,B) = 88; ^1J(C-3,F-3) = 263; ^2J(C-2,F-3) = 29
$C_4F_9{}^a$	D_2O	122.1 (q, C-1), 114.6 (C-2), 111.5 (q, C-3), 120.0 (qt, C-4)	^1J(C-1,B) = 87; 1J(C-4,F-4) = 262; ^2J(C-4,F-3) = 19; ^2J(C-3,F-4) = 29
C_8H_{17} [31]	DMSO-d_6	33.3, 31.6, 29.5, 29.0, 25.6, 22.3, 20.2, 14.0	
trans-$C_4F_9CF{=}CF^a$	DMSO-d_6	171.5 (q, C-1), 141.6 (C-2), 108.5 (C-3), 110.3 (C-4), 111.8 (C-5), 117.2 (C-6)	^1J(C-1,B) = 87
trans-$C_4F_9CF{=}CF$	DMSO-d_6	171.5 (C-1), 141.5 (tdd, C-2), 108.5 (m, C-3), 110.3 (m, C-4), 111.8 (m, C-5), 117.2 (tq, C-6)	^2J(C-2,F-3) = 27; ^2J(C-2,F-1) = 38; ^1J(C-2,F-2) = 227; ^2J(C-6,F-5) = 33; ^1J(C-6,F-6) = 288
cis-$C_2F_5CF{=}CF^a$	DMSO-d_6	165.8 (q, C-1), 139.8 (q, C-2), 109.6 (C-3), 118.7 (C-4)	^1J(C-1,B) = 90; ^2J(C-2,B) = 10
cis-$C_2F_5CF{=}CF$	DMSO-d_6	165.7 (C-1), 139.7 (d, C-2), 108.5 (t, C-3), 118.6 (tq, C-4)	^1J(C-2,F-2) = 252; ^2J(C-4,F-3) = 39; ^1J(C-4,F-4) = 287; ^1J(C-3,F-3) = 252
$C_4H_9C{\equiv}C^a$	acetone-d_6	91.9 (br m, C-1), 89.7 (C-2), 18.7 (C-3), 31.3 (C-4), 21.7 (C-5), 13.6 (C-6)	^1J(C-3,H-3) = 128; ^1J(C-4,H-4) = 125; ^1J(C-5,H-5) = 124; ^1J(C-6,H-6) = 125
$(CH_3)_3CC{\equiv}C^a$	DMSO-d_6	90.0 (C-1), 97.9 (C-2), 27.0 (C-3), 31.6 (q, C-4)	^1J(C-4,H-4) = 127
$CH_2ClCH_2CH_2$ [32]	DMSO-d_6	49.8, 30.9, 17.4 (m)	
trans-$CH_2ClCH{=}CH$ [33]	acetone-d_6	142.8 (m), 131.4, 49.7	

[a] Data from the $^{13}C\{^{19}F\}$ spectrum.

groups R_F = C_6F_5 (**15**), $CF_3CF{=}CF$ (**12**) caused a significant shift of the C-1 resonance to 117−118 and 123−125 ppm, respectively. It is an interesting coincidence that these values are very similar to those of α-difluoromethylene groups in the spectra of (perfluoroalkyl)trifluoroborates $K[R_FCF_2CF_2BF_3]$ (R_F = CF_3, C_2F_5), which themselves are strongly distinct from the chemical shifts of C-1 in (perfluoroalkenyl)trifluoroborates $K[R_FCF{=}CFBF_3]$, located at 165−172 ppm (Table 1). In all cases the C-1 signals appear as 1:1:1:1 quartets with $^1J_{CB}$ = 99−106 Hz for ((perfluoroorgano)ethynyl)-trifluoroborates and $^1J_{CB}$ = 87−90 Hz for perfluorinated alkyl- and alkenyltrifluoroborates. For comparison, the signals of C-1 and C-2 in the $^{13}C\{^{19}F\}$ NMR spectra of nonfluorinated alkynyltrifluoroborates $K[RC{\equiv}CBF_3]$ appear at lower frequencies. For example, the δ(C-1) and δ(C-2) values are equal to 91.9 and 89.7 ppm (R = C_4H_9) and 90.0 and 97.9 ppm (R = t-C_4H_9), respectively (Table 1). The resonances of C-1 and C-2 of alkyltrifluoroborates $K[RCH_2CH_2BF_3]$ are found at ca. 17−23 ppm and thus interfere with the ^{13}C chemical shifts of the methylene groups in the alkane chain (Table 1).

Experimental Section

Materials and Methods. 1,1,1,3,3-Pentafluoropropane (Honeywell), 2.5 M BuLi in hexanes (Aldrich), $K[HF_2]$ (Aldrich), $Me_3SiC{\equiv}CH$ (Aldrich), DMSO (Aldrich), 2-methyl-3-butyn-2-ol (Aldrich), 18-crown-6 (Aldrich), hexafluoropropene (Bristol Organics), zinc dust (Fluka), KF (Riedel-de Haën), 48% HF (Riedel-de Haën), CF_3CO_2H (Solvay), heptafluoropropyl iodide (ABCR), and heptafluoroisopropyl iodide (ABCR) were used as supplied. $B(OMe)_3$ (Fluka) and $B(O\text{-}i\text{-}Pr)_3$ (Fluka) were distilled over sodium before use. Solvents (ether, dichloromethane) were purified by standard procedures. All manipulations with organolithium compounds were performed under an atmosphere of dry argon.

The salts $K[RBF_3]$ (R = $C_4H_9C{\equiv}C$,[2] $(CH_3)_3CC{\equiv}C$,[25] C_3F_7,[6] C_4F_9[26]) and the alkene $C_6F_{13}CBr{=}CH_2$[22] were prepared as described in the literature. The yields of products were not optimized in all cases.

