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Trifluoromethylation of carbon and boron with CF_3SiMe_3/NMe_4F: formation of $NMe_4[\textit{trans}\text{-}CF_3\text{–}CF{=}CFB(CF_3)_3]$

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Dedicated to Professor Hans Bürger on the occasion of his 65th birthday.

Abstract

Trimethylamine-trifluoroethenyl-bis(trifluoromethyl)borane $[F_2C{=}CF(CF_3)_2B\cdot NMe_3]$ (**1**) reacts with $NMe_4[(CF_3)_2SiMe_3]$ in THF solution to form trimethylamine-bis(trifluoromethyl)pentafluoropropenylborane $[\textit{trans}\text{-}CF_3\text{–}CF{=}CF(CF_3)_2B\cdot NMe_3]$ (**3**), the fluoroborate $NMe_4[\textit{trans}\text{-}CF_3\text{–}CF{=}CF(CF_3)_2BF]$ (**4**), the novel borates $NMe_4[\textit{trans}\text{-}CF_3\text{–}CF{=}CFB(CF_3)_3]$ (**5**) and $NMe_4[\textit{cyclo}\text{-}(CF_3)_2B\text{–}CF_2\text{–}CF\text{–}CF_2\text{–}CF_3]$ (**6**). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NMR data; Boron; Fluorine; Small ring; Silicon

1. Introduction

In a preceding paper, we have reported on the formation of fluoroborates $[RB(CF_3)_2F]^-$ by cleavage of the BN bond of the corresponding trimethylamine-trifluoromethylboranes $[R(CF_3)_2B\cdot NMe_3]$ by $NEt_3\cdot 3HF$ [1]. The BN bond was cleaved thermally depending on R between 150 and 195 °C, the latter temperature was necessary for $R = F_2C{=}CF$. However, for this ligand another mechanism of BN bond cleavage and replacement of the trimethylamine by fluoride has been found [2]. Water-free NMe_4F cleaves the BN bond of $F_2C{=}CF(CF_3)_2B\cdot NMe_3$ (**1**) and replaces the trimethylamine ligand at 80 °C in 2-butanone rapidly to form the fluoroborate anion ion $[(F_2C{=}CF)B(CF_3)_2F]^-$. Here, a fluoride adds first to the CF_2 group of **1** and this adduct releases trimethylamine to form an intermediate alkylidene borate anion $[F_3C\text{–}CF{=}B(CF_3)_2]^-$. This subsequently rearranges by migration of fluoride from carbon to boron to yield $[(F_2C{=}CF)B(CF_3)_2F]^-$. Since, we are interested in the synthesis of borate anions surrounded by four perfluorinated ligands, we were looking for a suitable reagent that would allow an analogous reaction with the trifluoromethanide ion CF_3^- instead of F^-. Recently, it has been shown that CF_3SiMe_3 reacts with water-free NMe_4F in THF solution at −60 °C to form the bis(trifluoromethyl)siliconate $[(CF_3)_2SiMe_3]^-$ [3,4], which acts as a powerful source of the unstable trifluoromethanide ion. Here, we report on the reaction of $[(CF_3)_2SiMe_3]^-$ with **1**.

2. Results and discussion

When a THF solution of $NMe_4[(CF_3)_2SiMe_3]$ and **1** is warmed from −60 to 0 °C, the color of the reaction mixture turns black and elimination of NMe_3 is observed. After removing all volatile material in vacuo at 20 °C, a black tarry residue is obtained. ^1H, ^{19}F and ^{11}B NMR spectra of this material revealed that it consisted of both trimethylamine boranes and tetramethylammonium borates without any starting material. The product distribution and the possible reaction pathway is shown in Fig. 1. The reaction of **1** with $[(CF_3)_2SiMe_3]^-$ is initiated by a transfer of a formal trifluoromethanide ion CF_3^- from silicon to the CF_2 group. Under elimination of NMe_3 an intermediate alkylidene borate $[F_3C\text{–}F_2C\text{–}CF{=}B(CF_3)_2]^-$ (**2**) is formed. This reactive species is the key substance from which all identified products may derived (Scheme 1).

