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TRIFLUOROMETHYL-AMINOBORANES

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SUMMARY

The trifluoromethyl aminoboranes $CF_3B[N(CH_3)_2]_2$ (I), $CF_3B[N(CH_3)CH_2]_2$ (II) and $(CF_3)_2BN(CH_3)_2$ (III) have been prepared in yields between 8 and 25% by the reaction of the respective bromoboranes with a trifluoromethylating reagent prepared from $P[N(C_2H_5)_2]_3$ and CF_3Br in CH_2Cl_2. Mass, NMR, IR and Raman spectra are reported. The compounds (I) to (III) are monomeric and stable at room temperature, thermal decomposition beginning at about 100 °C.

INTRODUCTION

Bonds between CF_3 groups and electropositive elements E are difficult to form because repulsion between the positively charged C atom of the CF_3 group and the element E weakens the E - C bond [1]. Elimination of $:CF_2$ and formation of E - F derivatives is the usual pathway for the easy decomposition of such E - CF_3 compounds. For trifluoromethylboron compounds (E = B), the positive atomic charge on boron may be removed either by coordination of a fourth ligand or eventually by dative $(p \rightarrow p)\pi$ bonds. Thus, it is not surprising that the majority of the hitherto known trifluoromethylboron compounds is derived from tetracoordinate boron, e.g. $CF_3BF_3^-$ [2], $(CF_3)_2BF_2^-$[3] $CF_3BF_2 \cdot N(CH_3)_3$ [4].

No trifluoromethyl derivative of tricoordinate boron has been reported except CF_3BF_2 and its precursor $CF_3B(n\text{-}C_4H_9)_2$ [5,6]. These compounds first prepared in 1961 were however not fully characterized, and a discrepancy concerning the properties of $CF_3BF_2 \cdot N(CH_3)_3$ from which CF_3BF_2 was prepared has been noted [4].

Keeping in mind the possible increase in stability of CF_3B compounds by ligands capable of dative $(p \rightarrow p)\pi$ bonding, we attempted the synthesis of

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trifluoromethyl aminoboranes $CF_3B(NR_2)_2$(A) and $(CF_3)_2BNR_2$(B). With this goal, the respective haloboranes were reacted with different trifluoromethylating agents. In the following we report on the synthesis of the first three reasonably stable and fully characterized trifluoromethylboranes and some of their physical properties.

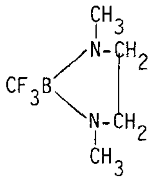
SYNTHESES

Preparation of trifluoromethyl aminoboranes (A) and (B) was attempted by transfer of CF_3 groups to the appropriate aminoboron halides R_2NBX_2 and $(R_2N)_2BX$, X = Cl and Br. Searching for a suitable CF_3 transfer agent, $Hg(CF_3)_2$, $(CH_3)_3SnCF_3$ and Burton's reagent prepared from $(C_6H_5)_3P$, CF_2Br_2 and KF in triglyme [7] were tested. Though these reagents have been successfully employed for the synthesis of CF_3 derivatives of group IV elements and tetracoordinated boron, they did not afford an (A) or (B). Only very low yields of $CF_3B[N(CH_3)_2]_2$ (I) were obtained from the photochemical reaction of $B_2[N(CH_3)_2]_4$ with CF_3I.

Substantial though unsatisfactory yields of (I), the analogous borolidine (II) and bis(trifluoromethyl) dimethylaminoborane (III) were obtained by reacting the appropriate halides at low temperature with the reagent prepared according to Ruppert _et al_. [8] from $P[N(C_2H_5)_2]_3$ and CF_3Br in the presence of a suitable solvent, preferentially CH_2Cl_2.

$CF_3B[N(CH_3)_2]_2$

(I)



(II)

$(CF_3)_2BN(CH_3)_2$

(III)

This reagent evidently reacts as a phosphonium salt (IV) by transfer of its CF_3^- anion [8], eqn. (1):

$$\begin{array}{llll} P[N(C_2H_5)_2]_3 + CF_3Br \longrightarrow & \{[(C_2H_5)_2N]_3PBr^+ \; CF_3^-\} & (IV) & \\ & & & (1) \\ (IV) + XB\langle \quad \longrightarrow & CF_3B\langle \; + [(C_2H_5)_2N]_3PBr^+ \; X^- & & \end{array}$$

The reagent (IV) has been successfully employed for the synthesis of trifluoromethylsilicon compounds, and yields up to 90% have been reported [8].

