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Preparation of Trifluoromethyl Aryl Sulfides Using Silver(I) Trifluoromethanethiolate and an Inorganic Iodide

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Reaction of silver(I) trifluoromethanethiolate ($AgSCF_3$) with KI or tetra-*n*-butylammonium iodide in acetonitrile leads to the formation of a nucleophilic source of trifluoromethanethiolate. This source is capable of converting activated fluoro-, chloro-, bromo-, and iodoaromatics into the corresponding trifluoromethyl aryl sulfides under mild conditions. After successful reaction with tetra-*n*-butylammonium iodide, crystals of $Bu_4N[Ag_3I_4]$ precipitate from the reaction mixture. With less activated aromatic compounds, decomposition of the trifluoromethanethiolate anion occurs preferentially, giving bis(trifluoromethyl)disulfide, tetrakis(trifluoromethylthio)ethene, and 3,4,5,6-tetrakis(trifluoromethylthio)-1,2-dithiine. The use of copper(I) trifluoromethanethiolate and mercury(II) trifluoromethanethiolate for such reactions has also been investigated.

Introduction

Trifluoromethyl aryl sulfides are potentially important target molecules for the pharmaceutical and agrochemical industries, due to the electronic effects and high lipophilicity imparted by the $-SCF_3$ group.[1] Many of the methods for introducing these groups into aromatic compounds involve harsh reaction conditions, which can lead to low product yields and mixtures of isomers and restricts the use of molecules containing sensitive functional groups.[2,3,4] It is clear that there is still a need for new, efficient routes for the introduction of the SCF_3 group.

Jellinek and Labrowski describe the reaction of tetramethylammonium or potassium iodide with bis(trifluoromethylthio)mercury to give a 1:1 complex anion of the form $[Hg(SCF_3)_2I]^-$.[5] They also describe how the use of a ratio of KI to $Hg(SCF_3)_2$ of greater than 1:1 leads to irreversible reactions, including the elimination of trifluoromethyl sulfide,[6] Scheme 1. The $[SCF_3]^-$ was found to have a lifetime that was dependent on the quality of the solvent. The half-life in acetone was estimated at 30 min, with decomposition occurring to fluoride and thiocarbonyl fluoride. We report that the addition of KI or tetra-*n*-butylammonium iodide (Bu_4NI) to a solution of silver(I) trifluoromethanethiolate results in the formation of a source of nucleophilic trifluoromethanethiolate.

Scheme 1

$$[Hg(SCF_3)_2I]^- + I^- \longrightarrow [Hg(SCF_3)I_2]^- + SCF_3^-$$

These systems can be used to generate trifluoromethyl aryl sulfides from activated haloaromatics.

Results and Discussion

$AgSCF_3$ has been used as a source of $[SCF_3]^-$ for reactions with alkyl halides.[7] However, no successful reactions have been reported for aromatic halide substrates. It was thus unsurprising to find that mixing acetonitrile solutions of 4-chloro-3,5-dinitrobenzotrifluoride (**1**), 2,4-dinitrochlorobenzene (**3b**), or 1,3-dichloro-4,6-dinitrobenzene (**5**) with $AgSCF_3$ resulted in only starting materials being recovered after 24 h at both 25 and 60 °C. The chlorine atoms of these substrates are known to be highly labile under S_NAr conditions,[4a,8] indicating that $AgSCF_3$ is a poor nucleophilic source of $[SCF_3]^-$. Upon addition of KI or Bu_4NI to the reaction mixtures, conversion to the corresponding trifluoromethyl aryl sulfides (Figure 1) occurred, Table 1. This demonstrates that the system can indeed be used as an active source of $[SCF_3{}^-]$. Unusually, the system can be used to convert fluoro-, chloro-, bromo-, and iodoaromatics to trifluoromethyl aryl sulfides. Other nucleophilic sources of $[SCF_3]^-$ are limited in that $CuSCF_3$ will only react with iodo- and bromoaromatics[3a] while $KSCF_3$ has only been reported to react with fluoro- and chloroaromatics.[4] The yields achieved here compare well to those previously reported using other methods.

