172 *Organometallics* **2004,** *23,* 172−174

Efficient Synthesis of Salts of the Tetrakis(perfluoroorgano)borate Anion, $[B(CF{=}CF_2)_4]^-$

Nicolay Yu. Adonin and Vadim V. Bardin

N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, SB RAS,
Acad. Lavrentjev Avenue, 9, 630090 Novosibirsk, Russia

Ulrich Flörke

Department of Chemistry, University Paderborn, Warburger Strasse 100,
D-33098 Paderborn, Germany

Hermann-Josef Frohn*

Institute of Chemistry, Inorganic Chemistry, University Duisburg-Essen,
Lotharstrasse 1, D-47048 Duisburg, Germany

Received September 24, 2003

Summary: The synthesis and the NMR spectra of the tetrakis(trifluorovinyl)borate salts $M[B(CF{=}CF_2)_4]$ (M = Li, K, Cs, $[NR^1R^2_3]$) as well as the X-ray crystal structure of the tetramethylammonium salt are reported. These salts were prepared by the reaction of boron trichloride with bis(trifluorovinyl)di-n-butyltin in the presence of tri- and tetraalkylammonium or alkali-metal chlorides in dichloromethane.

Weakly coordinating anions have been studied intensively in the past decade because to their importance in pure and applied chemistry.[1] The tetrakis(perfluoroorgano)borates $M[B(R_F)_4]$ contain such weakly coordinating anions.[1a] Until 2000 they have been represented only by the tetrakis(pentafluorophenyl)borate salts $M[B(C_6F_5)_4]$ (M = Li, Na, K, $(C_6H_5)_3C$, $HNRR'_2$, etc.) and related perfluoroaryl compounds, which were prepared by the reaction of the respective aryllithium reagent with boron trihalide.[2]

In 2001 the synthesis of the first tetrakis(perfluoroalkyl)borate salts, $M[B(CF_3)_4]$, was reported.[3] In contrast to $M[B(C_6F_5)_4]$, the $M[B(CF_3)_4]$ salts could not be prepared by stepwise introduction of nucleophilic CF_3 groups. Salts of the $[B(CF_3)_4]^-$ anion were obtained by the fluorination of the cyano groups in $M[B(CN)_4]$ using ClF_3 in anhydrous HF. The $M[B(CF{=}CF_2)_4]$ salts and related (perfluoroalkenyl)borates have remained unknown, although the first (trifluorovinyl)boranes, $(CF_2{=}CF)_nBX_{3-n}$ ($n = 1-3$; X = F, Cl, Br), were synthesized more than 40 years ago.[4] Other (trifluorovinyl)boranes, $(CF_2{=}CF)_nBX_{3-n}$ (n = 1, 2; X = OAlk, Me), were prepared later.[5] Recently, the donor−acceptor complexes $CF_2{=}CFB(CF_3)_2{\cdot}NRMe_2$ (R = H, Me, Bz),[6] the series of (alken-1-yl)trifluoroborates $M[RCF{=}CFBF_3]$[7] (R = F, Cl, C_2F_5, C_6F_{13}, C_4F_9, C_4H_9, C_6H_5), and the $Cs[CF_2{=}CFB(CF_3)_2F]$ salt[6] were prepared and characterized. To our knowledge, borates that contain more than one trifluorovinyl substituent on boron have not been described to date.[8]

We report here the synthesis and the NMR spectra of tetrakis(trifluorovinyl)borate salts, $M[B(CF{=}CF_2)_4]$ (**1**), as well as the X-ray crystal structure of the tetramethylammonium salt. These salts were prepared by the reaction of boron trichloride with bis(trifluorovinyl)di-*n*-butyltin (**2**) in the presence of a tri- or tetraalkylammonium or alkali-metal chloride in dichloromethane (eq 1).

