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THE REACTION OF BORON TRIHALIDES WITH $CF_3Sn(CH_3)_3$ IN THE PRESENCE OF TRIMETHYLAMINE

H. BÜRGER, M. GRUNWALD and G. PAWELKE

Anorganische Chemie, FB 9, Universität-Gesamthochschule,
D-5600 Wuppertal 1 (F.R.G.)

SUMMARY

The reaction of $CF_3Sn(CH_3)_3$ with BCl_3 and BBr_3 in the presence of trimethylamine has been investigated. The volatile adducts $CF_2XBF_2 \cdot N(CH_3)_3$ (X = F, Cl and Br) have been isolated from the complex reaction mixture while the anions $BF_4^\ominus$, $CF_2XBF_3^\ominus$, $CF_3BF_2CF_2X^\ominus$ and $(CF_2X)_2BF_2^\ominus$ have been identified in the residue. $[(CH_3)_3NH][CF_2ClBF_3]$ has been isolated. The formation of the CF_2XB derivatives is likely to occur via CF_2 insertion, which is promoted by the presence of $N(CH_3)_3$. NMR, IR, Raman and mass spectra of the novel fluoromethyl borane derivatives are reported.

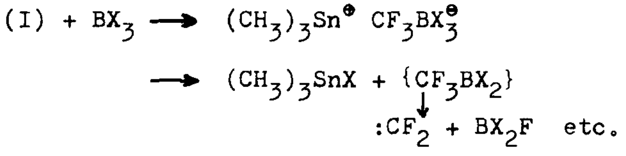
INTRODUCTION

Only very few trifluoromethylboron compounds have been reported in the literature [1]. Among these are the anions $CF_3BF_3^\ominus$ (I) and $(CF_3)_2BF_2^\ominus$ (II) obtained from the reaction of BF_3 with $CF_3Sn(CH_3)_3$ (III) in the presence of $F^\ominus$ [2, 3]. It has been reported that CF_3BF_2 (IV) is formed when $CF_3B(n\text{-}C_4H_9)_2$ is treated with BF_3, and (IV) has been characterized by its IR spectrum, vapor pressure and a fluorine analysis [4]. Furthermore, complexes of (IV) with $O(CH_3)_2$ [5] and tertiary amines [4] have been mentioned.

Apparently, (III) is a reactant particularly suited to transfer CF_3 groups to strong Lewis acids [6]. However, its use in the synthesis of CF_3B compounds is mainly limited by the instability of the intermediates involved rather than an inertness towards boron trihalides. We describe the following experiments aimed at synthesizing new fluoroalkyl boron compounds by means of the reaction of (III) with BCl_3 and BBr_3.

THE REACTION OF (III) WITH BCl_3 AND BBr_3

A solution of (III) in pentane reacts at -90°C vigorously with BCl_3 and BBr_3 to form a white precipitate. This precipitate is supposedly salt-like and may have the constitution $(CH_3)_3Sn^{\oplus}\ CF_3BX_3^{\ominus}$, X = Cl, Br. It decomposes rapidly when the temperature is raised above -70°C. At room temperature all CF_3B compounds have been converted into the well-known anions (I) and (II). The reaction scheme, eq. (1), with sequential halogen exchange would account for the observed product balance.



$$\begin{aligned} \mathrm{(I)} + \mathrm{BX_3} &\longrightarrow \mathrm{(CH_3)_3Sn^{\oplus}\ CF_3BX_3^{\ominus}} \\ &\longrightarrow \mathrm{(CH_3)_3SnX} + \{\mathrm{CF_3BX_2}\} \\ &\qquad\qquad\qquad\qquad\ \ \downarrow \\ &\qquad\qquad\qquad\quad \mathrm{:CF_2 + BX_2F}\quad \mathrm{etc.} \end{aligned} \tag{1}$$

This sequence is repeated until all BX_3 has been converted into BF_3, (I) and (II), provided (III) is available in sufficient amounts. We believe that the reactivity of the tricoordinate boron intermediate CF_3BX_2 is of major importance for this halogen exchange process. Such a species may be stabilized by a Lewis base, e.g. NMe_3. Indeed the complexes $BF_3 \cdot NMe_3$ (V) and $CF_2XBF_2 \cdot NMe_3$, X = F (VI), Cl (VII) and Br (VIII), are formed when NMe_3 is added to the above-mentioned reaction mixture at -40°C.