Physical and Analytical Measurements. NMR spectra were recorded on a Bruker AVANCE 300 (300.13 MHz, ^1H; 96.29 MHz,^{11}B; 75.47 MHz,^{13}C; 282.40 MHz,^{19}F) and a Bruker DRX 500 (125.75 MHz, ^{13}C; 470.59 MHz, ^{19}F) FT 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. FT-IR (pellets in KBr) and FT-Raman (powder) spectra were measured on a Bruker VECTOR 22 and Bruker IFS 66/FRA 106 spectrometer, respectively. Elemental analysis was performed with a

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HEKAtech EA3000 analyzer on the complexes [K·18-crown-6][$R_FC{\equiv}CBF_3$]. The latter were prepared in 70−80% yield by reaction of K[$R_FC{\equiv}CBF_3$] (1 equiv) and 18-crown-6 (1.1 equiv) in dichloromethane and subsequent crystallization by slow evaporation (over days) of the solvent at 20 °C.

Synthesis of K[$CF_3C{\equiv}CBF_3$] (16). A 2.5 M solution of BuLi in hexanes (95 mL, 237 mmol) was added dropwise to the stirred solution of $CF_3CH_2CHF_2$ (11.8 g, 88 mmol) in ether (300 mL) at −35 °C within 40 min, and the solution was kept at −35 °C for 1 h before it was warmed to −15 °C and $B(OMe)_3$ (9.9 g, 95 mmol) in ether (15 mL) was added dropwise with a syringe. The reaction mixture was warmed to 0 °C during 2 h. The ^{19}F and ^{11}B NMR spectra showed the presence of $[CF_3C{\equiv}CB(OCH_3)_3]^-$ (δ(F) −47.6 (s, F^3) ppm; δ(B) 0.8 (s) ppm) (main product)), $[(CF_3C{\equiv}C)_2B(OCH_3)_2]^-$ (δ(F) −47.8 (s, F^3) ppm; δ(B) −4.0 (s) ppm), $CF_2{=}C{=}CF_2$ (δ(F) −63.4 (s) ppm), the starting compounds $B(OMe)_3$ (δ(B) 18.3 (s) ppm) and $CF_3CH_2CHF_2$ (δ(F) −62.5 (m, 3F) and −115.2 (m, 2F) ppm), and admixtures of unknown products (singlets at δ(F) −50.6, −57.4, and −60.7 ppm). The solvents were partially evaporated under reduced pressure at ca. 0 °C, and the solution was poured into a solution of $K[HF_2]$ (20 g, 256 mmol) in water (50 mL) and 40% HF (12 mL). The resulting suspension was stirred overnight, diluted with water (50 mL), neutralized with K_2CO_3, and saturated with KF. The product was extracted with acetonitrile (3 × 50 mL), and the combined extracts were dried with $MgSO_4$. After evaporation of the solvent the brown solid residue was washed with toluene (3 × 50 mL) and with hexane (2 × 50 mL) and dried in a vacuum desiccator over Sicapent to yield the white solid **16** (8.4 g, 53%). ^{19}F NMR (CD_3CN): δ −48.3 (s, 3F, F^3), −137.0 (q $^1J_{FB}$ = 32 Hz, 3F, B*F*$_3$) ppm. ^{11}B NMR (CD_3CN): δ −2.8 (q $^1J_{BF}$ = 32 Hz) ppm.^{19}F NMR (acetone-d_6): δ −47.3 (s, 3F, F^3), −135.5 (q $^1J_{FB}$ = 31 Hz, 3F, B*F*$_3$) ppm. ^{11}B NMR (acetone-d_6): δ −2.4 (q $^1J_{BF}$ = 31 Hz) ppm. ^{19}F NMR (DMSO-d_6): δ −47.9 (s, 3F, F^3), −134.3 (q $^1J_{FB}$ = 31 Hz, 3F, B*F*$_3$) ppm. IR: ν_{max}/cm^{-1} 2241 (w) ν(C≡C), 1724 (w), 1626 (m), 1286 (s), 1263 (s), 1223 (s), 1128 (s), 1080 (s), 1022 (s), 968 (s), 839 (s), 699 (w), 612 (w), 585 (s). Raman: ν_{max}/cm^{-1} 2236 ν(C≡C), 1404, 701, 279, 191. Anal. Calcd for C_3BF_6K (199.93): C, 18.02; F, 57.01. Found: C, 18.0; F, 56.5.

Synthesis of $CF_3CF{=}CFC{\equiv}CSiMe_3$ (10). A 2.5 M solution of BuLi in hexanes (18 mL, 45 mmol) was added dropwise to a cold (−50 °C) stirred solution of ethynyltrimethylsilane (5.0 g, 50 mmol) in ether (50 mL) at <−35 °C. The colorless solution was kept at −15 to −20 °C for 30 min. After it was cooled to −70 °C, the solution was added to a cold (−70 °C) stirred solution of hexafluoropropene (10 g, 66 mmol) in ether (50 mL) within 5 min. The solution was stirred at −75 °C for 1 h and then warmed to ambient temperature overnight. After it was washed with water and acidified with HCl, the aqueous phase was extracted with ether (50 mL). The combined extracts were washed with water and dried with $MgSO_4$. The product **10** (6.2 g, 60%; cis:trans = 31:69) was isolated by distillation (bp 100−118 °C) (lit.[27] bp for *trans*-$CF_3CF{=}CFC{\equiv}CSiMe_3$ 105−107 °C) and contained an admixture (4%) of the isomer $CF_2{=}CFCF_2C{\equiv}CSiMe_3$.