$$2\underset{\mathbf{2}}{(CF_2{=}CF)_2SnBu\text{-}n_2} + MCl + BCl_3 \rightarrow \underset{\mathbf{1}}{M[B(CF{=}CF_2)_4]} + n\text{-}Bu_2SnCl_2 \quad (1)$$

$$M = NR^1R^2_3\ (R^1 = H, Bz, Me, n\text{-}Bu;\ R^2 = Me, Et, n\text{-}Bu), Li, K, Cs$$

NMR-scale reactions for elucidating the reaction parameters were carried out under either homogeneous ($M = NR^1R^2_3$ (R^1 = H, Bz, Me, *n*-Bu; R^2 = Me, Et, *n*-Bu)) or heterogeneous (M = Li, K, Cs) conditions at 25 °C. The addition of a solution of BCl_3 into a mixture of $(CF_2{=}CF)_2SnBu\text{-}n_2$ and $[C_6H_5CH_2N(CH_3)_3]Cl$ in dichloromethane gave salt **1** in 98% yield (Table 1, entry 1). Both trifluorovinyl groups of $(CF_2{=}CF)_2SnBu\text{-}n_2$ can be transferred to boron (Table 1, entries 1−3).

The order of mixing of the reagents is important. When BCl_3 was added to a slight excess of $[NR^1R^2_3]Cl$ before the tin compound was added, the formation of **1**

---

[1] (a) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927−942. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133−139. (c) Piers, W. E. *Chem. Eur. J.* **1998**, *4*, 13−18.

[2] For recent reviews, see: (a) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391−1434. (b) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345−354.

[3] Bernhardt, E.; Henkel, G.; Willner, H.; Pawelke, G.; Bürger, H. *Chem. Eur. J.* **2001**, *7*, 4696−4705.

[4] (a) Kaesz, H. D.; Stafford, S. L.; Stone, F. G. A. *J. Am. Chem. Soc.* **1959**, *81*, 6336. (b) Stafford, S. L.; Stone, F. G. A. *J. Am. Chem. Soc.* **1960**, *82*, 6238−6240. (c) Coyle, T. D.; Stafford, S. L.; Stone, F. G. A. *Spectrochim. Acta* **1961**, *17*, 968−976.

[5] (a) Sterlin, R. N.; Isaev, V. L.; Zakharov, G. M.; Martin, B.; Knunyanz, I. L. *Zh. Vses. Khim. Obshch.* **1967**, *12*, 475−477; *Chem. Abstr.* **1968**, *68*, 13025r. (b) Stampf, E. J.; Odom, J. D. *J. Organomet. Chem.* **1976**, *108*, 1−11.

[6] Brauer, D. J.; Pawelke, G. *J. Organomet. Chem.* **2000**, *604*, 43−51.

[7] Frohn, H.-J.; Bardin, V. V. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2499−2505.

[8] Independently, G. Pawelke et al. obtained $[B(CF{=}CF_2)_4]^-$ and related anions by a different route (private communication).

10.1021/om030610i CCC: $27.50

Table 1. Reaction of $(CF_2{=}CF)_2SnBu\text{-}n_2$ (2) and BCl_3 in CH_2Cl_2 in the Presence of MCl

		amt of reagent, mmol			yield, %	
entry	M	2	BCl_3	MCl	$M[B(CF{=}CF_2)_4]^a$	$B(CF{=}CF_2)_3^b$
1	$[C_6H_5CH_2NMe_3]$	0.40	0.11	0.10	>98	traces
2	$[C_6H_5CH_2NMe_3]$	0.20	0.11	0.10	80	18
3	$[C_6H_5CH_2NMe_3]$	0.22	0.11	0.10	95	9
4	$[C_6H_5CH_2NMe_3]$	0.20	0.10	0.11	*c*	
5	$[Bu_4N]$	0.22	0.11	0.10	85	10
6	$[Me_4N]$	0.22	0.11	0.10	92^d	
7	Li	0.22	0.10	0.28	$30^{b,d}$	
8	K	1.42	0.50	0.51	$26^{b,d}$	
9	Cs	0.22	0.10	0.86	$25^{b,d}$	
10	–	0.22	0.1		traces	>98

[a] The yield was calculated based on MCl. [b] The yield was calculated based on BCl_3. [c] First the BCl_3–CH_2Cl_2 solution was added to MCl in CH_2Cl_2, followed by $(CF_2{=}CF)_2SnBu\text{-}n_2$. [d] Preparative yield.

was suppressed owing to the formation of the $[BCl_4]^-$ anion, which is stable in dichloromethane (shown by ^{11}B NMR)[9] (Table 1, entry 4).