Much poorer yields, 20, 25 and 8% for (I), (II) and (III), respectively, were obtained for trifluoromethyl aminoboranes. Several reasons are responsible for the limited selectivity of the reaction eqn. (1). In agreement with previous observations [9], the reagent (IV) itself isomerizes to $F_3CP[N(C_2H_5)_2]_3^+Br^-$, and the cation $FP[N(C_2H_5)_2]_3^+$ as well as $F_3CP[N(C_2H_5)_2]_2$ are formed in minor quantities. Furthermore, the solvent (CH_2Cl_2) may be attacked by (IV), and HCF_3 is formed in varying amounts depending on the reaction conditions.

The aminoboron bromides are more suited as starting materials than the corresponding chlorides because, though both react in a comparable way, unreacted bromides can be easier separated by distillation from the desired reaction products.

Ligand scrambling involving both the boron and phosphorus atoms also accounts for the poor yields. Thus, $B[N(CH_3)_2]_3$ has been identified as major by-product in the synthesis of (I), while (I) is found in the reaction of $(CH_3)_2NBBr_2$ with (IV). In the latter reaction, cleavage of the solvent CH_2Cl_2 by $(CH_3)_2NBBr_2$ is more pronounced than in the synthesis of (I) and (II). This cleavage is evident in the formation of mixtures of (yet unidentified) by-products which are similarly volatile as (III) and which contain $N(CH_3)_2$ groups, boron, CF groups and ~20% chlorine, but no bromine.

The compounds (I) to (III) are separated from the reaction mixture by condensation in vacuo and purified by repeated distillation employing a slit tube column. However, purification is accompanied by loss of material due to dismutation.

PROPERTIES

Compounds (I), (II) and (III) are colourless liquids which are readily soluble in organic solvents. Their physical properties are set out in Table 1. They are apparently monomeric and readily decomposed by H_2O, HCF_3 being formed. They are thermally stable at room temperature, but decomposed at elevated temperature under elimination of $:CF_2$. Heating of (I) to 140° C for 80h results in 40% decomposition and formation of $FB[N(CH_3)_2]_2$, while a total of 15% of monomeric and dimeric fluoroborolidine [10] were identified by ^{19}F NMR spectroscopy when (II) was heated to 100° C for 40h. The thermolysis of (III) (65h at 118° C) yields a black, obviously polymeric material in which monomeric and dimeric $F_2BN(CH_3)_2$ were identified by ^{19}F NMR spectroscopy.

TABLE I

Physical properties and NMR spectra of compounds (I) to (III)

	$CF_3B[N(CH_3)_2]_2$ (I)	$CF_3B[N(CH_3)CH_2]_2$ (II)	$(CF_3)_2BN(CH_3)_2$ (III)
bp [°C/Torr]	25/16	47/30	25/25
$^{1}H^{a}$			
$\delta(CH_3/CH_2)$ [ppm]	2.72	2.33/2.87	2.70
$^{5}J(HF)$ [Hz]	0.7		
$^{19}F^{b}$			
δ [ppm]	-61.0	-62.3	-63.0
$^{13}C^{c}$			
$\delta(CH_3/CH_2)$ [ppm]	39.9	33.4/51.6	41.8
$^{1}J(CH_3/CH_2)$ [Hz]	135	135/140	140
$\delta(CF_3)$ [ppm]	128.2	126.7	125.5
$^{1}J(CF)$ [Hz]	301	297	299
$^{1}J(CB)$ [Hz]	99	97	100
$^{11}B^{d}$			
δ [ppm]	26.3	24.9	30.2
$^{14}N^{e}$			
δ [ppm]	-337		

[a] At 90 MHz, ext. std. TMS. [b] At 84.67 MHz, ext. std. $CFCl_3$. [c] At 75.47 MHz, int. std. $CDCl_3$ = 77 ppm. [d] At 25.52 MHz, ext. std. $BF_3 \cdot O(C_2H_5)_2$. [e] At 5.75 MHz, ext. std. NO_3^-.

