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POTASSIUM-BIS (TRIFLUOROMETHYL) AMINO TRIFLUOROBORATE

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## SUMMARY

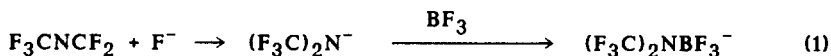
Potassium-bis (trifluoromethyl) amino trifluoroborate  $K[(F_3C)_2NBF_3]$  has been prepared from perfluoroazapropene, potassium fluoride and boron trifluoride in acetonitrile. The new compound was characterised by elemental analyses, NMR and IR spectra.

## INTRODUCTION

Stable boron compounds with a  $(F_3C)_2N$ -ligand are still unknown. Attempts to prepare  $(F_3C)_2NBX_2$  ( $X = F, Cl, Br, I$ ) by reaction of  $(F_3C)_2NH$  with the corresponding boron halides were unsuccessful or yielded unstable  $(F_3C)_2NBBR_2$  which decomposed into  $BF_3$  and  $F_3CNCBr_2$  [1]. Studies on the behaviour of perfluorotrimethylamine towards  $SbF_5$  [2] have shown that the carbocation  $(F_3C)_2NCF_2^+$ , formed by fluoride abstraction, is unstable as well. This may be attributed to the low basicity of a nitrogen atom carrying two electron-withdrawing  $F_3C$ -groups. In accord with this observation, we assumed that a bis(trifluoromethyl)amino trifluoroborate anion, which is isoelectronic with perfluorotrimethylamine, should be a stable species.

## RESULTS

It is known that  $F_3CNCF_2$  adds a fluoride ion in  $H_3CCN$  solution to form a  $(F_3C)_2N^-$  anion, which was characterised by its  $^{19}F$  NMR-spectrum [3]. If  $BF_3$  is condensed onto such a solution at low temperatures, the bis (trifluoromethyl) amino trifluoroborate anion is generated according to eqn. (1).



Though the yield is only moderate and considerable  $\text{BF}_4^-$  is formed as well,  $\text{K}[(\text{F}_3\text{C})_2\text{NBF}_3]$  is easily separated from  $\text{KBF}_4$  due to the solubility of the former in ether. The structure of the novel trifluoroborate follows from elemental analyses,  $^{19}\text{F}$  and  $^{11}\text{B}$  NMR spectra which are detailed in Table 1.

TABLE 1

NMR spectra of  $[(\text{F}_3\text{C})_2\text{NBF}_3]^-$ 

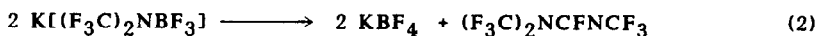
$^{19}\text{F}^*$	$\delta \text{F}_3\text{C}$ [ppm]	a)	-50.9	b)	-51.4
	$\delta \text{F}_3\text{B}$ [ppm]	a)	-144.9	b)	-143.8
	$^4\text{J}(\underline{\text{FCNBF}})$ [Hz]	a)	8.7	b)	8.8
	$^1\text{J}(\underline{\text{BF}})$ [Hz]	a)	14.2	b)	16.1
$^{11}\text{B}^{**}$	$\delta \text{B}$ [ppm]	a)	-0.66	b)	-0.62

\*against  $\text{FCCl}_3$ , internal  $\text{F}_3\text{CCOOCH}_3 = -76.2$  ppm

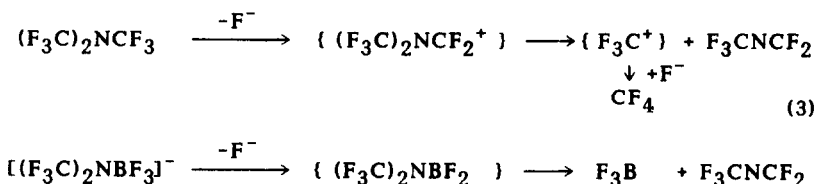
\*\*against  $\text{F}_3\text{B O}(\text{C}_2\text{H}_5)_2$  external

a)  $\text{H}_3\text{CCN}$  solution; b) ether solution

The  $^{19}\text{F}$  NMR spectrum proves the presence of two different F atoms in a 2:1 ratio. It should be noted that shifts and coupling constants vary considerably with the solvent. The salt is sensitive to moisture and must be handled under nitrogen. It is stable at room temperature but decomposes in a sealed tube in vacuo within two weeks at  $70^\circ\text{C}$  quantitatively into  $\text{KBF}_4$  and  $(\text{F}_3\text{C})_2\text{NCFNCF}_3$  according to eqn. (2).



Attempts to obtain  $(\text{F}_3\text{C})_2\text{NBF}_2$  by reaction with traces of  $\text{SbF}_5$  yielded only the decomposition products  $\text{F}_3\text{CNCF}_2$  and  $\text{BF}_3$ . In this respect the decomposition reaction resembles those observed for perfluoro-trimethylamine [2] as illustrated in eqn. (3).



## EXPERIMENTAL

1.75 g (30 mmol) KF were dried in an ampoule connected to a vacuum system and 20 ml dry  $H_3CCN$  and 4.0 g (30 mmol)  $F_3CNCF_2$  were added. The mixture was stirred for 30 min. in an ice bath, and 1.7 g (25 mmol)  $BF_3$  were added slowly to the suspension. All volatile materials were removed in vacuo at room temperature. The solid residue was suspended in dry ether and filtered under nitrogen.

$KI(F_3C)_2NBF_3$  crystallised as the ether evaporated; yield 1.7 g (26%)

$C_2BF_9NK$ . Required/found; %C, 9.27/9.1; %F, 66.04/66.0; %N, 5.41/5.3.  
IR ( $cm^{-1}$ ): 655 s/ 706 s/ 755 s/ 880,895,909 vs/ 950 vs/ 1025 vs/  
1050 vs/ 1220 vs/ 1258 vs/ 1305 vs/ 1365 vs.

## ACKNOWLEDGEMENT

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