(i) The alkylidene borate (**2**) eliminates fluoride and re-adds trimethylamine to form the trimethylamine borane $[\textit{trans}\text{-}F_3C\text{–}CF{=}CF\text{–}B(CF_3)_2\cdot NMe_3]$ (**3**).
(ii) Alternately, the intermediate **2** can rearrange under migration of fluorine from carbon to boron to yield the propenylfluoroborate $[\textit{trans}\text{-}F_3C\text{–}CF{=}CF\text{–}B(CF_3)_2F]^-$ (**4**).

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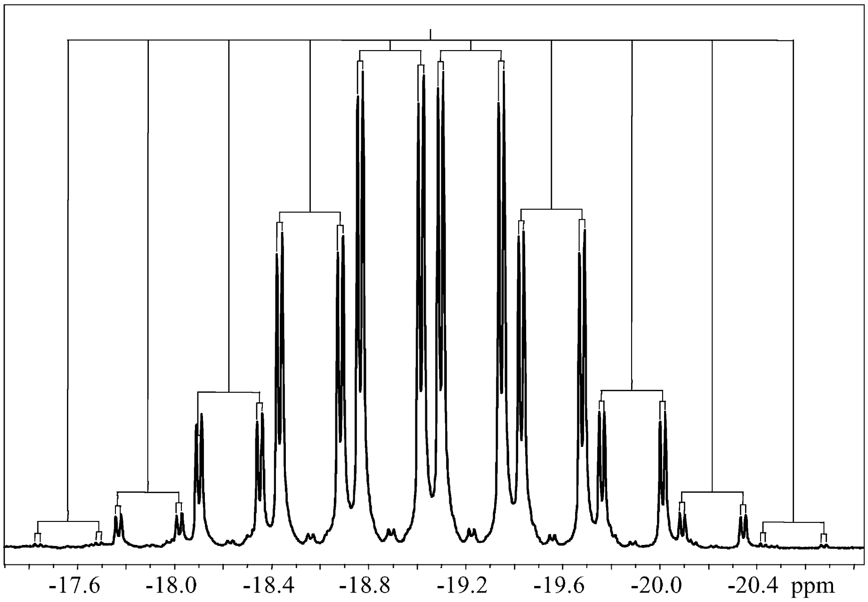
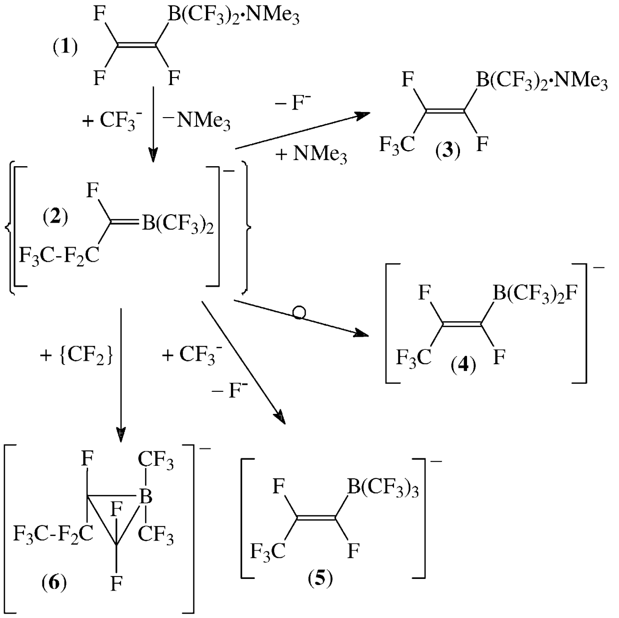


Fig. 1. ^{11}B NMR spectrum of **5**.

(iii) With transfer of one more trifluoromethanide ion and elimination of fluoride the novel tris(trifluoromethyl)-borate [*trans*-$F_3C–CF=CF–B(CF_3)_3]^-$ (**5**) is formed which is the main product under appropriate reaction conditions.

(iv) A side reaction is the addition of difluorocarbene to the BC double bond of **2** to yield the novel cyclopropanylborate [*cyclo*-$(CF_3)_2B–CF_2–CF–CF_2–CF_3]^-$ (**6**).

