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Reactions of silver(I) trifluoromethanethiolate with halotrimethylsilanes: in situ generation of trimethylsilyl trifluoromethyl sulfide

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Abstract

Silver(I) trifluoromethanethiolate reacts with halotrimethylsilanes to produce silver halide, fluorotrimethylsilane and an oligomeric species of formula $(CS)_3(SCF_3)_2$. Variable temperature ^{19}F NMR spectroscopy reveals that the reaction proceeds via trimethylsilyl trifluoromethyl sulfide (Me_3SiSCF_3), which rapidly decomposes on warming. This acts as a source of nucleophilic trifluoromethanethiolate, reacting with highly activated haloaromatics to produce trifluoromethyl aryl sulfides.

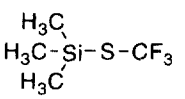
Keywords: Silver(I); Halotrimethylsilanes; Silver halide; Haloaromatics; Sulfides

1. Introduction

The introduction of trifluoromethanethio groups into aromatic and aliphatic substrates is of interest to the agricultural and pharmaceutical industries as it has good chemical stability as well as imparting high lipophilicity and strong electron withdrawing effects [1]. The current industrial method for the preparation of trifluoromethyl aryl sulfides involves the use of Swartz type chemistry, which requires the treatment of trichloromethylthioaromatics with the aggressive fluorinating agent antimony trifluoride [2]. Other routes to trifluoromethyl aryl sulfides include the decarboxylation of potassium trifluoroacetate in the presence of an aryldisulfide [3] and the reaction of iodoaromatics with toxic mercury(II) trifluoromethanethiolate [4,5] or with copper(I) trifluoromethanethiolate [6]. We have recently reported a cheap and convenient method for the preparation of such compounds from fluoro and chloroaromatics by use of potassium fluoride and thiophosgene to generate a source of nucleophilic trifluoromethanethiolate, although this requires the presence of electron withdrawing groups on the aromatic ring of the substrate [7].

Ruppert's reagent, trifluoromethyltrimethylsilane, has found applications as a trifluoromethide precursor in a wide range of reactions, including aromatic nucleophilic substitution and the preparation of α-trifluoromethylated alcohols from ketones [8]. The reaction is promoted by addition of a source of fluoride (typically KF or tetra-*n*-butylammonium fluoride), and is, at least in part, driven by formation of a strong silicon–fluorine bond. Other perfluoroalkyltrialkylsilanes have been used in a similar manner [8], but until now no $-SCF_3$ version has been reported.

A trifluoromethanethiolate analogue of Ruppert's reagent should have synthetic applications as a nucleophilic source of trifluoromethanethiolate anion, and as such could be used as a new reagent for the production of trifluoromethyl aryl sulfides. There are relatively few reports of silicon–sulfur bonds in organic compounds in the literature, although silyl trifluoromethyl sulfide (H_3SiSCF_3) has been reported [9]. Silver(I) trifluoromethanethiolate ($AgSCF_3$) is expected to react with halotrimethylsilanes to produce the silver halide and trimethylsilyl trifluoromethyl sulfide (**I**). The silver thiolate is conveniently prepared by reaction of silver(I) fluoride with carbon disulfide (typically in acetonitrile) with the formation of silver(I) sulfide as a by-product [10]. We have performed this reaction with both chloro- and iodotrimethylsilanes in acetonitrile and pyridine solvents, and used the resultant mixture as a source of nucleophilic trifluoromethanethiolate.