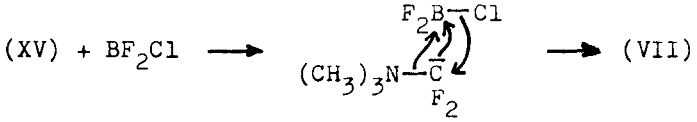
The ^{19}F NMR spectrum of the non-volatile residue dissolved in acetonitrile confirms the presence of further ionic fluoroalkyl boron compounds in addition to the well-known anions (I) and (II). The following species have been identified in a more detailed investigation:

$CF_2XBF_3^{\ominus}$, X = Cl (IX), Br (X)
$CF_3(CF_2X)BF_2^{\ominus}$, X = Cl (XI), Br (XII)
$(CF_2X)_2BF_2^{\ominus}$, X = Cl (XIII), Br (XIV)

The separation and isolation of these anions turned out to be difficult if not impossible and has only been achieved for (IX) with the counterion $(CH_3)_3NH^{\oplus}$.

While the formation of (VI) is not unexpected, the appearance of CF_2Cl and CF_2Br groups bonded to boron both in the anions and the trimethylamine complexes is somewhat surprising. Since the formation of CF_2X groups is unequivocally associated with the presence of $N(CH_3)_3$, it is most likely that CF_2X groups result from an intermediate in which CF_2, formed according to eq. (1), is trapped by $N(CH_3)_3$. This intermediate, which may be denoted '$(CH_3)_3NCF_2$' (XV), suppresses the usual oligomerization of CF_2 to form C_2F_4 and cyclo-C_3F_6.

The intermediate (XV) supposedly inserts into the BX bond of BXF_2 as is demonstrated for (VII), eq. (2).



(2)

The constitution of (XV) may well be that of a free or complexed ylid because in the course of the above-mentioned reactions performed in the presence of $N(CH_3)_3$, the cation $(CH_3)_3NCF_2H^{\oplus}$ has always been detected as a side product. The properties and the structure of this cation will be the subject of a forthcoming contribution.

PROPERTIES OF THE COMPLEXES (VI), (VII) and (VIII)

The complexes (VI), (VII) and (VIII) are low-melting, colourless solids which may be purified by sublimation *in vacuo*. Physical and spectroscopic properties are set out in Table I. The ^1H, ^{11}B and ^{19}F NMR spectra are in agreement with the suggested constitution. The chemical shifts and coupling constants of (VI) to (VIII) are consistent and vary in a regular fashion. In the mass spectra the fragment m/e 107/108 ($M - CF_2X^+$) is the basis peak, followed by 58 ($CH_2N(CH_3)_2^+$), 91/92/93 ($CH_2NCH_3BF_2^+$)/($(CH_3)_2NBF_2^+$), 59 ($(N(CH_3)_3)^+$) and 42 ($CH_2NCH_2^+$). The fragment (CF_2X^+) appears with relatively low intensity.

The IR and Raman spectra are just as indicative of a complexed $N(CH_3)_3$ molecule as they are in the case of $(CH_3)_3NBF_3$ [7]. Diagnostic vibrations due to the CF_2XBF_2 fragment are set out in Table 1.

The formation of the complex (VI) by the reaction of CF_3BF_2 with $N(CH_3)_3$ has been reported in the literature [4,5] (see however [8] for a misinterpretation of Ref. [4]), and it has been claimed [4,5] that this adduct is cleaved by anhydrous HCl with recovery of CF_3BF_2. However, no details are given for this reaction. We were unable to decompose (VI) with gaseous, dry HCl even by prolonged heating to 60°C. In this context the thermal stability of the related complex (V) and its resistance towards Lewis acids should be mentioned [9].

THE ANIONS (IX) TO (XIV)

After extraction of the trimethylamine complexes with ether a residue is obtained which is partly soluble in CH_3CN. The acetonitrile solution contains trimethylammonium salts of various fluoroborate anions. Typical yields, determined by ^{19}F NMR spectroscopy (Table 2), for the reactions with BCl_3/BBr_3 are: $BF_4^{\ominus}$ 6/4, (I) 25/30, (II) 8/22, (IX)/(X) 22/10, (XI)/XII) 5/8 and (XIII)/(XIV) 5/3 %. Due to this complex composition, the isolation of the individual species (IX) to (XIV) turned out to be extremely difficult. We have only been able to isolate (IX) analytically pure.

EXPERIMENTAL

Reaction of $CF_3Sn(CH_3)_3$ with BCl_3 and BBr_3 in the presence of $(CH_3)_3N$.