The intermediacy of **2** is further underscored by the observation that **3** does not react with $[(CF_3)_2SiMe_3]^-$ under cleavage of the BN bond. Obviously, a further nucleophilic attack of a trifluoromethanide ion to the C=C double bond of **3** is sterically hindered. The relative ratios in which **3**–**6** are formed vary considerably and are strongly depending on the reaction conditions. During the formation of the trifluoromethyl transfer reagent $[(CF_3)_2SiMe_3]^-$ at −60 °C the reaction with **1** is very slow. The successful transfer of the CF_3 groups seems to occur in a temperature window between −50 and −20 °C. At −15 °C, the siliconate is difficult to stabilize and sometimes exothermal decomposition has been observed which raised the temperature of the reaction mixture within a few seconds to +40 °C when a huge excess of $[(CF_3)_2SiMe_3]^-$ was employed. Under such circumstances, the yields of **4** and **6** were comparably high, whereas, under optimal conditions **5** and **3** were the main products. The formation of **3**, **4** and **6** could not completely be suppressed. However, the volatile **3** can be removed from the reaction mixture by sublimation at 80 °C/10^{-3} Torr and thus, easily separated.



Scheme 1. Reaction of $F_2C=CF(CF_3)_2B·NMe_3$ with $[(CF_3)_2SiMe_3]^-$ $\{CF_3^-\}$.

The ^{19}F, ^{11}B and ^{13}C NMR spectral data of **3**–**6** are collected in Table 1 and the ^{11}B NMR spectrum of **5** is displayed in Fig. 1. Amine-perfluoropropenylboranes and perfluoropropenylfluoroborates have recently been obtained according to Eqs. (1)–(3) in a *cis*/*trans* ratio of 75/25 and the ^{19}F NMR spectral data of **3** and **4** given in [1] are consistent with data of this investigation.

$$CF_3CF_2CFH_2 + (CF_3)_2BNMe_2 \xrightarrow[2.\,H_2O/-78\,^{\circ}C]{1.\,t\text{-BuLi}/-78\,^{\circ}C} CF_3-CF=CF-B(CF_3)_2 \cdot NHMe_2 \qquad (1)$$

$$CF_3-CF=CF-B(CF_3)_2 \cdot NHMe_2 \xrightarrow[-KI/-H_2O]{+KOH/+CH_3I} CF_3-CF=CF-B(CF_3)_2 \cdot NMe_3 \qquad (2)$$

Table 1
NMR spectral data of **3–6**

	3	**4**	**5**	**6**
^{19}F				
δ(BCF_3)	−59.6	−70.3	−61.6	−56.2, −56.4
^2J(BF)	25	28	26.7	
^4J(FF)			6.5	
^5J(FF)	14.5		10.6	
δ(CCF_3)	−68.4	−68.7	−68.1	−83.6
^3J(FF)	8.4	11.4	9.8	
^4J(FF)	22.1	22.9	22.8	13.4
δ(CCF_2−)				−117.8, −120.3
^2J(FF)				286.9
δ(BCF_2)				−148.4, −149.8
^2J(FF)				247.2
δ(BCFC)	−151.5	−156.6	−151.6	−232.7
$^3J(\mathrm{FF})_{trans}$	136.6	132.8	134.6	
^2J(BF)			20.1	
δ(=CF–CF$_3$)	−162.0	−178.5	−171.7	
^3J(BF)			1.8	
δ(BF)		−228.9		
^1J(BF)		58		
^{11}B				
δ(B)	−9.2	−6.3	−19.1	−24.6
^{13}C				
δ(NCH$_3$)	52.6			
δ(BCF$_3$)	130.3		134.1	
^1J(BC)	77		73.9	
^1J(CF)	305		305.3	
δ(CCF$_3$)	119.0		121.2	
^3J(BC)			2.5	
^3J(CF)				
^2J(CF)	37.8		38.1	
^1J(CF)	273.8		272.0	
δ(BCF=C)	158.6		164.6	
^1J(BC)	66		60.8	
^1J(CF)	254		271.2	
^2J(CF)	47		63.6	
δ(=CF–CF$_3$)	148.9		147.7	
^2J(BC)			3.8	
^2J(CF) CF$_3$	38.4		37.3	
^2J(CF) C=C	46.2		45.2	
^1J(CF)	249.9		238.2	

$$\mathrm{CF_3{-}CF{=}CF{-}B(CF_3)_2\cdot NMe_3} \xrightarrow[-\mathrm{NMe_3}]{\mathrm{NEt_3\cdot 3HF/195\,^{\circ}C}} \mathrm{HNEt_3[CF_3{-}CF{=}CF{-}B(CF_3)_2F]} \qquad (3)$$

