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Short communication

1-Fluoro-2,4,6-trichloro-1,3,5-triazinium tetrafluoroborate: synthesis, characterization, and ability to effect electrophilic aromatic substitution

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Abstract

The synthesis of 1-fluoro-2,4,6-trichloro-1,3,5-triazinium tetrafluoroborate, $[(ClCN)_3F]^+[BF_4]^-$ (**1**), from $(ClCN)_3$, BF_3 and F_2 is reported. Compound **1** was shown to be a useful reagent for the quantitative fluorination of aromatic substrates such as benzene, chlorobenzene, nitrobenzene, and methoxybenzene.

Keywords: Electrophilic fluorination; N–F reagents; Fluorine; Fluoroaromatics; Trichlorotriazinium salts

1. Introduction

Although details of the synthesis and characterization of the first *N*-fluoro-*sym*-triazinium salts were published in the early 1990s [1–4] no information appears to have been reported concerning their use as electrophilic fluorinating agents [5].[2] To provide a quantitative scale for the oxidizing strength of these oxidative fluorinators we previously computed the FPDE values (fluorine-plus detachment energy values) quantum-chemically at the DFT B3LYP hybrid level of theory at a 6-31G(d,p) basis [6]. Recently [6] we also indicated the potential of 1-fluoro-2,4,6-trichloro-1,3,5-triazinium tetrafluoroborate, $[(ClCN)_3F]^+[BF_4]^-$ (**1**), as a reagent for effecting electrophilic ring-fluorination of carboaromatic compounds. The experimentation involved, now detailed here, provides (to the best of our knowledge) the first examples of C–F bond synthesis via the agency of an *N*-fluorotriazinium salt.

2. Results and discussion

1-Fluoro-2,4,6-trichloro-1,3,5-triazinium tetrafluoroborate (**1**) was prepared in excellent yield by adapting the small-scale batch method employed originally [1,2] to convert cyanuric chloride to the corresponding *N*-fluorotriazinium hexafluoroarsenate, $[(ClCN)_3F]^+[AsF_6]^-$ (**2**), boron trifluoride being used in place of arsenic pentafluoride to provide the anionic moiety (Scheme 1). The tetrafluoroborate **1** is a brilliant white, moisture-sensitive solid (hence best manipulated in a dry-box under Ar or N_2) which decomposes at 153–155 °C when heated progressively in a melting point apparatus. Like its hexafluoroarsenate analogue [1], **1** is insoluble in $CFCl_3$ but readily soluble in liquified SO_2; it is also quite soluble in acetonitrile and in nitromethane but reacts slowly with the former at room temperature, hence our interest in the nitroalkane as a solvent (see Section 2.1).

In view of the disorder problem encountered during an X-ray diffraction study of the hexafluoroarsenate **2** [1,2], no attempt has been made to undertake similar work with $[(ClCN)_3F]^+[BF_4]^-$ (**1**) (complete reliable experimental X-ray data are available for only one *N*-fluoro-*sym*-triazinium salt, namely 1-fluoro-2,4,6-trimethoxy-1,3,5-triazinium hexafluoroantimonate [7]). The identity of this new salt rests, therefore, on its mode of synthesis, a good elemental analysis (C, B, N), NMR data, and its ability to act as a fluorine-plus (F^+) source.

The ^{19}F NMR spectrum of **1**, measured at 25 °C in SO_2, comprises an absorption at $\delta(CFCl_3)$ –141.7 (assignable to BF_4^-) and one of one-quarter relative intensity shifted to lower field at $\delta(CFCl_3)$ +18.3, which is reasonable for the cationic ^+NF moiety in **1**. The corresponding δ values for a solution of **1** in CD_3CN at −20 °C are −143.6 and

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[2] For recent in-depth reviews of electrophilic fluorinating agents of the N–F class, see [5].

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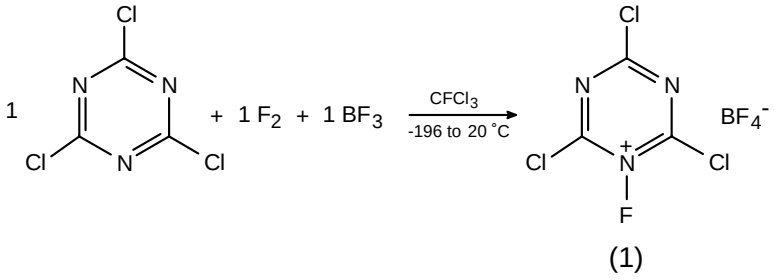


(1)

Scheme 1.