To a vigorously stirred solution of 76.4 g (0.33 mol) (III) in 100 ml 2-methylpentane, 15 g BCl_3 [33 g BBr_3] (0.13 mol), dissolved in 15 ml 2-methylpentane, are

TABLE I

Physical properties of the complexes (VI) to (VIII)

	$CF_3BF_2 \cdot N(CH_3)_3$ (VI)	$CF_2ClBF_2 \cdot N(CH_3)_3$ (VII)	$CF_2BrBF_2 \cdot N(CH_3)_3$ (VIII)
Mp. [°C]	35	46	58
NMR spectra			
$^1H^a$ δ [ppm]	2.83	2.84	2.88
$^{19}F^b$ δ(CF) [ppm]	-71.2	-62.6	-57.7
δ(BF) [ppm]	-173.4	-170.1	-168.0
$^1J(F^{11}B)$ [Hz]	51.2	48.5	47.0
$^2J(F^{11}B)$ [Hz]	32.6	25.5	23.7
$^{11}B^c$ δ [ppm]	-0.60	-0.37	-0.16
Selected IR^d/Raman^e frequencies of the CF_2XBF_2 part			
δ(CBN)	/158m	/148m	/126m
δ(BCX)		/213m	/184s
δ (BF_2)	607w/608s	585w/584w	580w/580w
$\delta_s(CF_3)$	710s/711vs		
δ (CF_2)		/647vs	637m/637s
ν(CX)		/409s	305m/306vs
ν(CF)	1196m/1190vw	1195m/-	1180m/-
	1323m/1321w	1231m/-	1225m/-

[a] In ether, ext. std. TMS. [b] In ether, int. std. $CFCl_3$. [c] In $CDCl_3$, ext. std. $BF_3 \cdot Et_2O$. [d] KBr pellets, ±2 cm^{-1}. [e] Solid, excitation 6471Å, ±2 cm^{-1}.

TABLE II

^{19}F NMR spectra[a] of the anions (IX) to (XIV)

	(IX)	(X)	(XI)	(XII)	(XIII)	(XIV)
$\delta(CF_2)$[ppm]	-66.5	-59.0	-63.3	-57.3	-61.1	-55.7
$\delta(CF_3)$[ppm]			-72.0	-70.2		
$\delta(BF)$[ppm]	-156.7	-155.0	-175.7	-175.2	-175.2	-169.2
$^1J(FB)$[Hz]	38.6	38.5	57.4	56.1	55.0	52.7
$^2J(F_2CB)$[Hz]	24.9	22.6	25.4	23.5	24.9	24.1
$^2J(F_3CB))$[Hz]			30.1	30.1		

[a] In CH_3CN, int. std. $CFCl_3$.

added at -70°C [-90°C]. Then the mixture is allowed to warm to -40°C, and 45.1 g (0.78 mol) $(CH_3)_3N$ are added. The solvent and an excess of $(CH_3)_3N$ are removed at room temperature. The residue, a brown oil, is repeatedly extracted with 50 ml portions of diethyl ether.

The ether extract is concentrated and treated at room temperature for 2 days with anhydrous KF in order to decompose (V) and $(CH_3)_3SnCl$, filtered, evaporated and worked up by repeated sublimation in vacuo (10^{-2} Torr). (VI), (VII) and (VIII) are obtained at -10, 0 and +45°C in yields of approximately 20, 30 and 50 %, respectively.

(VI): $C_4H_9BF_5N$. Required/found; %F, 53.69/53.0; %N, 7.92/7.8

(VII): $C_4H_9BClF_4N$. Required/found; %C, 24.84/24.8;
%H, 4.69/4.6; %Cl, 18.33/18.5; %N,7.24/7.3.

(VIII): $C_4H_9BBrF_4N$. Required/found; %C, 20.21/20.2;
%H, 3.81/3.8; %Br, 33.60/33.9; %F, 31.95/31.2;
%N, 5.89/6.0.

In the case of the reaction with BCl_3, the residue of the ether extraction is treated with CH_3CN, filtered, the solvent evaporated to dryness and stirred for 5 hours with a slurry of 6 g KF in 40 ml acetone, filtered again and the solution concentrated. The precipitate is collected and washed with

10-20 ml cold $CHCl_3$ to dissolve the $(CH_3)_3NH^+$ and $(CH_3)_3NCF_2H^+$ salts of the anions (II), (XI) and (XIII). The insoluble residue is extracted with acetone, and a solution of the $(CH_3)_3NH^+$ salts of (I) and (IX) is obtained. (IX) is isolated with a yield of 22 % as trimethylammonium salt by repeated recrystallisation from acetone/ether and acetone/-petrolether mixtures.

(IX): $C_4H_{10}BClF_5N$. Required/found; %Cl, 16.61/16.0.
IR: 1495s, 1182s, 1170s, 1080vs, 982vs, 970vs, 950vs, 840vs, 662s.
Raman: 1464s, 948s, 752s, 663m, 402m.

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