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A well feasible and general route to (organoethynyl)difluoroboranes, $R_HC{\equiv}CBF_2$, and their perfluorinated analogues, $R_FC{\equiv}CBF_2$ [☆]

Vadim V. Bardin [a], Nicolay Yu. Adonin [a], Hermann-Josef Frohn [b,*]

[a] N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS, Acad. Lavrentjev Ave. 9, 630090 Novosibirsk, Russia
[b] Department of Chemistry, Inorganic Chemistry, University of Duisburg-Essen, Lotharstr. 1, D-47048 Duisburg, Germany

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Dedicated to the 100th Anniversary of Professor I.L. Knunyants.

Abstract

A representative series of (organoethynyl)difluoroboranes $RC{\equiv}CBF_2$ ($R{=}C_4H_9$, $(CH_3)_3C$, CF_3, C_3F_7, $(CF_3)_2CF$, $CF_3CF{=}CF$, $C_4F_9CF{=}CF$, C_6F_5) was prepared by abstraction of fluoride from the corresponding $K[RC{\equiv}CBF_3]$ salts with BF_3 in appropriate solvents (1,1,1,3,3-pentafluoropropane, 1,1,1,3,3-pentafluorobutane, or dichloromethane).

Keywords: Fluoroboranes; Fluoroborates; Alk-1-ynylboron compounds; NMR spectroscopy

1. Introduction

Despite the important progress in organoboron chemistry during the last 50 years, some classes of organoboron compounds remained unknown or less investigated. For instance, the first communication on ethynyltrifluoroborate salts, $K[RC{\equiv}CBF_3]$ (R=Bu, Et_3Si), was published recently in 1999 [2]. Subsequently the related salts with hydrocarbon groups R_H=alkyl, alkenyl, and aryl were prepared [2–5]. Very recently, the syntheses of potassium (perfluoroorganoethynyl)-trifluoroborates, $K[R_FC{\equiv}CBF_3]$ (R_F represents perfluorinated alkyl, alkenyl, and aryl groups) were reported [1]. However, only two examples of hydrocarbon and no fluoro-containing alk-1-ynyldifluoroboranes were reported. To our knowledge, ethynyldifluoroborane, $HC{\equiv}CBF_2$, and propynyldifluoroborane, $CH_3C{\equiv}CBF_2$, are the only known representatives of this class. The former borane was prepared by photochemical dehydroborylation of *cis*-$Cl_2BCH{=}CHBCl_2$ and subsequent substitution of chlorine by fluorine in ethynyldichloroborane with antimony trifluoride [6] (Scheme 1) or by the reaction of ethynyltrimethyltin with BF_3 [7] (Scheme 2).

Prop-1-ynyldifluoroborane was obtained in low yield from bis(prop-1-ynyl)mercury and BF_2Cl or from prop-1-ynyldichloroborane by the Swarts reaction [8] (Schemes 3 and 4).

Both routes are not convenient and the products are obtained only in low yields. We were interested in alkylethynyldifluoroboranes, $R_HC{\equiv}CBF_2$, and their perfluorinated analogues, $R_FC{\equiv}CBF_2$, as starting materials for alk-1-ynylxenonium salts [9,10]. Therefore, we studied an alternative pathway to alk-1-ynyldifluoroboranes. Our approach is based on the abstraction of fluoride from $K[RBF_3]$ salts with an appropriate fluoride anion acceptor. This procedure was successfully employed in the preparation of alkyldifluoroboranes, alkenyldifluoroboranes, aryldifluoroboranes [11], and their partially fluorinated and perfluorinated analogues [12]. In order to demonstrate the general character of this method, a representative series of (organoethynyl)difluoroboranes, $RC{\equiv}CBF_2$, containing different types of alkyl and perfluoroorgano groups R was prepared in solutions and characterised by multi-NMR spectroscopy.

2. Results and discussion

Alk-1-ynyldifluoroboranes are very moisture sensitive molecules and strong Lewis acids. Due to these properties, anhydrous and weak-coordinating solvents (dichloromethane, 1,1,1,3,3-pentafluoropropane (PFP), or 1,1,1,3,3-pentafluorobutane (PFB)) were used as reaction media. $RC{\equiv}CBF_2$ boranes

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[☆] Part 15 in the series "(Fluoroorgano)fluoroboranes and -borates" [1].

[*] Corresponding author. Tel.: +49 203 379 3310; fax: +49 203 379 2231.
E-mail address: h-j.frohn@uni-due.de (H.-J. Frohn).