Tetramethyl- and tetra-*n*-butylammonium chlorides formed the corresponding salts **1** in high yield (Table 1, entries 5 and 6). In dichloromethane the insoluble chlorides MCl also promote the formation of $M[B(CF{=}CF_2)_4]$, but their yields were not greater than 30% (Table 1, entries 7–9).

In the absence of MCl the 2:1 molar reaction of **2** and BCl_3 gave, even when the correct stoichiometry was used, only tris(trifluorovinyl)borane (**3**) in 98% yield (Table 1, entry 10). It should be noted that the reaction of BCl_3 with an excess of the methyl derivative $(CF_2{=}CF)_2SnMe_2$ in the absence of a source of chloride afforded a mixture of (perfluorovinyl)chloroboranes that was difficult to separate.[4b]

For a preparative-scale synthesis we used a modified procedure for mixing the reagents and the tetramethylammonium chloride. The product $[NMe_4][B(CF{=}CF_2)_4]$ could be isolated easily from the reaction mixture as a white solid by addition of pentane, whereas in the case of the benzyltrimethyl- and tetra-*n*-butylammonium salts only oils were formed after the addition of pentane.

$[NMe_4][B(CF{=}CF_2)_4]$ is a white crystalline salt, which is soluble in CH_2Cl_2, acetone, acetonitrile, methanol, and water but insoluble in hydrocarbons.

The ^{19}F, ^{11}B, and ^{13}C NMR spectra of $M[B(CF{=}CF_2)_4]$ were measured and compared with those of the structurally related salts $K[CF_2{=}CFBF_3]$ and $Cs[CF_2{=}CFB(CF_3)_2F]$ and the borane $(CF_2{=}CF)_3B$ (**3**) (Table 2, see Supporting Information). The ^{19}F NMR spectra of $M[B(CF{=}CF_2)_4]$ consist of three signals with equal integrals at ca. −100, −124, and −183 ppm, and their positions are practically independent of the nature of the cation M = K, Cs, Me_4N or the solvent (Table 2). Replacement of BF_3 in $[CF_2{=}CFBF_3]^-$ by $B(CF_3)_2F$ or by $B(CF{=}CF_2)_3$ had practically no influence on the ^{19}F NMR chemical shift values of the fluorine atoms F^2 on carbon C-2 of the trifluorovinyl group. However, the fluorine atom F^1 at carbon C-1 in $[B(CF{=}CF_2)_4]^-$ is significantly deshielded relative to those in the $[CF_2{=}CFBX_2F]^-$ anions (X = F, CF_3). In contrast to the strongly deviating position of F^1 in **1** ($\Delta\delta$ approximately 13 ppm), the ^{13}C NMR chemical shift δ(C-1) of all three borate anions differs only by approximately 4 ppm, whereas δ(C-2) differs by approximately only 1 ppm (Table 2).