Located at −19.1 ppm with line width of 0.9 Hz the ^{11}B resonance of **5** appears as decet of doublets of doublets by coupling with the fluorine atoms of the BCF$_3$ and CF=CF group. The ^{19}F NMR spectrum consists of four signals with relative intensities of 9:3:1:1 at −61.6, −68.1, −151.6 and −171.7 ppm, respectively. The corresponding C-congener *trans*-F$_3$C–FC=CF–C(CF$_3$)$_3$ has been described in [5]. Its ^{19}F NMR spectrum shows fluorine resonances in the relative ratio of 9:3:2 at −63.3, −68.6 and −150 ppm, respectively. Here, the two fluorine atoms at the double bond coalesce accidentally presenting only one multiplet. Because of the slow relaxation of the boron nucleus in **5** the ^{13}C resonances are unusually sharp and ^{13}C-^{11}B and ^{13}C-^{19}F coupling constants are detectable (Table 1). The identification of **6** is based on ^{11}B and ^{19}F spectral data alone. The low frequency ^{11}B shift of −24.6 ppm is quite unusual. Tetraalkylborates show a ^{11}B resonance at −20 ppm, e.g. $[(\mathrm{CF_3})_4\mathrm{B}]^-$ δ ^{11}B = −18.9 ppm [6], $[(\mathrm{CH_3})_4\mathrm{B}]^-$ δ ^{11}B = −20.7 ppm [7]. Beyond that region only cyano, hydro and acetyleno borates possess ^{11}B shifts, e.g. $[\mathrm{B(CN)_4}]^-$ δ ^{11}B = −38.5 ppm, $[(\mathrm{CF_3})_2\mathrm{B(CN)_2}]^-$ δ ^{11}B = −26.5 ppm [6]. The ^{11}B shifts of organoborates can be directly correlated with the ^{13}C shifts of analogous alkanes following the empirical equation (δ ^{11}B = 0.5, δ ^{13}C = 34.7) [7]. Using this equation and the ^{13}C data of 1,1,2-trimethylcyclopropane, *cyclo*-CH$_2$CHCH$_3$C(CH$_3$)$_2$ [8], the ^{11}B shift of the hypothetical borate [*cyclo*-CH$_2$CHCH$_3$B(CH$_3$)$_2$]$^-$ is calculated to −27.2 ppm. If one takes a similar fluoro effect as observed for the couple $[(\mathrm{CH_3})_4\mathrm{B}]^-/[(\mathrm{CF_3})_4\mathrm{B}]^-$ into account, the ^{11}B shift of a hypothetical [*cyclo*-CF$_2$CFCF$_3$B(CF$_3$)$_2$]$^-$ anion should be close to −25 ppm. Thus, the observed value of −24.6 ppm for **6** is in line with a tetracoordinated boron atom incorporated into a three-membered ring. The ^{19}F NMR spectrum of **6** consists of eight signals with the relative intensities 3:3:3:1:1:1:1:1 at −56.2, −56.4, −83.6, −117.8, −120.3, −148.4, −149.8 and −232.7 ppm, respectively. The splitting of the boron-bonded CF$_3$ groups and the presence of two AB spin systems for the endo- and exocyclic CF$_2$ groups suggest the presence of a chiral atom in the three-membered ring. The resonance at −232.7 ppm is typical for a tertiary fluorine atom in a perfluorocyclopropane ring, e.g. the corresponding resonance in *cyclo*-CF$_3$–C*F*–CF$_2$–CF$_2$ is located at −221.2 ppm [9].