2-Chloro-5-nitrobenzonitrile (**8**) and 4-chloro-3-nitrobenzonitrile (**10**) can also be converted to the corresponding trifluoromethyl aryl sulfides in lower yields, although the reaction temperature had to be increased to 60 °C in order to induce reaction, Table 1. The formation of

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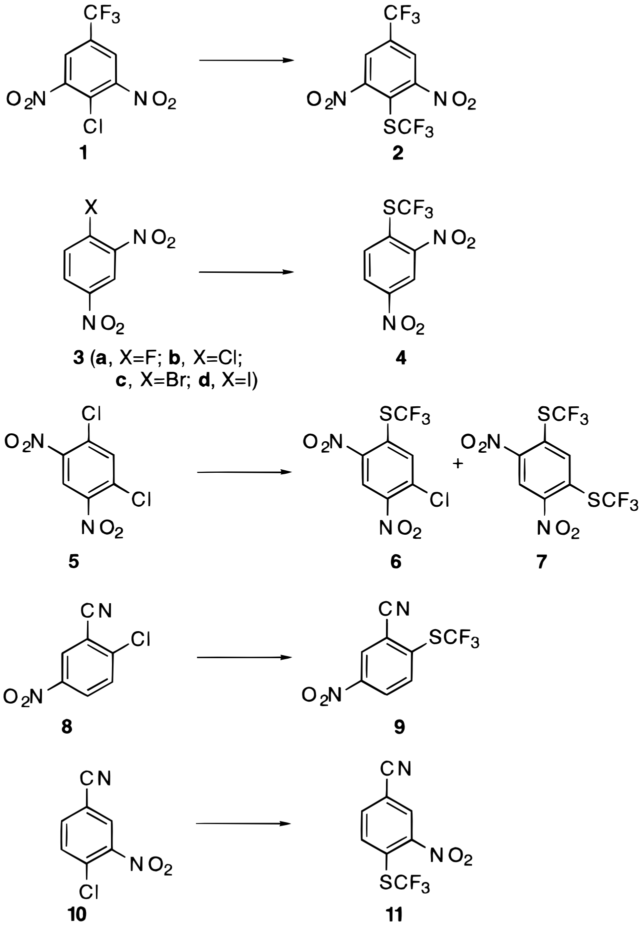

Figure 1.

Table 1. Reactions with AgSCF$_3$/Halide

substrate	halide (MX)	ratio[a]	product(s)	yield[b] (%)
1	KI	1:2:2	**2**	100
	KI	1:2:5	**2**	67
	KBr	1:2:5	**2**	32
	KCl	1:2:5	**2**	10
	KF	1:2:5	**2**	0
	NaI	1:2:5	**2**	0
	NaBr	1:2:5	**2**	0
3a	KI	1:5:5	**4**	26[c]
3b	KI	1:5:5	**4**	52
	Bu$_4$NI	1:3:3	**4**	64
3c	KI	1:5:5	**4**	85
3d	KI	1:5:5	**4**	97
5	KI	1:5:5	**6**	11
	KI	1:5:5	**7**	53
	Bu$_4$NI	1:3:3	**7**	100
8	KI	1:5:5	**9**	3[d]
	Bu$_4$NI	1:3:3	**9**	16[d]
10	KI	1:5:5	**11**	0[d]
	Bu$_4$NI	1:3:3	**11**	25[d,e]

[a] Ratio ArX/MX/AgSCF$_3$. [b] Yields calculated on the basis of GC area. Most reactions were stirred overnight for 24 h. [d] Reactions were stirred for 4 h at 60 °C. [c] 1% fluoronitrobenzene was also detected. [e] 15% 2-fluoro-5-nitrobenzonitrile was also detected.