+17.3 ppm (Table 1). The previously reported value of −45.2 ppm for the hexafluoroarsenate $[(ClCN)_3F]^+[AsF_6]^-$ (**2**) [1] is presumably incorrect due to decomposition of the sample.

2.1. Electrophilic fluorination of aromatics with 1-fluoro-2,4,6-trichloro-1,3,5-triazinium tetrafluoroborate (*1*)

Small-scale individual (i.e. no competitive runs were performed) reactions between **1** and benzene, methoxybenzene, chlorobenzene, and nitrobenzene were carried out, the objective being simply to estimate the N–F reagent's F^+ transfer capability. Reaction mixtures were monitored using ^{19}F NMR and by checking their abilities to liberate iodine from aqueous potassium iodide.

Initially, NMR-scale experiments were conducted in acetonitrile-d_3 with equimolar reactant ratios. Relative reaction rates ($C_6H_5OCH_3 \gg C_6H_6 \gg C_6H_5NO_2$) and orientation of attack ($C_6H_5OCH_3 \rightarrow$ 2:1 mixture of 4 and $2FC_6H_4OCH_3$; $C_6H_5NO_2 \rightarrow 3FC_6H_4NO_2$) consistent with electrophilic aromatic fluorination were established, but the ^{19}F NMR spectra of all the reaction mixtures contained a substantial number of unassignable absorptions in addition to those associated with "F^+" attack on the aromatics under study. This problem was resolved by dissolving the *N*-fluorotriazinium salt **1** in CD_3CN at room temperature and measuring the ^{19}F NMR spectrum (probe temperature 27 °C) of the solution immediately: the spectrum contained two major peaks assignable to **1** [$\delta(CFCl_3)$ 15.3 ppm (^+NF), −146.7 ppm (BF_4^-)] and minor absorptions in the range −1.0 to −110 ppm; the latter, which corresponded with absorptions found in the spectra of reaction mixtures involved in the fluorination of benzene and its derivatives with **1**, increased noticeably in overall intensity during the next 2 h at the expense of the ^+NF absorption at δ15.3, and the initially colourless solution turned yellow.

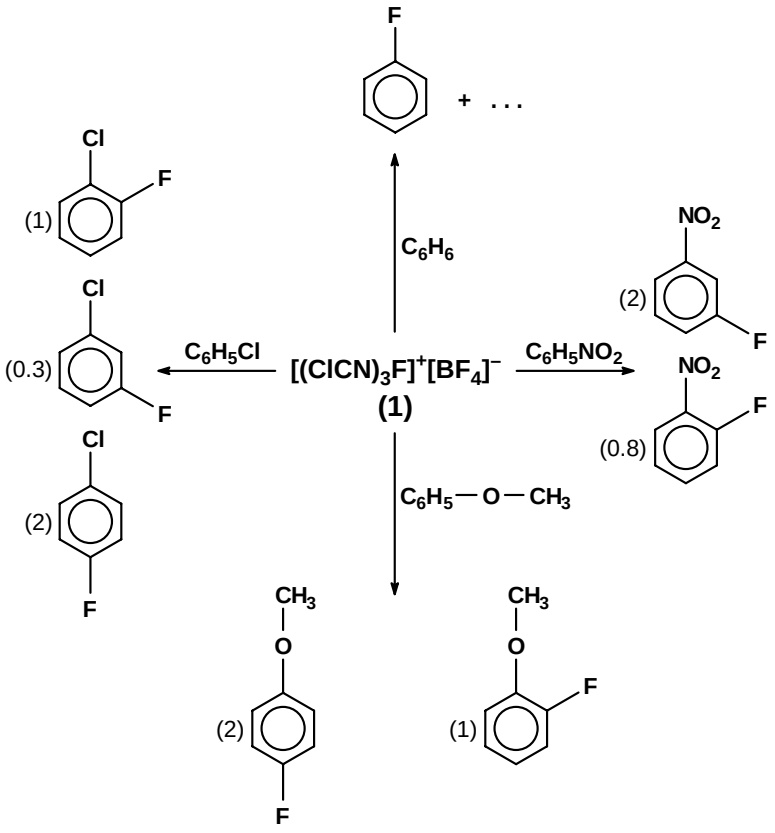
Table 1
NMR data for $[(ClCN)_3F]^+[BF_4]^-$ (**1**)[a]