***trans*-$CF_3CF{=}CFC{\equiv}CSiMe_3$ (*trans*-10).** ^{19}F NMR (neat): δ −68.7 (dd $^3J_{FF}$ = 11 Hz; $^4J_{FF}$ = 21 Hz, 3F, F^5), −140.2 (dq $^3J_{FF}$ = 141 Hz; $^4J_{FF}$ = 21 Hz, 1F, F^3), −162.3 (dq $^3J_{FF}$ = 141 Hz; $^3J_{FF}$ = 11 Hz, 1F, F^4) ppm. ^1H NMR (neat): δ 0.08 (s, 9H) ppm (lit.[27] ^{19}F NMR ($CDCl_3$): δ −68.4 (dd 12 Hz; 22 Hz, 3F, F^5), −139.9 (dq 142 Hz; 22 Hz, 1F, F^3), −161.8 (dq 142 Hz; 12 Hz, 1F, F^4) ppm. ^1H NMR ($CDCl_3$): δ 0.28 (s) ppm.

***cis*-$CF_3CF{=}CFC{\equiv}CSiMe_3$ (*cis*-10).** ^{19}F NMR (neat): δ −68.7 (dd $^3J_{FF}$ = 12 Hz; $^4J_{FF}$ = 7 Hz, 3F, F^5), −123.5 (dq $^3J_{FF}$ = 10 Hz; $^4J_{FF}$ = 7 Hz, 1F, F^3), −145.4 (dq $^3J_{FF}$ = 10 Hz; $^4J_{FF}$ = 12 Hz, 1F, F^4) ppm. ^1H NMR (neat): δ 0.05 (s, 9H) ppm.

$CF_2{=}CFCF_2C{\equiv}CSiMe_3$.$^{19}F$ NMR (neat): δ −85.3 (ddd $^4J_{FF}$ = 8 Hz; $^4J_{FF}$ = 20 Hz; $^3J_{FF}$ = 20 Hz, 2F, F^3), −95.9 (ddt $^2J_{FF}$ = 59 Hz; $^3J_{FF}$ = 38 Hz; $^4J_{FF}$ = 8 Hz, 1F, F^{5trans}), −107.2 (ddt $^2J_{FF}$ = 59 Hz; $^3J_{FF}$ = 117 Hz; $^4J_{FF}$ = 20 Hz, 1F, F^{5cis}), −187.2 (ddt $^3J_{FF(cis)}$ = 38 Hz; $^3J_{FF(trans)}$ = 117 Hz; $^3J_{FF}$ = 20 Hz, 1F, F^4) ppm. ^1H NMR (neat): δ 0.05 (s, 9H) ppm.

Synthesis of $CF_3CF{=}CFC{\equiv}CH$ (11). Silane **10** (6.0 g, 26 mmol) was added dropwise to a stirred solution of KF (6.1 g, 105 mmol) and water (2 mL, 111 mmol) in DMSO (42 mL). Under a slow flow of dry argon the reaction mixture was warmed to 40−50 °C for 2.5 h. The product was collected in a cold (−60 °C) trap which contained anhydrous ether (10 mL). The ^1H and ^{19}F NMR spectra showed the formation of $CF_3CF{=}CFC{\equiv}CH$ (13 mmol of *trans*-**11**, 6.7 mmol of *cis*-**11**) and Me_3SiF (8 mmol).

***trans*-$CF_3CF{=}CFC{\equiv}CH$ (*trans*-11).** ^{19}F NMR (ether): δ −67.4 (dd $^3J_{FF}$ = 11 Hz; $^4J_{FF}$ = 21 Hz, 3F, F^5), −140.2 (dqd $^3J_{FF(trans)}$ = 140 Hz; $^4J_{FF}$ = 21 Hz; $^4J_{FH}$ = 4 Hz, 1F, F^3), −161.2 (dq $^3J_{FF(trans)}$ = 140 Hz; $^3J_{FF}$ = 11 Hz, 1F, F^4) ppm. ^1H NMR (ether): δ 4.59 (d $^4J_{HF}$ = 4 Hz) ppm.

***cis*-$CF_3CF{=}CFC{\equiv}CH$ (*cis*-11).** ^{19}F NMR (ether): δ −67.4 (dd $^3J_{FF}$ = 12 Hz; $^4J_{FF}$ = 7 Hz, 3F, F^5), −123.3 (dqd $^3J_{FF(cis)}$ = 9 Hz; $^4J_{FF}$ = 7 Hz; $^4J_{FH}$ = 1 Hz, 1F, F^3), −143.4 (dqd $^3J_{FF(cis)}$ = 9 Hz; $^4J_{FF}$ = 12 Hz; $^5J_{FH}$ = 3 Hz, 1F, F^4) ppm. ^1H NMR (ether): δ 4.48 (m) ppm.