2-fluoro-5-nitrobenzonitrile in the reaction with **8** indicates that an active source of fluoride is also present in this reaction, presumably formed from the decomposition of $[SCF_3]^-$ to F_2CS and fluoride.[6] All of these systems were unaffected if rigorously anhydrous conditions were used or if no precautions were taken to preclude the presence of moisture. However, the reaction is dependent on the choice of solvent. The conversion of **3b** to **4** at room temperature was almost quantitative in *N*,*N*-dimethylacetamide (95%) and slightly less in ethylene glycol dimethyl ether (77%). Similar yields of **4** were achieved in both acetone and acetonitrile (49% and 52%, respectively, after stirring for 24 h). In *N*,*N*-dimethylformamide, a silver mirror formed around the flask, and the ^{19}F NMR spectrum showed that the only detectable fluorine-containing species was HF (by comparison with the values quoted by Hudlicky[9]). In pyridine, a black solution was formed that was found to contain a small amount of **4** (15%) with the major product being **3a** (60%), again demonstrating that decomposition to fluoride can occur. No conversion of substrate was detected in chloroform or cyclohexane. In the unsuccessful cases, ^{19}F NMR spectra demonstrated that $(F_3CS)_2CS$ was formed as the major SCF_3-containing product, along with bis(trifluoromethyl)disulfide. With significantly less activated chloroaromatics such as 2-chloronitrobenzene and 2,6-dichlorobenzonitrile, there was no conversion of the substrate, even in refluxing acetonitrile. Instead, decomposition of the $[SCF_3]^-$ occurs, with a range of trifluoromethylthiolated byproducts being formed, Figure 3. These include bis(trifluoromethyl)disulfide, tetrakis(trifluoromethylthio)ethene, and 3,4,5,6-tetrakis(trifluoromethylthio)-1,2-dithiine, all of which have been observed previously as decomposition products of KSCF$_3$.[4b] Interestingly, a cyclic condensation product of the formula $(CS)_3(SCF_3)_2$ was also formed in small amounts. This was not observed in the KSCF$_3$ systems, but was reported as

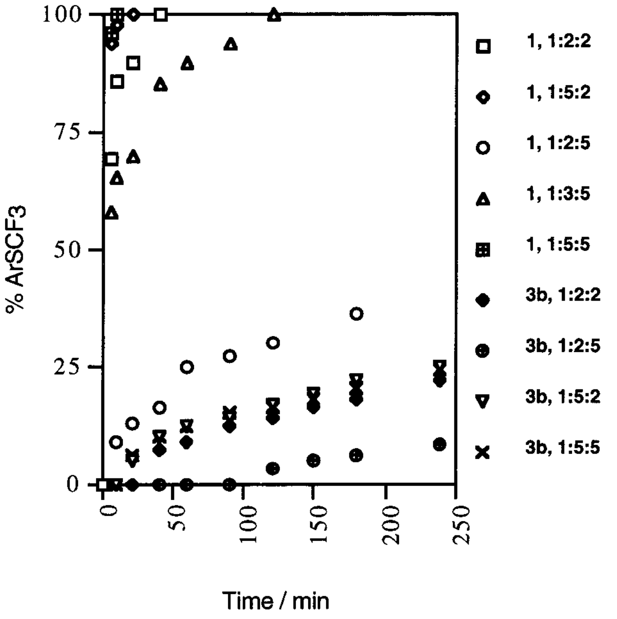

Figure 2. Reaction of **1** and **3b** with AgSCF$_3$/KI in varying ratios (ArCl/KI/AgSCF$_3$).

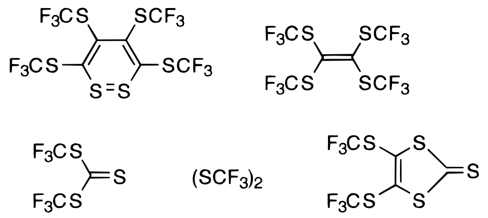

Figure 3.