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2. Results and discussion

2.1. Reaction of silver(I) trifluoromethanethiolate with halotrimethylsilanes

At room temperature in acetonitrile, $AgSCF_3$ reacts rapidly with chlorotrimethylsilane to produce a white precipitate of silver chloride. Analysis of the filtered solution by ^{19}F NMR showed a range of peaks around −40 ppm. We have observed similar peaks for the reaction of KF with thiophosgene to give condensation products of thiocarbonyl fluoride, believed to be of general formula $(SCF_2)_n$ [7]. Conducting the same reaction at a lower temperature (−40°C) allowed us to observe some of the intermediate species in this reaction. In addition to those for the polymeric species, peaks were observed for thiocarbonyl fluoride (SCF_2, +41.2 ppm [11]), fluorotrimethylsilane (Me_3SiF, −156.0 ppm [12]) and trifluoromethanethiol ($HSCF_3$, −31.4 ppm [13]; the identity of this compound was confirmed by bubbling dry HCl gas through a solution of $AgSCF_3$ in acetonitrile, which produced silver chloride and a foul smelling solution which gave a single resonance in the ^{19}F NMR spectrum at −31.4 ppm). On warming the reaction to room temperature and standing overnight, the ^{19}F NMR spectrum showed a disappearance of the peak due to the $HSCF_3$ accompanied by the formation of SCF_2 and an increase in the relative intensity of the peaks from the polymeric species. A reduction in the intensity of the fluorotrimethylsilane peak was also observed, although this is probably due to the volatility of that compound (n.b. Me_3SiF and $HSCF_3$ boil at +16 and −30°C, respectively). The appearance and subsequent oligomerisation of SCF_2 suggests that the $HSCF_3$ formed in this reaction decomposes via elimination of HF, rather than being lost through evaporation (Fig. 1). The formation of $HSCF_3$ instead of the desired Me_3SiSCF_3 presumably occurs because of some residual acidity in the system, which could be caused by hydrolysis of the water sensitive chlorosilane to produce HCl. Despite attempts to remove this acidity by distilling the silane from calcium hydride directly into the reaction, $HSCF_3$ was still produced. Emeléus and MacDuffie [14] have also reacted $AgSCF_3$ with Me_3SiCl, but at room temperature and in the absence of solvent, and report only AgCl and Me_3SiF as reaction products.

A similar reaction was performed using iodotrimethylsilane (Me_3SiI), which should be much more reactive than the chlorosilane because of the weaker silicon–iodine bond and the higher lattice energy of the silver iodide product. The reaction was vigorous even at −40°C, giving off white fumes as well as precipitating yellow silver iodide. NMR analysis showed that once again, SCF_2, $HSCF_3$, and Me_3SiF were the major reaction products. At this point, it was decided that the reaction might benefit from being run in a basic solvent to remove all traces of acidity. This also removes the possibility of reaction with the acetonitrile hydrogens, which are known to be labile under strongly basic conditions [15].

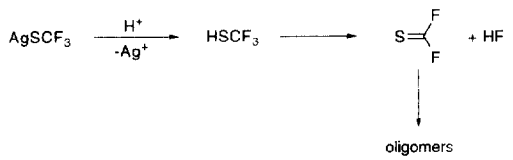


Fig. 1. Formation and decomposition of $HSCF_3$.

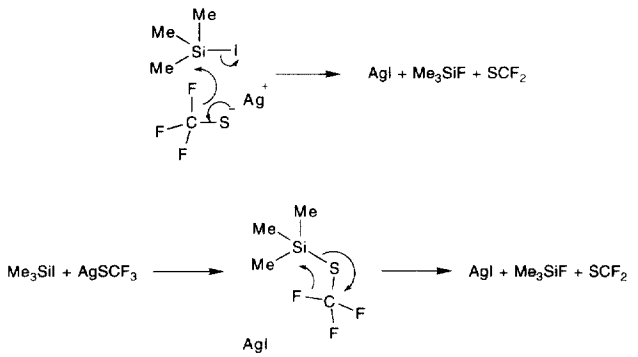


Fig. 2. Possible pathways for the reaction of $AgSCF_3$ with Me_3SiI.