SPECTRA

Mass spectra. (I) to (III) were investigated by E.I. mass spectroscopy. M^+ peaks were observed for (I) and (II) (73 and 12% relative intensities), while $(M\text{-}F)^+$ (12%) is the highest mass in the fragmentation of (III). Basis peaks are $(N(CH_3)_2)^+$, $(M\text{-}CF_2)^+$ and $(M\text{-}2CF_2)^+$ for (I), (II) and (III), respectively. The $(M\text{-}CF_2)^+$ peak of (I) has 56% relative intensity. The mass spectra are in agreement with the proposed constitution. The fragmentation pattern underscores the ease of thermal difluorocarbene elimination.

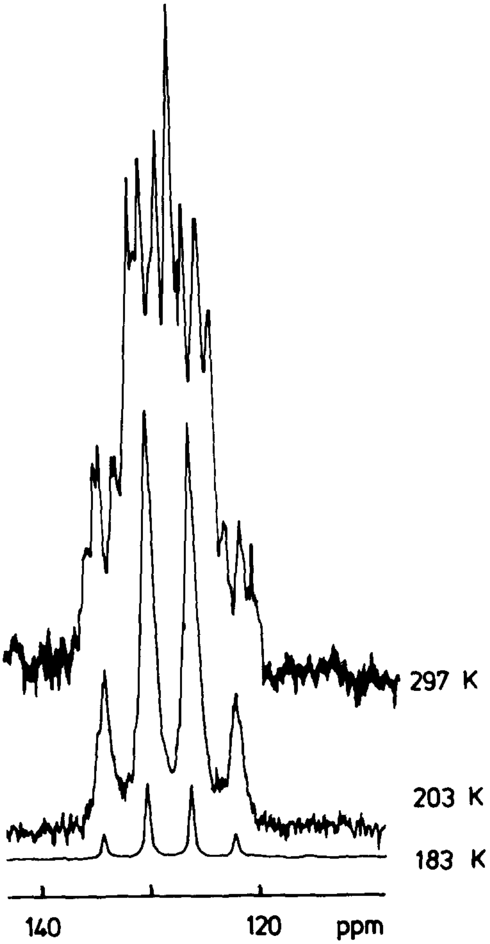


Fig. 1. CF_3 signal in the ^{13}C NMR spectrum of (I) at different temperatures.

NMR spectra. NMR spectra of the ^{1}H, ^{19}F, ^{13}C, ^{11}B and ^{14}N nuclei of (I) to (III) have been recorded (Table 1). They are in agreement with the suggested constitution. In contrast to the fluoroalkyl borate anions [4] the $^{2}J(BF)$ coupling is not resolved in tricoordinate CF_3-substituted boranes, only broad absorptions being observed in the ^{19}F and ^{11}B NMR spectra. Therefore most information is obtained from the ^{13}C NMR spectra which were recorded at different temperatures. Figure 1 illustrates the $^{13}C(CF_3)$ resonance of (I) at temperatures between 297 and 183K. At 183K, relaxation of the boron nucleus is fast, and a quartet with an intensity ratio of 1:3:3:1 and $^{1}J(^{19}F^{13}C)$ of 301 Hz is observed. On raising the temperature, coupling with the boron nucleus occurs. At 297K, a multiplet with $^{1}J(^{13}C^{11}B)$ of 99 Hz is observed.

Vibrational spectra. The vibrational frequencies of (I), (II) and (III) are given in Table 2. The Raman spectrum of (III) is illustrated in Fig. 2. The normal vibrations of the heavy atom skeletons of (I) and (III) without consideration of the CH_3 vibrations were assigned with the help of a normal coordinate analysis. The results are only discussed briefly. Details will be given in context with an electron diffraction investigation now in progress.

The BN stretching vibrations are easily detected by their $^{10/11}B$ shifts at 1552/1530, 1425/1404 (I), 1545/1522, 1430/1420 (II) and 1602/1571 cm^{-1} (III). The symmetric CF stretching vibrations are located at 1280 (I), 1300 (II) and 1273/1185 cm^{-1} (III), whereas their asymmetric counterparts are observed between 1100 and 1150 cm^{-1}. The latter are assigned by comparison

