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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).

$$F_3CNCF_2 + F^- \longrightarrow (F_3C)_2N^- \xrightarrow{BF_3} (F_3C)_2NBF_3^- \qquad (1)$$

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Though the yield is only moderate and considerable BF_4^- is formed as well, $K[(F_3C)_2NBF_3]$ is easily separated from KBF_4 due to the solubility of the former in ether. The structure of the novel trifluoroborate follows from elemental analyses, ^{19}F and ^{11}B NMR spectra which are detailed in Table 1.

TABLE 1

NMR spectra of $[(F_3C)_2NBF_3]^-$

^{19}F*	δ F_3C [ppm]	a)	-50.9	b)	-51.4
	δ F_3B [ppm]	a)	-144.9	b)	-143.8
	$^4J(\underline{F}CNB\underline{F})$ [Hz]	a)	8.7	b)	8.8
	$^1J(\underline{B}\underline{F})$ [Hz]	a)	14.2	b)	16.1
^{11}B**	δ B [ppm]	a)	-0.66	b)	-0.62

*against $FCCl_3$, internal $F_3CCOOCH_3$ = -76.2 ppm
**against $F_3B\,O(C_2H_5)_2$ external
a) H_3CCN solution; b) ether solution

The ^{19}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 °C quantitatively into KBF_4 and $(F_3C)_2NCFNCF_3$ according to eqn. (2).

$$2\ K[(F_3C)_2NBF_3] \longrightarrow 2\ KBF_4 + (F_3C)_2NCFNCF_3 \qquad (2)$$

Attempts to obtain $(F_3C)_2NBF_2$ by reaction with traces of SbF_5 yielded only the decomposition products F_3CNCF_2 and BF_3. In this respect the decomposition reaction resembles those observed for perfluorotrimethylamine [2] as illustrated in eqn. (3).

$$(F_3C)_2NCF_3 \xrightarrow{-F^-} \{(F_3C)_2NCF_2^+\} \longrightarrow \begin{matrix}\{F_3C^+\} + F_3CNCF_2 \\ \downarrow +F^- \\ CF_4\end{matrix} \qquad (3)$$

$$[(F_3C)_2NBF_3]^- \xrightarrow{-F^-} \{(F_3C)_2NBF_2\} \longrightarrow F_3B + F_3CNCF_2$$

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.
$K[(F_3C)_2NBF_3]$ 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.

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