We found that we could also successfully prepare $AgSCF_3$ in pyridine. The reaction with Me_3SiI was repeated in this solvent at −40°C and allowed to warm to room temperature. In this case, although peaks for fluorotrimethylsilane and the thiocarbonyl fluoride oligomers were still observed, neither $HSCF_3$ nor SCF_2 were detectable by ^{19}F NMR. The products from this reaction suggest that either the expected Me_3SiSCF_3 forms, then decomposes rapidly even at low temperatures, or that the Me_3SiI silicon centre reacts directly with one of the silver thiolate fluorine atoms to produce fluorotrimethylsilane directly (Fig. 2). In each of these two cases, the formation and decomposition of the transition state or intermediate could be either stepwise or concerted.

To distinguish between the two possible pathways, the reaction of Me_3SiI with $AgSCF_3$ in pyridine was studied by variable temperature ^{19}F NMR. The silane was added to a solution of the silver salt frozen in an NMR tube, and this was allowed to warm in the spectrometer, with spectra being recorded at 10°C increments (Fig. 3). The study shows a broad range of products even at −30°C: peaks are seen for unreacted $AgSCF_3$ (−17.9 ppm) and also, the decomposition products SCF_2 (+17.7 ppm; substantially shifted from its value of +41.2 ppm in acetonitrile) and Me_3SiF (−156.0 ppm, not shown). The peak at −45.0 ppm is assigned as Me_3SiSCF_3, expected to be at the most deshielded end of the $-SCF_3$ range [7,16,17]. At this temperature, numerous peaks due to oligomerisation products of SCF_2 can already be seen between −39 and −44 ppm. On warming, the intensity of the Me_3SiSCF_3 peak rapidly decreases, completely vanishing by 0°C. The disappearance of this peak is accompanied by production of more fluorotrimethylsilane and SCF_2, which itself rapidly reacts to form more oligomers. Warming further to room temperature causes the conversion of the many peaks due to the oligomers into a broader peak at −40.7 ppm, which we believe to be due to a single polymeric species, and a

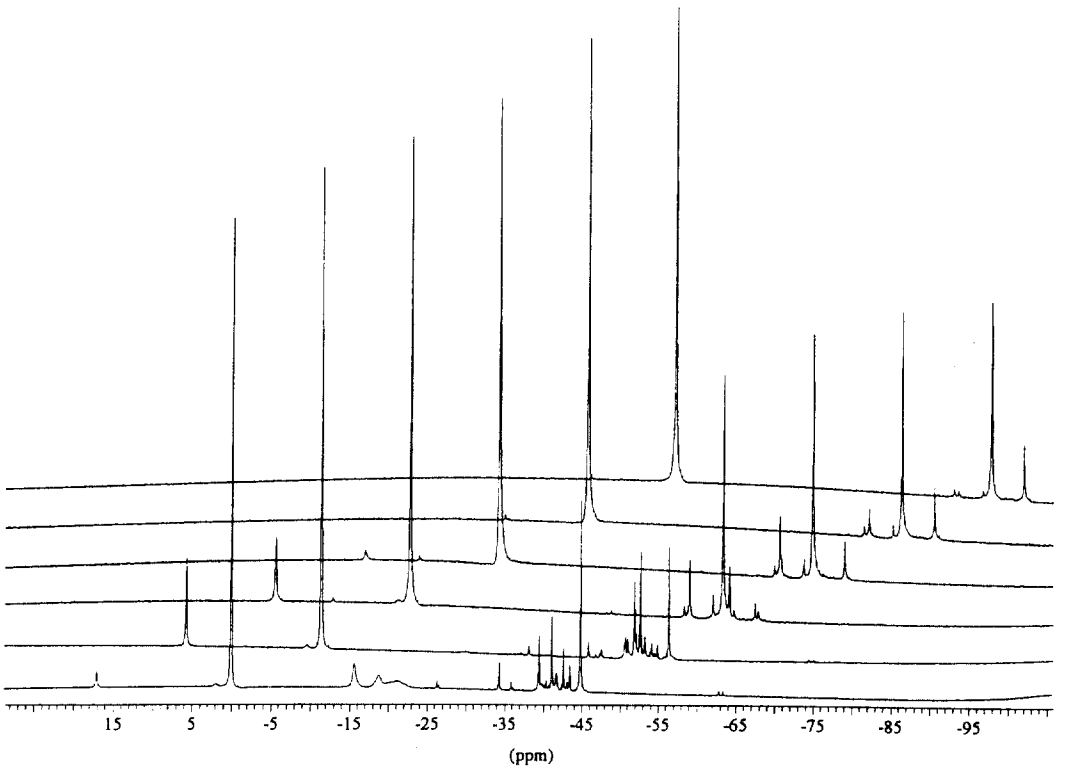
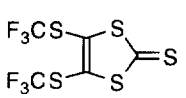