	^{11}B	^{13}C	^{14}N	^{19}F
Reference	$BF_3{\cdot}Oet_2$	TMS	$MeNO_2$	$CFCl_3$
δ (ppm)	+1.0	+173.4 (1)	−98[b]	−143.6 (4)
δ (ppm)		+158.3 (2)		+17.3 (1)

[a] CD_3CN solution, −20 °C; relative intensities in parentheses.
[b] One resonance due to fast N–F exchange.

Nitromethane (bp 101 °C), which has not to our knowledge featured previously in work with N–F reagents, proved to be a satisfactory replacement for acetonitrile, and reactions between **1** and our chosen aromatic substrates were effected in this solvent, even at elevated temperatures, without the complication experienced when using CD_3CN. Hence diversion of **1** down unwanted reaction channels was eliminated (no attempt has yet been made to determine the chemistry involved in attack of **1** on acetonitrile (possibly the formation of $[CH_3C{=}NF]^+$ occurs initially); the onset of reaction occurs at temperatures above ca. 0 °C (determined using temperature-programmed ^{19}F NMR)).

The results achieved using dilute solutions of **1** and an aromatic subtrate (6.8 μmol l^{-1} of **1** and of C_6H_5X (X = H, OCH_3, Cl, NO_2)) in nitromethane reinforced our conclusion based on the experiments conducted using acetonitrile as solvent that it is a more powerful electrophilic fluoromating agent than most of the "F^+" equivalents of the N–F class reported to date. In this respect, while **1** falls well short of the inorganic N–F reagents $NF_4^+X^-$ ($X^- = BF_4^-$, AsF_6^-, SbF_6^-) and $FN_2^+AsF_6^-$, which electrophilically fluorinate nitrobenzene in anhydrous HF at −78 °C [8,9] and methane in HF or pyridine-HF at room temperature [10], it appears to be at least as reactive as *N*-fluorobis(trifluoromethylsulfonyl)imide (**3**) and *N*-fluoropentachloropyridinium triflate (**4**), hitherto judged to be the most powerful F^+ delivery agents of the organic N–F class [11]. These two reagents (**3**, **4**) fluorinate benzene and its activated derivative $C_6H_5OCH_3$ under mild conditions, as does **1**, but neither has been demonstrated to attack deactivated benzenes under non-forcing conditions (**3** [12]: $C_6H_5Cl/CDCl_3$, 22 °C, 24 h; $C_6H_5COCH_3/CDCl_3$, 22 °C, 12 h; neat $C_6H_5NO_2$, 22 °C, 12 h and **4** [13]: $C_6H_5CO_2CH_3/CH_2Cl_2$, 2 h, reflux temperature). By contrast, $[(ClCN)_3F]^+[BF_4^-]$ (**1**) attacks chlorobenzene and (more slowly) nitrobenzene at ambient temperature in nitromethane, consumption of the reagent being complete (negative KI test) within 6 h at 70 °C in the case of the chloro-aromatic (→ a ca. 1:0.3:2 mixture of 2, 3, and $4FC_6H_4Cl$) and 90% (by ^{19}F NMR) under the same conditions with nitrobenzene (→ a ca. 2:0.8 mixture of 3



Scheme 2. Electrophilic fluorination reactions of $[(ClCN)_3F]^+[BF_4]^-$ (**1**) in dry nitromethane. After ca. 6 h the consumption of reagent **1** was complete, indicating a quantitative reaction. The relative molar ratios of the products formed are given in parentheses.

and $2FC_6H_4NO_2$) Since a swift exothermic reaction occurs between methoxybenzene and **1** at room temperature, solutions containing these reactants in CD_3CN or CH_3NO_2 were prepared at −20 °C (this precaution does not appear to have been necessary in the cases of fluorination with **3** [12] or **4** [13]). When allowed to warm up to room temperature, the colourless solutions turned yellow at about 0 °C then became brownish-violet during the next 2 h, by which time **1** had been completely consumed (negative KI test) and 4 and $2FC_6H_4OCH_3$ were present in the ratio of 2:1 (Scheme 2).