Synthesis of K[*cis*- and *trans*-$CF_3CF{=}CFC{\equiv}CBF_3$] (12). A solution of **11** (cis:trans = 1:2; 16 mmol) in ether (25 mL) was cooled to −40 °C, and 3.3 M EtMgBr (5 mL, 16.5 mmol) in ether was added using a syringe within 10 min. The reaction mixture was always kept below −35 °C. Immediately a white suspension was formed. Above −30 °C the complete dissolution of the precipitate occurred. Subsequently the solution was warmed to 20 °C within 1 h. After the mixture was cooled to −30 °C, $B(OMe)_3$ (2.2 g, 21 mmol) was added with a syringe. A suspension was formed, which was stirred at −25 °C for 5 min and at 0 °C for 10 min before being poured into a stirred suspension of $K[HF_2]$ (12 g, 153 mmol) in water (25 mL) and MeOH (5 mL). After 1 h the organic solvents were evaporated and the aqueous suspension was saturated with KF and extracted with MeCN (50 mL). The extract was dried with $MgSO_4$, evaporated to dryness, and suspended in 24% HF (4 mL) to complete the fluorodemethoxylation of (perfluoroorgano)fluoromethoxyborates. After 20 min the suspension was saturated with KF under cooling (cold water). Extraction with MeCN (3 × 10 mL) followed. The extracts were dried with dry KF, the solvent was removed under reduced pressure, and the solid residue was dried under vacuum (0.13 hPa) for 4 h. The salt K[$CF_3CF{=}CFC{\equiv}CBF_3$] (*cis*-**12**:*trans*-**12** = 1:2) was obtained in 21% yield (0.9 g). IR: ν_{max}/cm^{-1} 1698 (m), 1616 (w), 1377 (s), 1263 (s), 1215 (m), 1162 (s), 1055 (s), 1001 (s), 982 (s), 770 (w), 713 (w), 687 (w), 648 (w), 608 (w), 515 (w), 454 (w). Raman: ν_{max}/cm^{-1} 2197 ν(C≡C), 1699 ν(C=C), 1381, 671. ^{19}F NMR (MeCN) (*cis*-**12**): δ −67.6 (dd $^3J_{FF}$ = 12 Hz; $^4J_{FF}$ = 7 Hz, 3F, F^5), −116.4 (m, 1F, F^3), −136.2 (q $^1J_{FB}$ = 32 Hz, B*F*$_3$), −152.0 (dd $^3J_{FF(cis)}$ = 12 Hz; $^3J_{FF}$ = 12 Hz, 1F, F^4) ppm. ^{11}B NMR (MeCN) (*cis*-**12**): δ −2.2 (q $^1J_{BF}$ = 32 Hz) ppm. ^{19}F NMR (H_2O) (*cis*-**12**): δ −67.5 (dd $^3J_{FF}$ = 12 Hz; $^4J_{FF}$ = 7 Hz, 3F, F^5), −120.2 (m, 1F, F^3), −134.0 (q $^1J_{FB}$ = 32 Hz, B*F*$_3$), −147.0 (dd $^3J_{FF(cis)}$ = 12 Hz; $^3J_{FF}$ = 12 Hz, 1F, F^4) ppm. ^{11}B NMR (H_2O) (*cis*-**12**): δ −2.8 (q $^1J_{BF}$ = 32 Hz) ppm. ^{19}F NMR (DMSO-d_6) (*cis*-**12**): δ −67.5 (dd $^3J_{FF}$ = 13 Hz; $^4J_{FF}$ = 7 Hz, 3F, F^5), −115.8 (m, 1F, F^3), −134.8 (q $^1J_{FB}$ = 30 Hz, B*F*$_3$), −152.7 (dd $^3J_{FF}$ = 14 Hz; $^3J_{FF(cis)}$ = 15 Hz, 1F, F^4) ppm. ^{19}F NMR (MeCN) (*trans*-**12**): δ −67.7 (dd $^3J_{FF}$ = 12 Hz; $^4J_{FF}$ = 21 Hz, 3F, F^5), −134.5 (dd $^3J_{FF(trans)}$ = 140 Hz; $^4J_{FF}$ = 21 Hz, 1F, F^3), −136.1 (q $^1J_{FB}$ = 32 Hz, B*F*$_3$), −167.7 (dd $^3J_{FF}$ = 140 Hz; $^3J_{FF}$ = 12 Hz, 1F, F^4) ppm. ^{11}B NMR (MeCN) (*trans*-**12**): δ −2.2 (q $^1J_{BF}$ = 32 Hz) ppm. ^{19}F NMR (H_2O) (*trans*-**12**): δ −67.7 (dd $^3J_{FF}$ = 12 Hz; $^4J_{FF}$ = 21 Hz, 3F, F^5), −137.4 (dd $^3J_{FF(trans)}$ = 140 Hz; $^4J_{FF}$ = 21 Hz, 1F, F^3), −133.9 (q $^1J_{FB}$ = 32 Hz, B*F*$_3$), −164.0 (dd $^3J_{FF(trans)}$ = 140 Hz; $^3J_{FF}$ = 12 Hz, 1F, F^4) ppm. ^{11}B NMR (H_2O) (*trans*-**12**): δ −2.8 (q $^1J_{BF}$ = 32 Hz) ppm. ^{19}F NMR (DMSO-d_6) (*trans*-**12**): δ −67.8 (dd $^3J_{FF}$ = 13 Hz; $^4J_{FF}$ = 21 Hz, 3F, F^5),

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−134.4 (dd $^3J_{FF(trans)}$ = 141 Hz; $^4J_{FF}$ = 21 Hz, 1F, F^3), −134.8 (q $^1J_{FB}$ = 30 Hz, B*F*$_3$), −168.6 (dd $^3J_{FF(trans)}$ = 141 Hz; $^3J_{FF}$ = 12 Hz, 1F, F^4) ppm.

[K·18-crown-6][CF$_3$CF=CFC≡CBF$_3$]. Anal. Calcd for $C_{17}H_{24}BF_8KO_6$ (526.27): C, 38.80; H, 4.60. Found: C, 39.08; H, 4.62.

Synthesis of C$_3$F$_7$CH=ClC(OH)(CH$_3$)$_2$ (5). A three-necked flask (100 mL) equipped with a magnetic stirrer, a reflux condenser, and a septum inlet was charged with zinc dust (3.3 g, 50 mmol), CH_2Cl_2 (50 mL), 2-methyl-3-butyn-2-ol (4.2 g, 50 mmol), and C_3F_7I (14.8 g, 50 mmol) in succession. Then CF_3CO_2H (1.16 g, 10 mmol) was added with a syringe to the stirred suspension and the reaction mixture was refluxed gently. After 10 min the evolution of heat ceased and the suspension was stirred for a further 2 h at ambient temperature. Zinc was removed by filtration and washed with CH_2Cl_2 (20 mL). The combined CH_2Cl_2 solutions were evaporated under reduced pressure to give product **5** (*E*:*Z* = 86:14; yellow oil, 16.7 g), which was used for the preparation of **7** without further purification.