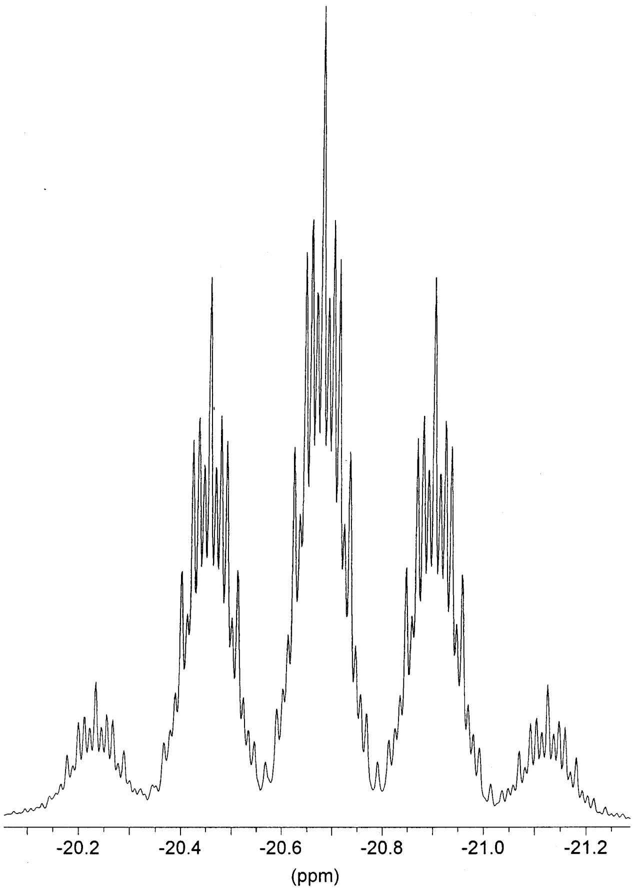

Figure 1. ^{11}B NMR spectrum of $K[B(CF{=}CF_2)_4]$ in CD_3CN: an overlapping quintet of quintets of quintets ($^2J_{B,F} = 21.5$, $^3J_{B,F} = 3.2$, $^3J_{B,F} = 2.2$ Hz).

The ^{11}B NMR signal of the tetrakis(trifluorovinyl)borate ion (Figure 1) is located at approximately −21 ppm as a quintet of overlapping quintets of quintets caused by the ^{11}B–^{19}F spin–spin coupling of four trifluorovinyl groups each with three magnetically inequivalent fluorine atoms (Figure 1). This $\delta(^{11}B)$ value is close to the chemical shift of the tetramethylborate anion (−20.2 ppm),[10,11] the tetrakis(trifluoromethyl)borate anion (−18.9 ppm),[3] and the tetravinylborate anion (−16.1 ppm)[11] and is strongly shifted to a low frequency relative to the ^{11}B signals of the anion $[CF_2{=}CFBF_3]^-$ (0.51 ppm) or of borane **3** (45.74 ppm) (see Table 2).

The structure of the $[B(CF{=}CF_2)_4]^-$ anion in its tetramethylammonium salt and important bond lengths and bond angles are presented in Figure 2 (for crystal data and details of the structure determination see the Supporting Information).[12] $[NMe_4][B(CF{=}CF_2)_4]$ (**1**) crystallizes in the tetragonal crystal system (space group $\bar{4}$) with $Z = 2$. The centers of the cation and anion are both located on special positions with point symmetry $\bar{4}$. At 153(2) K only the $[NMe_4]^+$ cation is disordered over

---

(9) Nöth, H.; Wrackmeyer, B. *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: Berlin, Heidelberg, New York, 1978; p 388.

(10) Nöth, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1968**, *12*, 23–36.

(11) Thompson, R. J.; Davis, J. C. *Inorg. Chem.* **1965**, *4*, 1464–1467.