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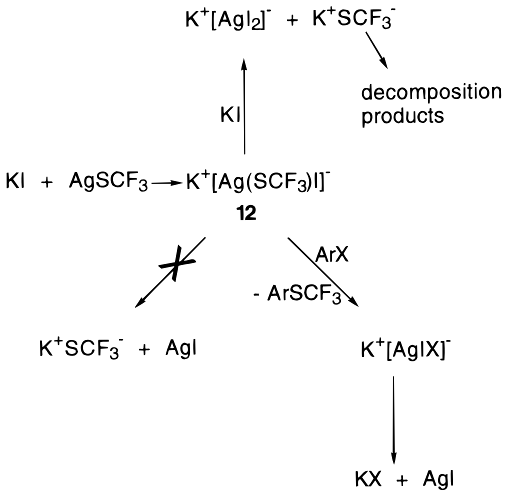
Scheme 2



a major byproduct in the reaction of $AgSCF_3$ with trimethyl silyl iodide.[10]

It is clear that the system is not simply a method of converting the chloroaromatic to the corresponding iodoaromatic, which then reacts with $AgSCF_3$, since neither KI nor Bu_4NI was found to react with any of the chloroaromatics under the conditions described here. $AgSCF_3$ will also not react directly with **3d** under these conditions. It is also clear from the above results that the reaction mixture is not simply a source of $KSCF_3$ or Bu_4NSCF_3. No precipitate of silver iodide is formed when Bu_4NI or KI is added to a solution of $AgSCF_3$ in acetonitrile (this differs to the case of silver(I) triflate, where quantitative conversion to tetrabutylammonium triflate occurs with the precipitation of silver iodide). That a direct conversion to $KSCF_3$ does not occur is also shown by the reactivity of the system. Tavener and Clark report that, with $KSCF_3$, fluoroaromatics are more reactive than the corresponding chloroaromatics.[4a] We have found that the yield of **4** is lower when $KSCF_3$ is reacted with **3c** (5%) compared to the reaction with **3a** (80%). However, in the $AgSCF_3$/KI system used here, while **3a** was found to react with the $AgSCF_3$/KI mixture, a much lower yield of **4** was achieved than reaction with **3b**. Reaction with iodo- and bromoaromatics was found to be even more favorable; indeed, the yields for the 2,4-dinitrohalobenzenes were found to increase in the order I > Br > Cl > F. These observations suggest that a mechanism different from that of the $KSCF_3$ system is occurring, presumably one similar to that reported for $Hg(SCF_3)_2$, Scheme 2.

Evidence for the formation of the anion **12** comes from electrospray mass spectrometry. A solution of a 1:1 ratio of Bu_4NI and $AgSCF_3$ showed the presence of this complex anion. Unfortunately, no bands due to such a species could be identified in the UV−vis spectrum. The IR spectrum of the 1:1 mixture of Bu_4NI and $AgSCF_3$ demonstrated a change in the contours of the C−F stretching band similar to that reported for the $[Hg(SCF_3)_2I]^-$ anion.[11] Little information could be deduced from the ^{19}F NMR spectrum, which demonstrated only a single peak at −17.1 ppm, shifted with respect to that found from $AgSCF_3$ alone (−23.0 ppm). This shift was found to be independent of the ratio of iodide to trifluoromethanethiolate. The presence of only a single peak demonstrates that all of the $AgSCF_3$ is in the same form, which is in agreement with previous work[11] where the complex formed between tetramethylammonium iodide and $Hg(SCF_3)_2$ was found to be completely dissociated and no unchanged $Hg(SCF_3)_2$ could be detected. Although the solution formed via the addition of Bu_4NI to $AgSCF_3$ was found to be stable for at least 1 week, with KI, the solution gradually became red. The ^{19}F NMR spectrum, which initially demonstrated a single peak at −19.2 ppm, showed many peaks characteristic of decomposition products of trifluoromethanethiolate.