***(E)*-C$_3$F$_7$CH=ClC(OH)(CH$_3$)$_2$ (*(E)*-5).** ^{19}F NMR (CH_2Cl_2): δ −81.9 (t $^4J_{FF}$ = 9 Hz, 3F,C*F*$_3$), −110.7 (qd $^4J_{FF}$ = 9 Hz; $^3J_{FF}$ = 13 Hz, 2F, $CF_3CF_2CF_2$), −128.8 (m, 2F, $CF_3CF_2CF_2$) ppm. ^{1}H NMR (CH_2Cl_2): δ 6.76 (t $^4J_{HF}$ = 13 Hz, 1H, C*H*=C), 3.10 (O*H*), 1.46 (m, 6H, 2C*H*$_3$) ppm.

***(Z)*-C$_3$F$_7$CH=ClC(OH)(CH$_3$)$_2$ (*(Z)*-5).** ^{19}F NMR (CH_2Cl_2): δ −82.0 (t $^4J_{FF}$ = 9 Hz, 3F, C*F*$_3$), −114.1 (qd $^4J_{FF}$ = 9 Hz; $^3J_{FH}$ = 11 Hz, 2F, $CF_3CF_2CF_2$), −129.3 (m, 2F, $CF_3CF_2CF_2$) ppm. ^{1}H NMR (CH_2Cl_2): δ 5.82 (t $^4J_{HF}$ = 11 Hz, 1H, C*H*=C), 3.10 (O*H*), 1.46 (m, 6H, 2C*H*$_3$) ppm.

Synthesis of C$_3$F$_7$C≡CC(OH)(CH$_3$)$_2$ (7). A three-necked flask (100 mL) equipped with a magnetic stirrer, a reflux condenser, and a dropping funnel was charged with KOH (2.9 g, 50 mmol), water (4 mL), and ethanol (10 mL). A solution of **5** in ethanol (2 mL) was added dropwise, and the reaction mixture was stirred for 1 h at ambient temperature, then diluted with water and acidified with HCl, and finally extracted with ether. The extract was dried with $MgSO_4$, and the solvent was removed on a rotary evaporator to give a yellow liquid (10 g) which contained residual ether (2 g), *cis*-**5** (3 mmol), and **7** (27 mmol) (^{1}H, ^{19}F NMR). This liquid was used for the preparation of **3** without purification.

C$_3$F$_7$C≡CC(OH)(CH$_3$)$_2$ (7). ^{19}F NMR (ether): δ −80.5 (t $^4J_{FF}$ = 8 Hz, 3F, C*F*$_3$), −98.4 (tq $^3J_{FF}$ = 5 Hz; $^4J_{FF}$ = 8 Hz, 2F, $CF_3CF_2CF_2$), −127.2 (t $^3J_{FF}$ = 5 Hz, 2F, $CF_3CF_2CF_2$) ppm.

Synthesis of C$_3$F$_7$C≡CH (3). NaOH pellets (1.8 g, 45 mmol) were added to a ether solution of **7** (27 mmol, see above). The mixture was stirred at 100−105 °C (bath) for 40 min. Product **3** (15 mmol, 56%) was collected in a cold (−40 °C) receiver with anhydrous ether (4 mL). ^{19}F NMR (ether): δ −79.9 (t $^4J_{FF}$ = 8.7 Hz, 3F, F^5), −99.1 (tdq $^3J_{FF}$ = 4 Hz; $^4J_{FH}$ = 5.7 Hz; $^4J_{FF}$ = 8.7 Hz, 2F, F^3), −126.5 (t $^3J_{FF}$ = 4 Hz, 2F, F^4) ppm. ^{1}H NMR (ether): δ 3.63 (t $^4J_{HF}$ = 5.6 Hz, 1H, H^1) ppm (lit. ^{19}F NMR (CCl_4): δ −81.5 (t 10 Hz), −101.5 (m), −128.4 (t 5 Hz) ppm. ^{1}H NMR (CCl_4): δ 2.9 ppm.[28] ^{19}F NMR (neat): δ −100.0 (F^3) ppm. ^{1}H NMR (neat): δ 3.0 ppm)[29]).

Synthesis of K[CF$_3$CF$_2$CF$_2$C≡CBF$_3$] (13). A solution of **3** (15 mmol) in ether (50 mL) was cooled to −60 °C, and 2.5 M BuLi (5 mL, 12.5 mmol) was added using a syringe within 10 min, ensuring that the internal temperature did not rise above −55 °C. The solution was stirred at −55 °C for 1 h and then cooled to −70 °C and transferred with a cannula into the cold (−80 °C) stirred solution of $B(OMe)_3$ (1.8 g, 17 mmol) in ether (50 mL). After additional stirring at −65 °C for 1 h, the solution was warmed to 0 °C within 2 h and then added to the stirred solution of $K[HF_2]$ (7.8 g, 100 mmol) in water (40 mL) and 48% HF (15 mL). The reaction mixture was stirred for 2 h, saturated with KF, and extracted with MeCN (3 × 40 mL). The combined extracts were dried with anhydrous KF and evaporated to dryness. Subsequent drying under vacuum gave the white solid **13** (2.0 g, 45%). ^{19}F NMR (CH_3CN): δ −80.3 (t $^4J_{FF}$ = 8.7 Hz, 3F, F^5), −95.3 (m, 2F, F^3), −126.9 (t $^3J_{FF}$ = 6 Hz, 2F, F^4), −136.6 (q $^1J_{FB}$ = 31 Hz, B*F*$_3$) ppm. ^{11}B NMR (CH_3CN): δ −2.6 (q $^1J_{BF}$ = 31 Hz) ppm. IR: ν_{max}/cm^{-1} 2228 (vw) ν(C≡C), 1612 (vw), 1352 (s), 1280 (s), 1248 (s), 1232 (s), 1182 (s), 1126 (s), 1041 (s), 996 (s), 945 (m), 772 (w), 727 (s), 687 (w), 659 (w), 627 (w), 601 (w), 536 (w). Raman: ν_{max}/cm^{-1} 2229 ν(C≡C), 1454, 774, 687, 189.