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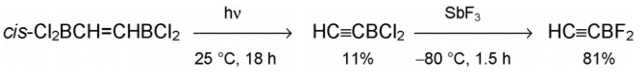
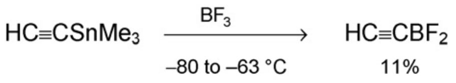
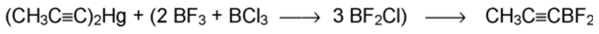


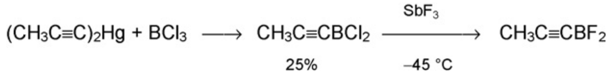
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

were obtained by bubbling of BF_3 gas (excess) into an intensively stirred suspension of the corresponding potassium (organoethynyl)trifluoroborate at −25 to −40 °C, and subsequent separation of the alk-1-ynyldifluoroborane-containing solution from insoluble $K[BF_4]$ (Scheme 5). The acidities of $RC{\equiv}CBF_2$ can be determined in the gas phase by their fluoride affinities. Thus, for $CF_3C{\equiv}CBF_2$ the fluoride affinity was calculated (B3LYP/6-31 + G*) to 89.0 kcal mol^{-1} [13]. This value exceeds that of BF_3 (78.8 kcal mol^{-1}) remarkably [13]. Consequently, the driving force for the formation of $RC{\equiv}CBF_2$ is the gain of lattice energy of $K[BF_4]$.

The preparative yield of $RC{\equiv}CBF_2$ was determined by ^{19}F NMR spectroscopy using the quantitative internal reference (1,1,2-trichlorotrifluoroethane). When the reaction (not optimised) was performed in CH_2Cl_2, the yield of (organoethynyl)difluoroboranes diminished to 30–40%.

We found a remarkable dependence of the stability of $RC{\equiv}CBF_2$ in solution on the nature of R. Thus, no decomposition of alk-1-ynyl- and perfluoroalk-1-ynyldifluoroboranes (R=C_4H_9, $(CH_3)_3C$, CF_3, C_3F_7, $(CF_3)_2CF$) in PFP was detected at 20–22 °C over days under an atmosphere of dry argon (^{19}F NMR). For distinction, brown coloration of solutions of $CF_3CF{=}CFC{\equiv}CBF_2$ and $C_4F_9CF{=}CFC{\equiv}CBF_2$ appeared within a few minutes at 22 °C. After 1 h, the degree of decomposition was 40 and 70%, respectively (^{19}F NMR). When a solution of $C_6F_5C{\equiv}CBF_2$ in PFP was kept at 22 °C for 5–10 min, a white precipitate was formed and only traces of pentafluorophenyl-containing products were still detected in the mother liquor by ^{19}F NMR spectroscopy. Detailed investigations of the reactivity of $RC{\equiv}CBF_2$ and the factors which influence the instability of (organoethynyl)difluoroboranes are in progress.

3. Experimental details

The NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (^1H at 300.13 MHz, ^{11}B at 96.29 MHz, ^{19}F at 282.40 MHz). The chemical shifts are referenced to TMS (^1H), $BF_3{\cdot}OEt_2/CDCl_3$ (15%, v/v) (^{11}B), and CCl_3F (^{19}F) [with C_6F_6 as a secondary reference (−162.9 ppm)]. The composition of the reaction mixtures and the yield of products were determined by ^{19}F NMR spectroscopy using 1,1,2-trichlorotrifluoroethane as an internal quantitative standard.

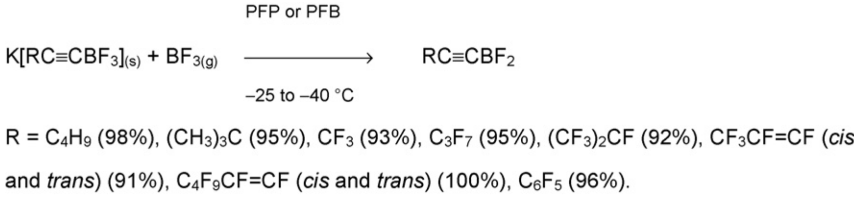
1,1,1,3,3-Pentafluorobutane (PFB) (Solvay), 1,1,1,3,3-pentafluoropropane (PFP) (Honeywell), 1,1,2-trichlorotrifluoroethane (Solvay K113), boron trifluoride (Messer Griesheim) were used as supplied. Dichloromethane (Baker) was purified by a standard procedure [14] (treatment in sequence by H_2SO_4, Na_2CO_3 (aq), H_2O, P_4O_{10}) and stored over molecular sieves 3 Å before use. Potassium (organoethynyl)trifluoroborates $K[RC{\equiv}CBF_3]$ (R=C_4H_9 [3], $(CH_3)_3C$ [4], CF_3, C_3F_7, $(CF_3)_2CF$, $CF_3CF{=}CF$, $C_4F_9CF{=}CF$, C_6F_5 [1] were prepared by literature procedures. All manipulations with (organoethynyl)difluoroboranes were performed in FEP (block copolymer of tetrafluoroethylene and hexafluoropropylene) equipment under an atmosphere of dry argon.