As can be seen from Table 1, sodium halides are ineffective at inducing the reaction of $AgSCF_3$ with chloroaromatics. We postulate that the sodium cation is too small to stabilize such large diffuse anions as **12**. The importance of the cation on the reaction is also highlighted by the observation that, upon successful reaction with Bu_4NI, crystals of tetra-*n*-butylammonium tetraiodotriargenate precipitate from the reaction mixture with time. The unit cell of a single crystal sample was determined at 150(1) K and was shown to be identical to the previously determined unit cell for tetra-*n*-butylammonium tetraiodotriargenate.[13] This was confirmed by a search of the Cambridge Structural Database.[14] With KI, a yellow/white powder precipitates, presumably a mixture of silver and potassium halides. This indicates that the larger Bu_4N^+ cation may be able to stabilize species that the smaller K^+ cannot. The use of potassium halides other than KI in the reaction of **1** with $AgSCF_3$ resulted in a reduced yield of **2**. The yield decreased in the order KI > KBr > KCl > KF, which may arise from the relative stabilities of either the $[Ag(SCF_3)X]^-$ anion or the $[AgClX]^-$ anion. The stability of the latter is certainly known to decrease in the order X = I > Br > Cl.[12]

The rate of reactions was found to be dependent on the ratio of KI to $AgSCF_3$. Even if both reagents were in excess with respect to **1** or **3**, lower yields and slower rates of reaction were found for a ratio of reagent/KI/$AgSCF_3$ of 1:2:5. The rate of reaction and overall conversions were increased dramatically when either a 1:2:2 or a 1:5:5 ratio was used. For example, a quantitative conversion to **2** was found to be possible in 10 min at 25 °C, Figure 2. This dependence on the ratio of KI to $AgSCF_3$ is more difficult to explain. It can be imagined that a ratio of substrate/KI/$AgSCF_3$ of 1:2:5 could be simply a 1:2:2 system with a “sink” of $AgSCF_3$. However, the rates of reaction and final yields obtained when both of these ratios are used imply that this is not so. It is likely that there are other equilibria not shown in Scheme 2 that complicate the system. However, we do not yet have evidence for the existence of these.

With regard to the mechanism for the displacement of a halide from an aromatic nucleus, the dependence of the success of the reaction on the choice of solvent initially implies a simple S_NAr-type process. However, under this process, it would be expected that the order of nucleo-

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Table 2. Reactions with $CuSCF_3$/KI and $Hg(SCF_3)_2$/KI

substrate	product(s)	yield (%) (KI/$CuSCF_a$)[a]	yield (%) (KI/$Hg(SCF_3)_2$)[b]
1	**2**	89[c]	100
3b	**4**	0	26
5	**6**	16	15
	7	12	39
8	**9**		1
10	**11**		2

[a] Yields calculated on the basis of GC area. Reactions stirred at room temperature for 24 h, ratio ($ArCl/KI/CuSCF_3$) = 1:2:2. [b]Reactions stirred at room temperature for 24 h with a ratio ($ArCl/KI/Hg(SCF_3)_2$) = 1:2:1. [c]A 4% yield was achieved in the absence of KI; all others resulted in no conversion in the absence of KI.

fugacity would be F > Cl > Br > I.[15] This is not the case with the $AgSCF_3$/KI system, which may well demonstrate the influence of a complex intermediate as postulated for copper nucleophiles.[16] Certainly, a benzyne process can be ruled out. Were this the case, then **1**, with no hydrogen atom ortho to the displaced chlorine, should not undergo reaction, whereas in fact it was found to be the most active of the substrates used in this study. Electron-transfer processes obviously can occur—the formation of a silver mirror when *N*,*N*-dimethylformamide is used as a solvent requires reduction. However, in acetonitrile, the inclusion of 1,4-dinitrobenzene as a radical trap has no effect on either the rate of reaction or the overall conversion of **3b**. This implies that the displacement of the halide does not occur by a $S_{RN}1$ mechansim or by any other mechanism requiring radical anion intermediates.