Fig. 3. Variable temperature ^{19}F NMR study of the reaction between $AgSCF_3$ and Me_3SiI in pyridine.

much smaller peak at −44.9 ppm (possibly F_3CSSCF_3). GCMS analysis of the reaction showed a single product with a MS base peak of 334 mass units, and a fragmentation pattern consistent with the formula $(CS)_3(SCF_3)_2$. After completion, the ^{19}F NMR was re-run at −30°C. This did not cause reappearance of the multiple peaks, demonstrating that these were due to separate species and not due to magnetic inequivalence of chemically equivalent fluorine environments caused by restricted rotation at low temperatures. Filtration of the reaction to remove silver salts followed by washing with dilute aqueous HCl and removal of the solvent under vacuum yielded a viscous red oil with mass spectrum identical to that seen in the GCMS described above, and a single peak in the ^{19}F NMR spectrum at −40.7 ppm.

Lentz et al. [18] have very recently reported the oligomerisation of carbon disulfide in the presence of tetramethylammonium fluoride to form a species with a five-membered cyclic skeleton. It is quite possible that something similar is occurring in our system: a possible structure for the oligomer is species **II**.



II

^{13}C NMR spectroscopy of the red oil showed that the compound contains three distinct carbon environments, and the chemical shifts assigned for the carbon atoms in the five-membered ring are in excellent agreement with those reported for the analogous unfluorinated compound, $(CS)_3(SCH_3)_2$ [19]. Many compounds with a similar C_3S_3 skeleton are known, but are usually formed by reductive polymerisation of carbon disulfide [20]. It is not clear how this species is formed in this system, but participation of small residual amounts of CS_2 seems likely. Attempts were made to remove excess CS_2 from the $AgSCF_3$ solution in pyridine by distillation, but even on heating the solution to 80°C evolved no CS_2. This suggests that the CS_2–pyridine mixture forms a high boiling azeotrope. Also, we found that formation of $(CS)_3(SCF_3)_2$ from $AgSCF_3$ and Me_3SiI in acetonitrile (from which the CS_2 was successfully distilled) was actually promoted by the addition of a few drops of CS_2.

2.2. Reaction of trimethylsilyl trifluoromethyl sulfide with haloaromatics

Pentafluoropyridine is known to be a facile substrate for aromatic nucleophilic substitution reactions, reacting with potassium trifluoromethanethiolate ($KSCF_3$) even at −20°C [7,16,17]. This was used to probe for the availability of trifluoromethanethiolate as a nucleophile in the Me_3SiSCF_3 system. A control reaction between $AgSCF_3$ and pentafluoropyridine in the absence of Me_3SiI showed no incorporation of $-SCF_3$ onto the pyridine ring. In contrast, the reaction with Me_3SiSCF_3 showed a mixture of mono-, di-, tri- and a trace of tetra- substituted products, as well as the polymeric product seen in the absence of substrate. While this is less selective than treatment with $KSCF_3$, where almost exclusive monosubstitution of pentafluoropyridine occurs [7,16,17], the formation of multiply substituted products demonstrates the high

nucleophilicity of the trifluoromethanethiolate supplied by Me_3SiSCF_3.