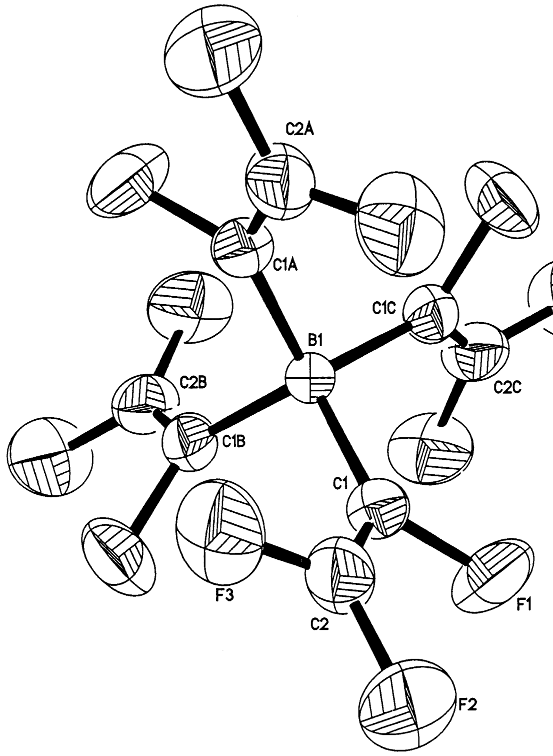

Figure 2. Anion in the $[NMe_4][B(CF{=}CF_2)_4]$ salt. Displacement ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg): B−C(1) = 1.618(3), C(1)−C(2) = 1.287(4), C(1)−F(1) = 1.381(4), C(2)−F(2) = 1.330(4), C(2)−F(3) = 1.321(4); C(2)−C(1)−B = 132.1(3), C(2)−C(1)−F(1) = 112.1(3), F(1)−C(1)−B = 115.7(2), C(1)−C(2)−F(2) = 126.3(4), C(1)−C(2)−F(3) = 125.0(3), F(2)−C(2)−F(3) = 108.7(3), C(1)−B−C(1A) = 108.01(11), C(1)−B−C(1B) = 112.4(2).

two positions, with occupation factors of 0.77(1) and 0.23(1).

The perfluorovinyl group of the anion has a strong structural similarity to that in the neutral adduct $CF_2{=}CFB(CF_3)_2{\cdot}NHMe_2$.[6] The main deviations involve the C−B and the F(2)−C(2) distance, which are trans to each other and longer in the anion than in the adduct. Additionally, the angle B−C(1)−C(2) is smaller, whereas F(1)−C(1)−B is larger in the anion than in the adduct. The long distance C(1)−F(1) in the anion of **1** may be caused by the opposite inductive effects of the F and B atom bonded to C(1), which reduces the polar component of the C(1)−F(1) bond.

Experimental Section. General Procedures. All reactions were carried out under an atmosphere of dry argon. A 2.5 M solution of *n*-BuLi in hexanes (Aldrich), di-*n*-butyltin dichloride (Fluka), 1.0 M BCl_3 in hexanes (Aldrich), 1.0 M BCl_3 in CH_2Cl_2 (Aldrich), and anhydrous ether (Baker) were used as supplied. NMR spectra were recorded on a Bruker AVANCE 300 (FT 300.13 MHz, ^{1}H; 96.29 MHz,^{11}B; 75.47 MHz,^{13}C; 282.40 MHz,^{19}F) spectrometer. The chemical shifts are referenced to TMS (^{1}H, ^{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.

Reaction of BCl_3 with $(CF_2{=}CF)_2SnBu\text{-}n_2$ in the Presence of MCl. MCl, $(CF_2{=}CF)_2SnBu\text{-}n_2$,[13] $C_6H_5CF_3$ (internal standard) (5 μL, 0.041 mmol), and CH_2Cl_2 (0.5 mL) were placed in sequence into a NMR tube under an atmosphere of dry argon. After addition of BCl_3 (1.0 M solution in hexanes), the reaction mixture was kept at 20 °C for 20 min and analyzed by ^{19}F (yields, see Table 1) and ^{11}B NMR spectroscopy.