3.1. *Hex-1-ynyldifluoroborane*

The stirred suspension of $K[C_4H_9C{\equiv}CBF_3]$ (84 mg, 0.45 mmol) in PFP (1 mL) in a 8 mm i. d. FEP trap was cooled to −40 °C and boron trifluoride was bubbled over a period of 15 min. The suspension was centrifuged at −78 °C, and the cold mother liquor was transferred to a cold (−78 °C) trap via a Teflon tube using a pressure of dry argon. The solution contained 0.44 mmol (98%) of $C_4H_9C{\equiv}CBF_2$ (^{19}F NMR). ^1H NMR (PFP, −40 °C): δ 2.28 (t, $^3J(H^3, H^4) = 7$ Hz, t, $^4J(H^3, H^5) = 2$ Hz, 2H, H^3), 1.57–1.36 (m, 4H, $H^{4,5}$), 0.92 (t, $^3J(H^6, H^5) = 7$ Hz, 3H, H^6). ^{19}F NMR (PFP, −40 °C): δ −77.3 (br s, $\tau_{1/2} = 60$ Hz, BF_2). ^{11}B NMR (PFP, −40 °C): δ 16.1 (br s, $\tau_{1/2} = 180$ Hz).

3.2. *3,3-Dimethylbut-1-ynyldifluoroborane*

(A) Boron trifluoride was bubbled into a stirred suspension of $K[(CH_3)_3CC{\equiv}CBF_3]$ (81 mg, 0.43 mmol) in PFP (1 mL)



Scheme 5.

at −40 °C over a period of 15 min. After centrifugation at −78 °C, the solution of $(CH_3)_3CC{\equiv}CBF_2$ in PFP was transferred to a cold (−78 °C) trap via a Teflon tube using a pressure of dry argon (95% yield, ^{19}F NMR). ^{1}H NMR (PFP, −40 °C): δ 1.24 (s, 3CH_3). ^{19}F NMR (PFP, −40 °C): δ −77.2 (br s, $\tau_{1/2}$ = 65 Hz, BF_2). ^{11}B NMR (PFP, −40 °C): δ 19.7 (br s, $\tau_{1/2}$ = 168 Hz).

(B) Boron trifluoride was bubbled into a stirred suspension of $K[(CH_3)_3CC{\equiv}CBF_3]$ (300 mg, 1.51 mmol) in CH_2Cl_2 (2 mL) at −40 °C for 30 min. The solution of $(CH_3)_3CC{\equiv}CBF_2$ (30% yield, ^{19}F NMR) in CH_2Cl_2 was separated after centrifugation at 0 °C.

3.3. *Perfluoroprop-1-ynyldifluoroborane*

(A) Boron trifluoride was bubbled into a stirred suspension of $K[CF_3C{\equiv}CBF_3]$ (57 mg, 0.28 mmol) in PFP (1.5 mL) at −40 °C for 10 min. After centrifugation at −78 °C, the solution of $CF_3C{\equiv}CBF_2$ in PFP was transferred to a cold (−40 °C) trap via a Teflon tube using a pressure of dry argon (93% yield, ^{19}F NMR). ^{19}F NMR (PFP, −30 °C): δ −52.0 (s, 3F, F^3), −72.0 (br s, $\tau_{1/2}$ = 82 Hz, 2F, BF_2). ^{11}B NMR (PFP, −30 °C): δ 15.6 (br s, $\tau_{1/2}$ = 98 Hz).