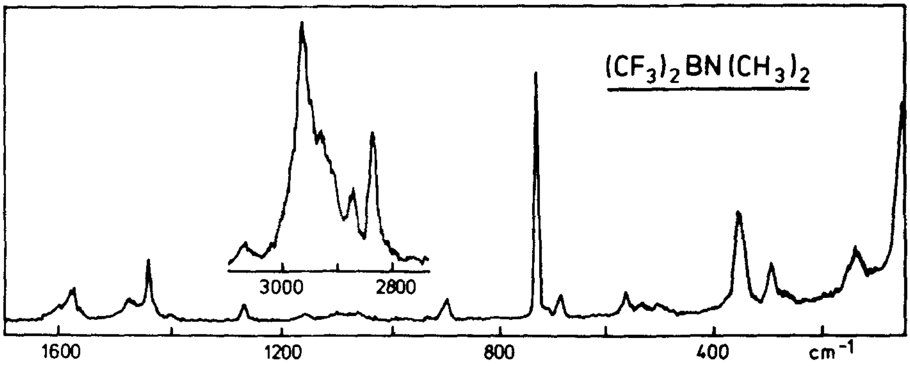


Fig. 2. Raman spectrum of $(CF_3)_2BN(CH_3)_2$.

with the corresponding bromoboranes, in which the CF_3 vibrations are absent, while the other skeletal vibrations appear in corresponding regions. Near 950 cm^{-1} several bands with $^{10/11}B$ shifts are observed and assigned to BC stretching vibrations. In the Raman spectrum, the most intense line is associated with the symmetric CF_3 deformation observed at 715 (I), 721 (II) and 729 cm^{-1} (III). In (III), the presence of a second CF_3 group is strongly suggested by the appearance of an infrared band at 690 cm^{-1}, which is assigned to the out-of-phase symmetric CF_3 deformation. Vibrations < 700 cm^{-1} with significant $^{10/11}B$ shifts correspond to out-of-plane vibrations of the boron atom. They are located at 696/674 (I), 675/650 (II) and 712/690 cm^{-1} (III). The CF_3 group vibrations δ_{as} and $\rho(CF_3)$ are associated with infrared absorptions near 510 and 350 cm^{-1}, but according to normal coordinate analysis they are mixed with other skeletal bending modes.

EXPERIMENTAL

Trifluoromethyl-bis(dimethylamino)borane (I) - 60.0g (402 mmol) CF_3Br are condensed upon a solution of 24.9 g (139 mmol) $BrB[N(CH_3)_2]_2$ in 30 ml CH_2Cl_2 at -70° C and 43.0 g (174 mmol) $P[N(C_2H_5)_2]_3$ added within 15 min. The mixture is warmed to room temperature within 3h and CH_2Cl_2 distilled off. Less volatile products are collected *in vacuo* (0.1 Torr) in a -78° C trap, while the residue is held at 60° C. The crude product is repeatedly distilled *in vacuo* ($p \leq 20$ Torr) employing a slit tube column. Yield 20%.

$C_5H_{12}BF_3N_2$. Required/found; %C, 35.75/36.0; %H, 7.20/7.2; %B, 6.44/6.5;
%F, 33.93/33.7; %N 16.68/16.8.

2-Trifluoromethyl-1,3-dimethyl-1,3-diaza-2-borolidine (II) was prepared similarly from 19.5g (110 mmol) bromoborolidine in 30 ml CH_2Cl_2, 40.0g (268 mmol) CF_3Br and 27.0g (110 mmol) $P[N(C_2H_5)_2]_3$. Yield 25%.

$C_5H_{10}BF_3N_2$. Required/found; %C, 36.19/36.2; %H, 6.07/5.9; %B, 6.51/6.6;
%F, 34.34/34.5; %N, 16.88/16.8.

Bis(trifluoromethyl)-dimethylaminoborane (III) At -78° C, 104.3g (700 mmol) CF_3Br are condensed upon a solution of 61.0g (284 mmol) $Br_2BN(CH_3)_2$ in 150 ml CH_2Cl_2, the solution cooled to -100° C and 140g (567 mmol) $P[N(C_2H_5)_2]_3$ added within 1.5h, stirred at -78° C for 1h and warmed to room temperature within 2h. Volatile products are condensed in a -78° C trap at 0.01 Torr, CH_2Cl_2

TABLE 2

Vibrational spectra of (I) to (III) (cm^{-1})