Other highly activated haloaromatic compounds reacted in a similar manner: 4-chloro-2,6-dinitrobenzotrifluoride and 4-chloro-7-nitrobenzofurazan both reacted with the Me_3SiSCF_3 at low temperature to give quantitative conversion to the corresponding trifluoromethyl aryl sulfides. However, less activated substrates such as 4-fluorobenzonitrile and 2-chloro-5-nitrobenzonitrile showed no conversion at all under these conditions. At these low temperatures there appears to be insufficient energy to overcome the activation barrier to nucleophilic aromatic substitution for all but the most active substrates, and as the temperature increases the reagent decomposes so that no substitution reaction occurs.

3. Experimental

3.1. Instrumentation

^{19}F NMR spectra were recorded at 20°C in CH_3CN with a few drops of C_6D_6 added as a signal lock and referenced to $CFCl_3$ on a Jeol EX270 spectrometer operating at 254 MHz unless otherwise stated. The ^{13}C [^1H] NMR of $(CS)_3(SCF_3)_2$ was run on a Bruker AMD 400 operating at 400 MHz for ^1H and 150 MHz for ^{13}C. Mass spectra were obtained on a VG Analytical Autospec instrument or on a Finnegan MAT Magnum GC-MS instrument.

3.2. Chemicals

Anhydrous solvents stored under nitrogen were obtained from Aldrich Chemical Co. and used without further purification. Chlorotrimethylsilane was distilled from calcium hydride directly into the reaction flask before use. Iodotrimethylsilane was purchased in sealed ampules which were opened and transferred to the reaction flask in an inert atmosphere glove box.

3.3. Preparation of silver(I) trifluoromethanethiolate solution in acetonitrile

Silver(I) fluoride (2.29 g, 18 mmol), carbon disulfide (2.3 ml, 2.9 g, 38 mmol) and acetonitrile (anhydrous, 25 ml) were placed together in a round bottomed flask fitted with a water condenser and argon purge. The reaction was then heated to reflux (measured to be 46°C, the boiling point of carbon disulfide) overnight. Excess carbon disulfide was then distilled from the reaction by fitting a distillation head and heating until the head temperature reached 80°C. The remaining solution was then filtered to remove the silver sulfide precipitate.

^{19}F NMR $\delta = -23.3$ ppm (s)

3.4. Preparation of silver(I) trifluoromethanethiolate solution in pyridine

Silver(I) fluoride (2.29 g, 18 mmol), carbon disulfide (2.3 ml, 2.9 g, 38 mmol) and pyridine (anhydrous, 25 ml) were placed together in a round bottomed flask fitted with a water condenser and argon purge. The reaction was then heated in an oil bath at 80°C (internal temperature was measured as 75°C) overnight. An attempt was made to distill excess carbon disulfide from the reaction by fitting a distillation head and heating at 80°C for 30 min. The remaining solution was then filtered to remove the black silver sulfide precipitate. The reagent was made up to a known concentration in a volumetric flask for the reactions involving haloaromatic substrates.

^{19}F NMR $\delta = -17.6$ ppm (s)

3.5. Variable temperature ^{19}F NMR study of the reaction between $AgSCF_3$ and Me_3Sil

C_6D_6 and $CFCl_3$ were added to 0.60 ml of a 0.30 molar solution of $AgSCF_3$ (0.18 mmol) in pyridine in an NMR tube, which was then cooled in a CO_2-acetone bath. Iodotrimethylsilane (0.18 mmol, 0.036 g, 26 μl) was added to the frozen mixture, the tube sealed and transferred to the NMR spectrometer pre-cooled to −30 °C, and allowed to equilibrate. Spectra were then recorded (64 scans each, recycle time of 5 s) at 10 °C intervals up to 20 °C. The reaction mixture was filtered to remove silver salts and then extracted with diethyl ether and 1M aqueous HCl. The phases were separated and the organic solvent removed on a rotary evaporator to give a viscous red oil with mass spectrum identical to that seen in the GCMS described above.

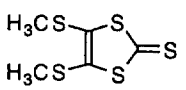
GCMS after reaction: m/z = 334(100), 145(65), 69(48), 189(46), 88(34), 76(28), 265(11), 257(8) consistent with formular $(CS)_3(SCF_3)_2$.