It is also possible to induce reaction of chloroaromatics with $CuSCF_3$ and $Hg(SCF_3)_2$ at room temperature by the addition of KI to the reaction mixture (Table 2). In the case of $CuSCF_3$, the reactions proceeded to a lesser degree than with $AgSCF_3$. No reaction occurred with **3b** and the yields for **5** were only modest. The yield was improved slightly by thorough degassing of the solutions before stirring. The yields achieved with $Hg(SCF_3)_2$, however, were found to be more similiar to those achieved with $AgSCF_3$.

Conclusions

The addition of KI or Bu_4NI to a solution of $AgSCF_3$, $CuSCF_3$, or $Hg(SCF_3)_2$ in acetonitrile results in the formation of a reactive source of $[SCF_3]^-$. These reagents are capable of converting activated haloaromatics to the corresponding trifluoromethyl aryl sulfides under mild conditions. Evidence suggests that the system is not simply a method of forming $KSCF_3$; rather the reactive species appears to be metal mediated. It is the first system described that is capable of reacting with fluoro-, chloro-, bromo-, and iodoaromatics. That good conversions can be achieved with some chloroaromatics has obvious advantages since it avoids the need for the more expensive iodo- and bromoaromatics that are used in the more conventional $CuSCF_3$ methodology.

Experimental Section

All solvents used were anhydrous grade. All reagents were purchased from Aldrich Chemical Co. and Apollo Scientific and used as received. ^1H NMR were recorded in $CDCl_3$ using a JEOL EX270 spectrometer. ^{19}F NMR were recorded in CH_3CN with C_6D_6 added as a lock. Chemical shifts are given in ppm relative to TMS (^1H) or $CFCl_3$ (^{19}F). Coupling constants are given in hertz. GC was performed on a HP5 column in a Hewlett-Packard HP6890. All mass spectrometry techniques were carried out using a VG Autospec. IR were recorded using a Bruker Equinox 55. $AgSCF_3$ and $CuSCF_3$ were obtained via literature procedures.[11,6] $Hg(SCF_3)_2$ was made via a variation of that of Man et al.[17] by stirring HgF_2 (2.38 g, 10 mmol) with carbon disulfide (2.3 mL) in acetonitrile in a sealed tube at 110 °C. After filtering and removal of the solvent, $Hg(SCF_3)_2$ was recovered in an 11% yield. Reactions with $KSCF_3$ were carried out using a literature procedure.[4]

General Procedure for the Preparation of Trifluoromethyl Aryl Sulfides. Silver(I) trifluoromethanethiolate in acetonitrile was added to the chloroaromatic and potassium iodide. The reaction was stirred at room temperature. A sample from the solution was added to diethyl ether and passed through a short silica column for GC analysis. The neat reaction mixture was used to analyze the reaction by ^{19}F NMR.

3,5-Dinitro-4-trifluoromethylthiobenzotrifluoride, 2. Compound **1** (0.27 g, 1.0 mmol), $AgSCF_3$ (0.406 g, 2.0 mmol), and KI (0.336 g, 2.0 mmol) in acetonitrile at room temperature showed a quantitative conversion of substrate after 1 h by GC and ^{19}F NMR. After column chromatography using cyclohexane/DCM (1:1) as eluant, **2** (0.286 g, 85%) was isolated as a yellow/orange solid: mp 55–56 °C; ν max/cm^{-1} 1551 (s, CNO_2), 1357 (s, CNO_2), 1092 (s, CF), 755 (m, CS); δ_F −39.1, −62.5; δ_H 8.274 (s); *m*/*z* (EI^+) 336 (M^+ 2%) amu. Anal. Calcd: C, 28.60; H, 0.60; N, 8.30. Found: C, 28.76; H, 0.54; N, 8.26. **Tetra-*n*-butylammonium tetraiodotriargenate** was isolated by filtration of the precipitated crystals from the neat reaction mixture. Anal. Calcd: C, 17.90; H, 3.40; N, 1.30. Found: C, 18.03; H, 3.42; N, 1.28. The unit cell was determined using a Rigaku AFC6S diffractometer indexed by least-squares refinement on diffractometer angles for 20 automatically centered reflections,[18] γ = 0.71069 Å. Monoclinic, primitive, a = 9.387(5) Å, b = 15.707(9) Å, c = 18.529(3) Å, α = 89.99(4)°, β = 100.84(20)°, γ = 90.03(6)°. U = 2683(2) Å^3.