Compounds **3–6** are air- and water-stable. Despite their ionic character the tetramethylammonium salts are insoluble in water, but excellently soluble in polar organic solvents like acetone, acetonitrile or alcohol. The novel perfluorinated borates **5** and **6** are congeners of the of the perfluorinated cycloalkanes and alkenes, where one carbon atom is replaced by a formally negatively charged boron atom [10]. The cylopropanylborate **6** is also the first example of a three-membered ring with two carbon atoms and a tetracoordinated boron atom. The chemistry of perfluoroalkenes is well-developed and further experiments will show whether similar reactions can be applied to these related borates.

3. Experimental

3.1. General

NMR: Bruker ARX 400 (400, 100.6 and 376.5 MHz, for ^{1}H, ^{13}C and ^{19}F, respectively), Bruker AC 250 (79.8 MHz for ^{11}B). [D$_3$]Acetonitrile as solvent and internal standard (^{1}H: δ_H = 1.95, ^{13}C: δ_C = 1.30), ^{19}F: external standard CFCl$_3$, ^{11}B: external standard BF$_3$·OEt$_2$. IR/Raman: Bruker Equinox 55 (laser 9394.8 cm^{-1}). MS: Varian MAT 311 (70 eV).

3.2. Preparation of compounds

Onto a mixture of 1.40 g (15 mmol) of anhydrous NMe_4F [11], 1.4 g (5.4 mmol) of $F_2C{=}CF(CF_3)_2B{\cdot}NMe_3$, 15 ml of dry THF (directly distilled from $LiAlH_4$) and 5.0 g (35.2 mmol) of CF_3SiMe_3 were condensed in vacuo. The light yellow solution was stirred at −60 °C and then allowed to warm to 0 °C within 7 h, upon which the color of the reaction mixture slowly turned black. All volatile material was removed in vacuo. The black tarry residue was dissolved in water/acetone (2/8) and the acetone evaporated at room temperature. The organic residue which consists according to ^{19}F NMR spectra of 40 mol% of **5**, 45 mol% of **3**, 10 mol% of **4** and 5 mol% of **6** was subjected to a sublimation in vacuo at 80 °C by which most of **3** was removed. Pure **3** was obtained by repeated sublimation followed by crystallization from $CHCl_3$. The non-volatile residue which contained the tetramethylammonium salts was dissolved in hot CH_2Cl_2. Upon cooling to −40 °C, a black solid layer was obtained from which the dark solution was decanted. The solid material contained ca. 80% of **5** and was further purified by thin layer chromatography on silica plates (Merck 60F 20 cm × 20 cm/2 mm) using CH_2Cl_2. Besides tarry material which could not be eluted, the lower zone (R_F ca. 0.08) on the plates contained a ca. 1:1 mixture of **4** and **6**, whereas, **5** (95% purity) was isolated from the upper zone of the plates (R_F ca. 0.159). Finally, pure **5** was obtained after crystallization from di-(*n*-butyl ether).

3—mp: 49 °C; *m/z*: 108(100)$[F_2BN(CH_3)_3]^+$, 59(89)-$[N(CH_3)_3]^+$, 58(52)$[H_2CN(CH_3)_2]^+$, 152(19)$[C_6H_9F_3N]^+$, 220(29)$[M - C_2F_5]^+$, 270(3)$[M - CF_3]^+$, 339(1)$[M]^+$; Raman cm^{-1}: 2995 s, 2979 s ν(CH), 1685 s ν(C=C), 1480 s, 1457 s δ(CH), 823 m $\delta(CCF_3)$, 718 s $\delta(BCF_3)$. Anal. calcd. for $C_8H_9BF_{11}N$: H, 2.68; C, 28.35; N, 4.13. Found: H, 2.6; C, 28.2; N, 4.1.

5—mp: 158–160 °C; Raman cm^{-1}: 3049 s, 2992 s, 2905 s ν(CH), 1691 s ν(C=C), 1455 s δ(CH), 754 s $\delta(CCF_3)$, 722 s $\delta(BCF_3)$. Anal. calcd. for $C_{10}H_{12}BF_{14}N$: H, 2.86; C, 28.39; N, 3.31. Found: H, 2.9; C, 28.3; N, 3.4.

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