Isolated red oil: 26% yield (based on fluorine content).

^{19}F NMR: $\delta = -40.7$ ppm (s).

^{13}C [1H] NMR: $\delta = 210.1$ (s, C=S); 135.3 (s, C=C); 128.3 (q, $|^1J_{FC}| = 313$ Hz, -SCF_3) ppm. (^{13}C spectrum run on 400 MHz instrument in CD_3CN, referenced to CD_3CN).

For comparison, values for



from ref. 19: $\delta = 211$ (C=S); 136 (C=C) ppm.

3.6. Reaction of Me_3SiSCF_3 with other haloaromatic substrates

A solution of $AgSCF_3$ in pyridine (1.00 ml of a 0.12 M solution) was added to 0.12 mmol of the haloaromatic substrate in a sample tube, which was agitated until the aromatic dissolved. A total of 0.60 ml of this solution was then trans-

Table 1
GCMS data for the reaction between $AgSCF_3$ and Me_3SiI in the presence of pentafluoropyridine

Product	Relative GC area/%	ms data
$C_5NF_4(SCF_3)$	35	251(53), 69(100), 138(27), 87(18), 93(12), 163(12), 232(12), 182(9)
$C_5NF_3(SCF_3)_2$	14	333(92), 195(100), 264(35), 226(33), 87(30), 314(20), 151(19), 69(15)
$C_5NF_2(SCF_3)_3$	17	415(100), 277(78), 396(34), 208(26), 346(20), 308(16), 327(12) 258(8)
$(CS)_3(SCF_3)_2$	34	334(100), 145(66), 69(53), 189(46), 88(37), 76(29), 265(13), 258(9)
$C_5NF(SCF_3)_4$	trace	497(100), 69(75), 88(73), 308(50), 352(46), 251(43), 283(30), 145(28)

Table 2
^{19}F NMR data for the reaction between $AgSCF_3$ and Me_3SiI in the presence of pentafluoropyridine

δ/ppm	Assignment
−38.3, 38.5, −38.5, −39.9, −40.5, −41.3, −42.0	Py–SCF_3
−40.8	$(CS)_3(SCF_3)_2$
−84.2, −87.5, −88.1	Py-2-F
−133.0	Py-3-F
−156.1	Me_3Si–F
−160.6	Py-4-F

ferred to an NMR tube which was cooled by immersion in a CO_2–acetone bath. Iodotrimethylsilane (0.07 mmol, 0.014 g, 10 μl) was added to the frozen mixture, the tube sealed and allowed to warm to room temperature. GCMS analysis and ^{19}F NMR spectra were obtained (Tables 1 and 2, respectively).

3.7. Reaction with 4-chloro-2,6-dinitrobenzotrifluoride

GCMS after reaction: $m/z = 336(4), 267(100), 251(86), 69(22), 175(18), 106(15), 317(12), 81(11)$. ^{19}F NMR: $\delta = -39.2$ (s, $-SCF_3$); -62.4 (s, $-CF_3$) ppm.

3.8. Reaction with 4-chloro-7-nitrobenzofurazan

GCMS after reaction: $m/z = 265(92), 69(100), 196(68), 120(28), 180(27), 80(23), 207(19), 136(16)$. ^{19}F NMR: $\delta = -39.6$ ppm (s, $-SCF_3$).

Both sets of data indicate the replacement of –Cl with $-SCF_3$.

4. Conclusions

Trimethylsilyl trifluoromethyl sulfide may be prepared by the reaction of $AgSCF_3$ with Me_3SiI in pyridine. This compound is very reactive and unstable, decomposing rapidly on warming to produce Me_3SiF and a SCF_2 condensation product of empirical formula $(CS)_3(SCF_3)_2$. In the presence of highly activated substrates, Me_3SiSCF_3 will act as a source of nucleophilic trifluoromethanethiolate. However, its instability at ambient temperatures means that this reagent is unlikely to find the widespread application of Ruppert's reagent.

Acknowledgements

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