(B) Boron trifluoride was bubbled into a stirred suspension of $K[CF_3C{\equiv}CBF_3]$ (500 mg, 2.61 mmol) in CH_2Cl_2 (4 mL) at −40 °C for 30 min. The suspension was centrifuged at −78 °C and the mother liquor was decanted at −40 °C into a cold (−40 °C) FEP trap. The precipitate was washed with cold (−40 °C) CH_2Cl_2 (2 mL). The combined extracts contained 0.80 mmol (30%) of borane $CF_3C{\equiv}CBF_2$ (^{19}F NMR) in CH_2Cl_2.

3.4. *Perfluoropent-1-ynyldifluoroborane*

Boron trifluoride was bubbled into a stirred suspension of $K[C_3F_7C{\equiv}CBF_3]$ (444 mg, 1.48 mmol) in PFP (2 mL) at −35 °C for 30 min. The suspension was stirred at 0 °C for 5 min and centrifuged at −78 °C. The mother liquor was separated at −40 °C as described above and the residue was washed with cold (−40 °C) PFP (1 mL). The combined solutions of $C_3F_7C{\equiv}CBF_2$ in PFP were collected in a cold (−40 °C) FEP trap (100% yield, ^{19}F NMR). ^{19}F NMR (PFP, −20 °C): δ −72.2 (br s, $\tau_{1/2}$ = 153 Hz, BF_2), −79.1 (t, $^4J(F^5, F^3)$ = 8 Hz, 3F, F^5), −100.6 (t, $^3J(F^3, F^4)$ = 4 Hz, q, $^4J(F^3, F^5)$ = 8 Hz, 2F, F^3), −125.6 (t, $^3J(F^4, F^3)$ = 4 Hz, 2F, F^4). ^{11}B NMR (PFP, −20 °C): δ 15.5 (br s, $\tau_{1/2}$ = 100 Hz).

3.5. *Perfluoro-3-methylbut-1-ynyldifluoroborane*

(A) Boron trifluoride was bubbled into a stirred suspension of $K[(CF_3)_2CFC{\equiv}CBF_3]$ (82 mg, 0.26 mmol) in PFP (1.5 mL) at −40 °C for 10 min. After centrifugation at −78 °C, the solution of $(CF_3)_2CFC{\equiv}CBF_2$ in PFP was transferred to a cold (−40 °C) trap via a Teflon tube using a pressure of dry argon (92% yield, ^{19}F NMR). ^{19}F NMR (PFP, −10 °C): δ −72.3 (br s, $\tau_{1/2}$ = 80 Hz, 2F, BF_2), −75.3 (d, $^3J(CF_3, F^3)$ = 10 Hz, 6F, 2CF_3), −169.0 (septet, $^3J(F^3, CF_3)$ = 11 Hz, t, $^5J(F^3, BF_2)$ = 3 Hz, 1F, F^3). ^{11}B NMR (PFP, −10 °C): δ 15.7 (br s, $\tau_{1/2}$ = 101 Hz).

(B) Boron trifluoride was bubbled into a stirred suspension of $K[(CF_3)_2CFC{\equiv}CBF_3]$ (155 mg, 0.51 mmol) in CH_2Cl_2 (2 mL) at −40 °C for 40 min. After centrifugation at 0 °C, the solution of $(CF_3)_2CFC{\equiv}CBF_2$ was transferred to a cold (0 °C) trap via a Teflon tube using a pressure of dry argon and the residue was washed with cold (0 °C) CH_2Cl_2 (1 mL). The combined extracts contained 0.17 mmol (30%) of borane $(CF_3)_2CFC{\equiv}CBF_2$ (^{19}F NMR) in CH_2Cl_2.