3. Experimental

3.1. General experimental procedures

Raman and NMR data for $[(s\text{-}ClCN)_3F]^+[BF_4]$ (**1**) were obtained using a Perkin-Elmer 2000 NIR FT instrument and a Jeol Eclipse 400 spectrometer, respectively; ^{19}NMR analysis of reaction mixtures produced via the interaction of **1** with benzene and its derivatives was performed with a Bruker AC-200 machine (188.8 MHz). Elemental analyses were performed with a Vario EL analyser (for C and N) and by ICP (for B). The mp of **1** was determined using a Büchi B-540 apparatus.

3.2. Caution

The safe handling of elemental fluorine requires a high level of expertise and special apparatus [14]. Only experimentalists with appropriate know-how and equipment, plus facilities for dealing with F_2 and HF burns [14], should attempt to prepare **1**.

Care must be taken when using nitromethane to avoid accidents arising from inhalation of its vapour, fire and explosion [15].

3.3. Preparation of 1-fluoro-2,4,6-trichloro-1,3,5-triazinium tetrafluoroborate (*1*)

Several reactions were carried out on a 4–5 mmol scale. In a typical experiment, boron trifluoride (0.271 g, 4.0 mmol) and difluorine (0.151 g, 4.0 mmol) were condensed separately, in vacuo, onto a frozen solution of cyanuric chloride (0.738 g, 4.0 mmol) in trichlorofluoromethane (20 cm^3) contained in a pre-passivated (with F_2) T316 stainless steel autoclave (120 cm^3) cooled to −196 °C (liq. N_2). The reaction vessel was sealed, warmed to room temperature during 3 h, then stored at that point for 5 days (an excessive time). Volatile material was removed from the reaction vessel under vacuum, leaving a white residual solid that was shown to be virtually pure 1-fluoro-2,4,6-trichloro-1,3,5-triazinium

tetrafluoroborate (nc) (**1**; 1.10 g, 3.8 mmol, 95% yield), mp (decomp.) 153–155 °C. Anal. Calcd. for $C_3BCl_3F_5N$: C, 12.42; B, 3.72, N, 14.47: Found. C, 12.40; B, 3.58; N, 14.61%. ^{19}F NMR (376.0 MHz, CD_3CN at −20 °C; $CFCl_3$ ref.): δ 17.3 (s, 1F, NF), −143.6 (s, 4F, BF_4). ^{13}C NMR (67.9 MHz, CD_3CN at −20 °C; TMS): δ 173.4 (s, C-1), 158.3 (s, C-3.5).

*3.4. Fluorination of aromatic substrates with 1-fluoro-2,4,6-trichloro-1,3,5-triazinium tetrafluoroborate (**1**)*

3.4.1. In CD_3CN

Cold (0 °C) solutions of the aromatic substrates under study in CD_3CN were added to weighed amounts of **1** contained in a Pyrex vials under argon in a dry-box to provide 1:1 molar reaction mixtures in the cases of benzene, chlorobenzene, and nitrobenzene, and both 1:1 and 1:2 (**1**: $C_6H_5OCH_3$) in the case of methoxybenzene. Reaction mixtures were then allowed to warm to room temperature before samples were transferred by syringe to standard stoppered NMR tubes and their ^{19}F spectra measured.

3.4.2. In CH_3NO_2

Solutions containing equimolar quantities of **1** (0.1 g, 0.34 mmol) and an aromatic substrate in nitromethane (20 cm^3) were prepared at room temperature (for benzene, chlorobenzene and nitrobenzene) or −20 °C (for methoxybenzene) in a dry-box under argon. Samples of the solutions were transferred to standard stoppered NMR tubes for ^{19}F NMR analysis; samples were also tested for unreacted **1** using KI. Some reaction mixtures were heated (water bath) to 70 °C (in sealed NMR tubes) to drive the fluorination to completion.

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