[K·18-crown-6][CF$_3$CF$_2$CF$_2$C≡CBF$_3$]. Anal. Calcd for $C_{17}H_{24}BF_{10}KO_6$ (564.27): C, 36.19; H, 4.29. Found: C, 36.37; H, 4.36.

Synthesis of CF$_3$CF(CF$_3$)CH=ClC(OH)(CH$_3$)$_2$ (6). Product **6** (*E*:*Z* = 88:12; yellow oil, 16.2 g, 42 mmol, 76%) was prepared as described for compound **5** from zinc dust (3.3 g, 50 mmol), CH_2Cl_2 (50 mL), 2-methyl-3-butyn-2-ol (4.3 g, 51 mmol), *i*-C_3F_7I (16.7 g, 56 mmol), and CF_3CO_2H (1.15 g, 10 mmol) and used for the preparation of **8** without further purification.

***(E)*-CF$_3$CF(CF$_3$)CH=ClC(OH)(CH$_3$)$_2$ (*(E)*-6).** ^{19}F NMR (CH_2Cl_2): δ −78.3 (d $^3J_{FF}$ = 8.3 Hz, 6F, 2C*F*$_3$), −189.0 (dsept $^3J_{FH}$ = 22 Hz; $^3J_{FF}$ = 8.3 Hz, 1F, C*F*) ppm. ^{1}H NMR (CH_2Cl_2): δ 6.73 (d $^3J_{HF}$ = 22 Hz, 1H, C*H*=C), 2.3 (br, O*H*), 1.45 (m, 6H, 2C*H*$_3$) ppm.

***(Z)*-CF$_3$CF(CF$_3$)CH=ClC(OH)(CH$_3$)$_2$ (*(Z)*-6).** ^{19}F NMR (CH_2Cl_2): δ −78.9 (d $^3J_{FF}$ = 7.6 Hz, 6F, 2C*F*$_3$), −187.3 (dsept $^3J_{FH}$ = 21 Hz; $^3J_{FF}$ = 7.6 Hz, 1F, C*F*) ppm. ^{1}H NMR (CH_2Cl_2): δ 6.37 (d $^3J_{HF}$ = 16 Hz, 1H, C*H*=C), 2.3 (br, O*H*), 1.45 (m, 6H, 2C*H*$_3$) ppm.

Synthesis of CF$_3$CF(CF$_3$)C≡CC(OH)(CH$_3$)$_2$ (8). The preparation of **8** from **6** (42 mmol), KOH (3.0 g, 53 mmol), water (4 mL), and ethanol (25 mL) was performed analogously to the synthesis of **7**. After removal of the solvent on a rotary evaporator (25 °C, bath), the yellow liquid residue (15 g) was distilled. The fraction which boiled in the range 90−105 °C (9.1 g) consisted of ethanol (3.5 g), **8** (4.8 g, 19 mmol), and *trans*-$CF_3CF(CF_3)CH{=}CHC(OH)(CH_3)_2$ (**9**; 0.8 g, 3 mmol) (^{1}H, ^{19}F NMR) was used for the preparation of **4** without further purification.

CF$_3$CF(CF$_3$)C≡CC(OH)(CH$_3$)$_2$ (8). ^{19}F NMR (EtOH): δ −77.8 (d $^3J_{FF}$ = 10.5 Hz, 6F, 2C*F*$_3$), −167.1 (sept $^3J_{FF}$ = 10.5 Hz, 1F, C*F*) ppm. ^{1}H NMR (EtOH): δ 1.44 (m, 6H, 2C*H*$_3$) ppm.

***trans*-CF$_3$CF(CF$_3$)CH=CHC(OH)(CH$_3$)$_2$ (9).** ^{19}F NMR (EtOH): δ −77.9 (d $^3J_{FF}$ = 7.3 Hz, 6F, 2C*F*$_3$), −186.0 (dsept $^3J_{FH}$ = 21 Hz; $^3J_{FF}$ = 7.5 Hz, 1F, C*F*) ppm. ^{1}H NMR (EtOH): δ 6.34 (d $^3J_{HH}$ = 15.7 Hz; 1H, $R_FCH{=}CH$), 5.75 (dd $^3J_{HH}$ = 15.7 Hz; $^3J_{HF}$ = 21 Hz, 1H, $R_FCH{=}CH$), 1.25 (m, 6H, 2C*H*$_3$) ppm.

Synthesis of CF$_3$CF(CF$_3$)C≡CH (4). NaOH powder (4.5 g, 112 mmol) was added to the solution of **8** (19 mmol, see above). The mixture was stirred at 75−80 °C (bath) for 40 min. Product **4** (12 mmol, 64%) was collected in a cold (−50 °C) receiver with anhydrous ether (1 mL). ^{19}F NMR (ether): δ −77.0 (d $^3J_{FF}$ = 10 Hz, 6F, 2C*F*$_3$), −168.1 (dsept $^4J_{FH}$ = 6 Hz; $^3J_{FF}$ = 10 Hz, 1F, F^3) ppm. ^{1}H NMR (ether): δ 3.66 (d $^4J_{HF}$ = 6 Hz, 1H, H^1) ppm. (lit.[30] ^{19}F NMR (neat): δ −90.7 and −171.8 ppm; J_{FF} = 9.9 Hz; J_{FH} = 6.0 Hz; J_{FH} = 0.4 Hz. ^{1}H NMR (neat): δ 2.35 ppm).