3.6. *Perfluoropent-3-en-1-ynyldifluoroborane*

Boron trifluoride was bubbled into a stirred suspension of $K[CF_3CF{=}CFC{\equiv}CBF_3]$ (80 mg, 0.30 mmol) (*cis*:*trans* = 1:2) in PFP (1 mL) at −40 °C for 15 min. After centrifugation at −78 °C, the solution of $CF_3CF{=}CFC{\equiv}CBF_2$ (*cis*:*trans* = 1:2) in PFP was separated at −40 °C as described above and collected in a cold (−40 °C) FEP trap (91% yield, ^{19}F NMR). ^{19}F NMR (PFP, −40 °C): δ −67.5 (d, $^3J(F^5, F^4)$ = 11 Hz, d, $^4J(F^5, F^3)$ = 21 Hz, 3F, F^5), −73.6 (br s, $\tau_{1/2}$ = 51 Hz, 2F, BF_2), −144.0 (d, $^3J(F^3, F^4)$ = 139 Hz, q, $^4J(F^3, F^5)$ = 21 Hz, t, $^5J(F^3, BF_2)$ = 2 Hz, 1F, F^3), −154.5 (d, $^3J(F^4, F^3)$ = 139 Hz, q, $^3J(F^4, F^5)$ = 11 Hz, 1F, F^4) (*trans*-isomer); −67.6 (d, $^3J(F^5, F^4)$ = 12 Hz, d, $^4J(F^5, F^3)$ = 6 Hz, 3F, F^5), −73.9 (br s, $\tau_{1/2}$ = 51 Hz, 2F, BF_2), −127.9 (d, $^3J(F^3, F^4)$ = 7 Hz, q, $^4J(F^3, F^5)$ = 6 Hz, 1F, F^3), −135.3 (d, $^3J(F^4, F^3)$ = 7 Hz, q, $^3J(F^4, F^5)$ = 12 Hz, 1F, F^4) (*cis*-isomer). ^{11}B NMR (PFP, −40 °C): δ 16.1 (br s, $\tau_{1/2}$ = 175 Hz).

3.7. *Perfluorooct-3-en-1-ynyldifluoroborane*

Boron trifluoride was bubbled into a stirred suspension of $K[C_4F_9CF{=}CFC{\equiv}CBF_3]$ (72 mg, 0.17 mmol) (*cis*:*trans* = 46:54) in PFB (1.5 mL) at −25 °C for 10 min. The solution of $C_4F_9CF{=}CFC{\equiv}CBF_2$ (*cis*:*trans* = 46:54) in PFB was separated at −40 °C as described above and collected in a cold (−40 °C) FEP trap (100% yield, ^{19}F NMR). ^{19}F NMR (PFB, −10 °C): δ −73.4 (br s, $\tau_{1/2}$ = 42 Hz, 2F, BF_2), −80.2 (t, $^3J(F^8, F^7)$ = 2 Hz, t, $^4J(F^8, F^6)$ = 10 Hz, 3F, F^8), −117.1 (d, $^3J(F^5, F^4)$ = 12 Hz, t, $^4J(F^5, F^7)$ = 12 Hz, d, $^4J(F^5, F^3)$ = 25 Hz, 2F, F^5), −123.4 (m, 2F, F^6), −125.4 (m, 2F, F^7), −141.8 (d, $^3J(F^3, F^4)$ = 139 Hz, t, $^4J(F^3, F^5)$ = 25 Hz, t, $^5J(F^3, BF_2)$ = 6 Hz, 1F, F^3), −150.8 (m, d, $^3J(F^4, F^3)$ = 139 Hz, 1F, F^4) (*trans*-isomer); −73.8 (br s, $\tau_{1/2}$ = 51 Hz, 2F, BF_2), −80.2 (t, $^3J(F^8, F^7)$ = 2 Hz, t, $^4J(F^8, F^6)$ = 10 Hz, 3F, F^8), −115.5 (d, $^3J(F^5, F^4)$ = 14 Hz, t, $^4J(F^5, F^7)$ = 14 Hz, 2F, F^5), −122.2 (m, 1F, F^4), −122.7 (m, 2F, F^6), −125.4 (m, 2F, F^7), −131.2 (m, 1F, F^3) (*cis*-isomer). ^{11}B NMR (PFB, −10 °C): δ 16.1 (br s, $\tau_{1/2}$ = 138 Hz).

3.8. *Pentafluorophenylethynyldifluoroborane*

Boron trifluoride was bubbled into a stirred suspension of $K[C_6F_5C{\equiv}CBF_3]$ (106 mg, 0.35 mmol) in PFP (1.5 mL) at −35 °C for 10 min. After centrifugation at −78 °C, the solution of $C_6F_5C{\equiv}CBF_2$ in PFP was separated at −50 °C as described above and collected in a cold (−50 °C) FEP trap (96% yield, ^{19}F NMR). ^{19}F NMR (PFP, −30 °C): δ −74.9 (br s, $\tau_{1/2} = 45$ Hz, 2F, BF_2), −134.0 (m, 2F, F^{ortho}), −148.1 (t, $^3J(F^{para}, F^{meta}) = 19$ Hz, t, $^4J(F^{para}, F^{ortho}) = 4$ Hz, 1F, F^{para}), −161.2 (m, 2F, F^{meta}). ^{11}B NMR (PFP, −30 °C): δ 16.4 (br s, $\tau_{1/2} = 178$ Hz).

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