(I), IR	(I), Raman	(II), IR	(II), Raman	(III), IR	(III), Raman	Assignment
3037 vw						$\nu(\mathrm{CH})$
3009 w	3005 wp	3015 w	3008 vw	3008 vvw		
2941 m	2942 mp	2970 m		2978 w	2985 mp	
		2935 m	2945 w	2960 w		
2900 m	2898 mp		2922 w	2925 w	2930 wp	
2871 m	2865 s	2902 sh				
	2840 vwp	2875 s	2884 m	2885 vw	2878 wp	
2826 m	2816 mp		2857 w	2838 w	2835 wp	
	2793 mp	2820 s	2813 m			
1552 1530 s		1545 1522 s		1602 1571 w	1603 1573 mp	$\nu(\mathrm{BN})\substack{{}^{10}\mathrm{B}\\{}^{11}\mathrm{B}}$
	1492 w		1515 m	1534 w		
1472 m	1470 m	1463 s	1463 s	1472 w	1475 m	$\delta_{as}(\mathrm{CH_3})$
	1450 m		1436 s	1425 w	1442 s	
1425 1404 s	1422 1407 wp	1430 1420 s				$\nu(\mathrm{BN})\substack{{}^{10}\mathrm{B}\\{}^{11}\mathrm{B}}$
	1395 sp	1360 w	1361 w	1406 w	1400 wp	$\delta_s(\mathrm{CH_3})$
				1350 1333 m		$\nu_{as}(\mathrm{NC})$
1280 m	1275 wp	1300 s	1304 vw	1273 s	1270 mp	$\nu_s(\mathrm{CF_3})$
1204 s		1220 s				$\nu_{as}(\mathrm{NC})$
				1185 s		$\nu_s(\mathrm{CF_3})$
1145 m	1148 vwp					$\nu(\mathrm{NC})$
1110 vs	1108 vwp	1110 vs		1150 vs		$\nu_{as}(\mathrm{CF_3})$
				1106 vs		$\nu_{as}(\mathrm{CF_3})$

1073 vs 1046 m	1071 w	1085 vs	1078 w	1075 m 1060 w	1070 vw	$\rho(CH_3)$
					1060 vw	$\nu_{as}(CF_3)$
920 907 m		986 m	985 w	935 913 s		$\nu(BN,C)\,{}^{10}B$ ^{11}B
		937 w	936 m			$\nu_s(CC)$
	919 903 mp				907 898 mp	$\nu(BN,C)\,{}^{10}B$ ^{11}B
		846 vw 786 vw 750 w				$\delta(CH_2)$
716 w	715 vsp	719 m	721 sp	729 w	729 vsp	$\delta_s(CF_3)$
696 674 w		675 650 m		712 690 m		$\delta_{op}(B)\,{}^{10}B$ ^{11}B
				690 m	687 m	$\delta_s(CF_3)$
		617 w	620 w			$\delta(CH_2)$
	565 mp	557 m	559 s		564 mp	$\nu_s(CN)$
563 w						$\delta(NC_2)$
512 w	515 wp	505 m		503 w	505 wp	$\delta_{as}(CF_3)$
385 vw	380 mp	395 vw			380 sh	$\delta(BNC)$
	340 mp	348 vw	351 w		352 sp	$\rho(CF_3)$
285 w	290 wp	278 w 257 vw	279 w 260 w		294 mp	$\delta(CNC)$
	175 vwp 135 vwp				138 mp	$\delta(CBN)/(CBC)$

distilled off and (III) obtained by distillation *in vacuo*, yield 8%.
$C_4H_6BF_6N$. Required/found; %C, 24.91/25.8; %H, 3.14/3.3; %B 5.60/5.4; %F, 59.09/57.5; %N, 7.26/7.5.

Physical measurements

Mass spectra: Varian CH5 and Varian MAT 311; EI; 70eV
NMR spectra: ^{1}H, ^{19}F Varian EM 390; ^{13}C Bruker WP 300; ^{11}B and ^{14}N Varian CFT 80.
Raman spectra: Cary 82, 1mm i.d. capillaries, excitation Ar^+ 514.5 nm (II) and Kr^+ 647.1 nm (I, III), ±2 cm^{-1}.
IR spectra: Perkin-Elmer 580B, 200 - 4000 cm^{-1}, 18.7 cm gas cells, KBr and polythene windows, ±2 cm^{-1}.

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