Synthesis of K[CF$_3$CF(CF$_3$)C≡CBF$_3$] (14). Salt **14** was obtained by metalation of **4** (12 mmol) in ether solution (50 mL) with 2.5 M BuLi (4.8 mL, 12 mmol), subsequent alkynylation of $B(OMe)_3$ (1.6 g, 15 mmol) in ether (50 mL), and

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fluorodemethoxylation of lithium (perfluoroalkynyl)trimethoxyborate with K[HF_2] (7.1 g, 91 mmol) in water (30 mL) and 48% HF (10 mL), as described for the synthesis of salt **13**. The yield of **14** was 2.6 g (72%). ^{19}F NMR (CH_3CN): δ −77.6 (d $^3J_{FF}$ = 10.8 Hz, 6F, 2CF_3), −136.5 (q $^1J_{FB}$ = 31 Hz, BF_3), −162.5 (sept $^3J_{FF}$ = 11 Hz, 1F, F^3) ppm. ^{11}B NMR (CH_3CN): δ −2.6 (dq $^4J_{BF}$ = 2 Hz; $^1J_{BF}$ = 31 Hz) ppm. ^{19}F NMR (DMSO-d_6): δ −77.1 (d $^3J_{FF}$ = 11 Hz, 6F, 2CF_3), −134.0 (q $^1J_{FB}$ = 29 Hz, BF_3), −162.1 (qsept $^5J_{FB}$ = 2 Hz; $^3J_{FF}$ = 11 Hz, 1F, F^3) ppm. IR: ν_{max}/cm^{-1} 1616 (w), 1326 (s), 1299 (s), 1245 (s), 1212 (s), 1232 (s), 1180 (s), 1164 (s), 1091 (s), 1015 (s), 997 (s), 972 (s), 725 (m), 637 (m), 596 (w), 558 (w), 527 (w), 483 (w). Raman: ν_{max}/cm^{-1} 2218 ν(C≡C), 1271, 1171, 779, 723, 640, 561, 331, 168.

[K·18-crown-6][$CF_3CF(CF_3)C{\equiv}CBF_3$]. Anal. Calcd for $C_{17}H_{24}BF_{10}KO_6$ (564.27): C, 36.19; H, 4.29. Found: C, 36.44; H, 4.28.

Synthesis of K[$C_6F_{13}C{\equiv}CBF_3$] (18). A solution of diisopropylamine (1.01 g, 10 mmol) in 40 mL of ether was cooled to −78 °C, and BuLi (2.5 M in hexanes, 4 mL, 10 mmol) was gradually added. The resulting solution was stirred at −78 °C for 15 min, warmed to 10 °C within 30 min, and stirred at this temperature for 10 min. After the mixture was cooled to −78 °C, a solution of $C_6F_{13}CBr{=}CH_2$ (2.15 g, 5 mmol) in 10 mL of ether was added dropwise. The solution was stirred at −78 °C for 1 h before B(O-*i*-Pr)$_3$ (940 mg, 5 mmol) was added. After it was stirred at −78 °C for 1 h, the solution was gradually warmed to 20 °C. The ether solution was poured into a solution of K[HF_2] (4 g) and 48% aqueous HF (1.5 mL) in water (20 mL). The reaction mixture was stirred at 20 °C until ether was evaporated. The mixture was extracted with acetonitrile (5 × 10 mL). The combined extracts were dried with KF, and the solvent was evaporated to give the salt **18** (450 mg, 20%). ^{19}F NMR (CH_3CN): δ − 80.0 (tt $^4J_{FF}$ = 10 Hz; $^3J_{FF}$ = 2 Hz, 3F, F^8), − 93.0 (m, 2F, F^3), −120.0 (m, CF_2), −121.4 (m, CF_2), −121.7 (m, CF_2), −125.0 (m, CF_2), −135.5 (q $^1J_{FB}$ = 31 Hz, BF_3) ppm. ^{11}B NMR (CH_3CN): δ −2.5 (q $^1J_{BF}$ = 31 Hz) ppm.

Synthesis of K[$C_6F_5C{\equiv}CBF_3$] (15). A three-necked flask (100 mL) equipped with a magnetic stirrer, a thermometer, and a septum inlet was charged with (pentafluorophenyl)-acetylene (**1**; 910 mg, 4.74 mmol) and ether (60 mL). The solution was cooled to −95 °C (acetone−liquid N_2 bath) and 2.5 M BuLi in hexanes (1.8 mL, 4.5 mmol) was added slowly with a syringe, precluding an internal temperature above −90 °C. The mixture was stirred at −90 to −95 °C for 2 h before B(O-*i*-Pr)$_3$ (940 mg, 5.0 mmol) was added with a syringe. A white suspension resulted, which was stirred at −90 °C for 1 h, warmed to −20 °C, and poured into a solution of K[HF_2] (8 g, 102 mmol) in water (45 mL) and 48% HF (3 mL). The mixture was stirred at 20 °C for 1 h, before being extracted with acetonitrile (5 × 20 mL). The combined extracts were treated with 10 g of KF and formed two phases. The organic phase was separated, and the aqueous phase was again extracted with acetonitrile (2 × 10 mL). The combined extracts were evaporated under reduced pressure. The solid residue was dried under high vacuum (0.013 hPa) for 2 h and then over Sicapent in a vacuum desiccator overnight. The white salt **15** (910 mg, 64%) was obtained as a powder. ^{19}F NMR (CH_3CN): δ −134.3 (q $^1J_{FB}$ = 33 Hz, BF_3), −138.4 (m, 2F, $F^{2,6}$), −156.9 (t $^3J_{FF}$ = 20 Hz, 1F, F^4), −163.6 (m, 2F, $F^{3,5}$) ppm. ^{11}B NMR (CH_3CN): δ −1.9 (q $^1J_{BF}$ = 34 Hz) ppm. ^{19}F NMR (acetone-d_6): δ −134.3 (q $^1J_{FB}$ = 33 Hz, BF_3), −137.9 (m, 2F, $F^{2,6}$), −156.9 (t $^3J_{FF}$ = 20 Hz, 1F, F^4), −163.6 (m, 2F, $F^{3,5}$) ppm. IR: ν_{max}/cm^{-1} 2206 (vw) ν(C≡C), 1634 (w), 1528 (s), 1500 (s), 1378 (w), 1301 (w), 1239 (w), 1142 (s), 1086 (s), 1055 (s), 989 (s), 952 (s), 744 (w), 702 (w), 596 (w), 561 (w), 534 (w), 522 (w), 483 (w), 470 (w). Raman: ν_{max}/cm^{-1} 2207 ν(C≡C), 1657, 1442, 955, 563, 435, 390, 172.