2,4-Dinitrotrifluoromethylthiobenzene, 4. Compound **3b** (0.202 g, 1.0 mmol), $AgSCF_3$ (0.406 g, 2.0 mmol), and KI (0.336 g, 2.0 mmol) in acetonitrile at room temperature showed a 52% conversion of substrate after 24 h by GC. After column chromatography using hexane/DCM (1:1) as eluant, **4** was isolated as a low-melting solid: mp 46–48 °C; ν max/cm^{-1} 1531 (s, CNO_2), 1347 (s, CNO_2) 1082 (s, CF), 724 (m, CS); δ_F −41.1; δ_H 9.075 (d, J = 2.5), 8.522 (dd, J = 2.4, 9.0), 8.038 (d, J = 8.5); *m*/*z* (EI^+) 268 (M^+ 27%) amu; found 267.976563, requires 267.976193.

1,3-Di(trifluoromethylthio)-4,6-dinitrobenzene, 7. Compound **5** (0.236 g, 1.0 mmol), $AgSCF_3$ (1.046 g, 5.0 mmol), and KI (0.830 g, 5.0 mmol) in acetonitrile at room temperature showed a 64% conversion of substrate after 24 h by GC. After column chromatography using hexane/DCM (1:1) as eluant, **6** was isolated as a yellow solid: mp; δ_F −40.1; *m*/*z* (EI^+) 302 (M^+, 27) 69 (100), 233 (80), 97 (58), 106 (52), 129 (43), 302 (27), 175 (26), 141 (15) amu; found 301.938128, requires 301.937591. **7** (recrystallized from hexane, yellow needles) was also isolated: mp 87–88 °C (); ν max/cm^{-1} 1571 (s, CNO_2), 1338 (s, CNO_2), 1073 (s, CF), 755 (m, CS); δ_H 9.14 (s) 8.24 (s); δ_F −41.71; *m*/*z* (EI^+) 398 (M^+, 18) amu; found 397.934814, requires 397.934877.

4-Trifluoromethylthio-3-nitrobenzonitrile, 9. Compound **8** (0.182 g, 1.0 mmol), $AgSCF_3$ (1.046 g, 5.0 mmol), and KI (0.830 g, 5.0 mmol) in acetonitrile at 60 °C showed a 16% conversion of substrate after 4 h by GC to **9**: δ_F −41.0; *m*/*z* (EI^+) 248 (M^+ 23%) amu; found 247.98950, requires 247.987214.

2-Trifluoromethylthio-5-nitrobenzonitrile, 11. Compound **10** (0.182 g, 1.0 mmol), $AgSCF_3$ (1.046 g, 5.0 mmol),

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and KI (0.830 g, 5.0 mmol) in acetonitrile at 60 °C showed a 15% conversion of substrate after 4 h by GC to **11**: δ_F −40.2; m/z (EI^+) 248 (M^+, 100) amu.

Anion 12. Bu_4NI (2.4 mmol) and $AgSCF_3$ (2.4 mmol) in acetonitrile at room temperature showed the presence of a single peak in the ^{19}F NMR spectrum: ν max/cm^{-1} 1071 (s, broad, CF),749 (m, CS); δ_F −17.1; m/z (electrospray) 335/337 amu consistent with the anion $[AgI(SCF_3)]^-$, with an ^{107}Ag/^{109}Ag isotope pattern.

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