Preparation of $[Me_4N][B(CF{=}CF_2)_4]$. To a stirred solution of $(CF_2{=}CF)_2SnBu\text{-}n_2$ (400 μL, 561.6 mg, 1.42 mmol) in CH_2Cl_2 (2 mL) was added a BCl_3 solution (1.0 M in CH_2Cl_2, 0.5 mL, 0.5 mmol) in one portion. The mixture was stirred for 10 min at 20 °C and formed a light brown solution. Anhydrous $[Me_4N]Cl$ (61 mg, 0.55 mmol) was added in 5 portions within 50 min. The resulting solution was stirred at 20 °C for an additional 2 h and was then diluted with pentane (7 mL). The white precipitate was filtered, washed with pentane (3 × 10 mL), and dried in a vacuum desiccator overnight. The yield of $[Me_4N][B(CF{=}CF_2)_4]$ was 184 mg (90%). Mp: 156−157 °C (recrystallized from CH_2Cl_2, sealed capillary). T_{onset}(endothermic) = 158.9 °C (DSC). 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%.

Crystals for X-ray Structural Analysis. $[Me_4N][B(CF{=}CF_2)_4]$ (30 mg) was dissolved in boiling CH_2Cl_2 and filtered into a glass tube, which was placed in a closed flask over pentane. Within 3 weeks crystals of quality sufficient for X-ray analysis were obtained.

Acknowledgment. We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft, the Russian Foundation for Basic Research, and the Fonds der Chemischen Industrie.

Supporting Information Available: Table 2 containing NMR spectral data of $M[B(CF{=}CF_2)_4]$ and related compounds, and details of the X-ray crystal structure study, including tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for $[NMe_4][B(CF{=}CF_2)_4]$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030610I

---

(12) Crystal structure analysis of $[NMe_4][B(CF{=}CF_2)_4]$: $C_{12}H_{12}BF_{12}N$, SMART APEX (Bruker), Mo Kα radiation (λ = 0.710 73 Å, graphite monochromator), T = 153(2) K, colorless crystal (0.35 × 0.20 × 0.15 mm^3), tetragonal, space group $\bar{4}$, a = 9.9305(9) Å, c = 8.2531(10) Å, V = 813.88(14) Å^3, Z = 2, ρ_{calcd} = 1.669 Mg m^{-3}, μ(Mo Kα) = 0.194 mm^{-1}, $F(000)$ = 408, 4751 measured reflections ($2.90 < \theta < 28.22°$), absorption correction (SADABS[14]), minimum/maximum transmission 0.524/0.589, 981 independent intensities, structure solution by direct and conventional Fourier methods, refinement based on F^2 and 981 intensities, 70 parameters, all but hydrogen atoms refined anisotropically, H atoms located from difference maps and refined at idealized positions with riding model, R1($I > 2\sigma(I)$) = 0.049, wR2(all data) = 0.130, maximum $\Delta/\sigma < 0.001$, minimum/maximum height in ΔF map = −0.16/0.26 e/Å^3. In the absence of significant anomalous scattering effects, the Flack parameter and thus the determination of absolute structure is essentially meaningless. Accordingly, Friedel pairs were merged. Programs for solution and refinement were from the SHELXTL suite.[14] Crystallographic data, excluding structure factors, have been deposited as Supporting Information with the Cambridge Crystallographic Data Centre, with deposition number CCDC-212214. Data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1 EZ, U.K. (e-mail: deposit@ccdc.cam.ac.uk).

(13) The stannane $(CF_2{=}CF)_2SnBu\text{-}n_2$ was prepared by trifluorovinylation of $Cl_2SnBu\text{-}n_2$ with $CF_2{=}CFLi$ (generated from CF_3CFH_2 and *n*-BuLi[15]) in ether in 95% preparative yield.

(14) SADABS (Version 2.03) and SHELXTL (Version 6.10); Bruker AXS Inc., Madison, WI, 2002.

(15) (a) Burdon, J.; Coe, P. L.; Haslock, I. B.; Powell, R. L. *J. Chem. Soc., Chem. Commun.* **1996**, 49−50. (b) Banger, K. K.; Brisdon, A. K.; Gupta, A. *J. Chem. Soc., Chem. Commun.* **1997**, 139−140. (c) Burdon, J.; Coe, P. L.; Haslock, I. B.; Powell, R. L. *J. Fluorine Chem.* **1997**, *85*, 151−153.