[K·18-crown-6][$C_6F_5C{\equiv}CBF_3$]. Anal. Calcd for $C_{20}H_{24}BF_8KO_6$ (562.30): C, 42.72; H, 4.30. Found: C, 42.0; H, 4.76.

Synthesis of K[$C_4F_9CF{=}CFC{\equiv}CBF_3$] (19). (A) BuLi (2.5 M in hexanes, 8 mL, 20 mmol) was added to the precooled solution of $C_6F_{13}CBr{=}CH_2$ (4.30 g, 10 mmol) in 50 mL of ether at −70 °C. The reaction mixture was stirred at −78 °C for 2 h, and B(O-*i*-Pr)$_3$ (1.88 g, 10 mmol) was added in one portion. Stirring was continued for an additional 1 h. After it was gradually warmed to −20 °C, the mixture was poured into a solution of K[HF_2] (8 g, 102 mmol) in water (45 mL) and 48% HF (3 mL). This mixture was stirred at 20 °C for 1 h and then extracted with acetonitrile (5 × 20 mL). The combined extracts were treated with 10 g of KF and formed two phases. The organic phase was separated, and the aqueous phase was extracted once more with acetonitrile (2 × 10 mL). The combined extracts were evaporated under reduced pressure. The solid residue was dried under high vacuum (0.013 hPa) for 2 h and then over Sicapent in a vacuum desiccator overnight. Salts *cis*-**19** and *trans*-**19** (1:2) (1.81 g, 44%) were obtained.

(B) When the above synthesis was repeated with 50% more BuLi (2.5 M in hexanes, 12 mL, 30 mmol), the salts *cis*-**19** and *trans*-**19** (5:6) were obtained in 66% yield (2.7 g). ^{19}F NMR (CH_3CN) (*cis*-**19**): δ −80.1 (tt $^3J_{FF}$ = 2.5 Hz; $^4J_{FF}$ = 10 Hz, 3F, F^8), −109.1 (d $^3J_{FF(cis)}$ = 13 Hz, 2F, F^3), −114.9 (dt $^3J_{FF}$ = 13 Hz; $^4J_{FF}$ = 13 Hz, 2F, F^5), −122.9 (m, 2F, F^6), −125.4 (m, 2F, F^7), −135.3 (q $^1J_{FB}$ = 33 Hz, BF_3), −148.3 (m, 2F, F^4) ppm. ^{11}B NMR (CH_3CN) (*cis*-**19**): δ −2.2 (q $^1J_{BF}$ = 32 Hz) ppm. ^{19}F NMR (CH_3CN) (*trans*-**19**): δ −80.2 (tt $^3J_{FF}$ = 2.5 Hz; $^4J_{FF}$ = 10 Hz, 3F, F^8), −131.3 (dt $^3J_{FF}$ = 141 Hz; $^4J_{FF}$ = 25 Hz, 2F, F^3), −116.3 (dt $^3J_{FF}$ = 14 Hz; $^4J_{FF}$ = 13 Hz, 2F, F^5), −123.6 (m, 2F, F^6), −125.4 (m, 2F, F^7), −135.2 (q $^1J_{FB}$ = 33 Hz, BF_3), −163.9 (dt $^3J_{FF}$ = 141 Hz; $^3J_{FF}$ = 14 Hz, 2F, F^4) ppm. ^{11}B NMR (CH_3CN) (*trans*-**19**): δ −2.1 (q $^1J_{BF}$ = 32 Hz) ppm. IR: ν_{max}/cm^{-1} 1692 (m), 1614 (w), 1363 (s), 1340 (s), 1243 (s), 1212 (s), 1140 (s), 1087 (s), 1031 (s), 1001 (s), 943 (m), 860 (m), 814 (m), 747 (m), 727 (m), 646 (w), 624 (w), 601 (w), 579 (w), 533 (w). Raman: ν_{max}/cm^{-1} 2198 ν(C≡C), 1692 ν(C=C), 1342, 749, 621, 386, 152.

[K·18-crown-6][$C_4F_9CF{=}CFC{\equiv}CBF_3$]. Anal. Calcd for $C_{20}H_{24}BF_{14}KO_6$ (676.29): C, 35.52; H, 3.58. Found: C, 35.4; H, 3.58.

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Supporting Information Available: Tables S1−S3, compiling the ^{11}B and ^{19}F NMR spectra of K[R_FBF_3] (R_F = polyfluoroalkyl, polyfluoroalk-1-enyl, polyfluoroaryl). This material is available free of charge via the Internet at http://pubs.acs.org.

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