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Silver(I) Fluoride and Related Compounds in Chemical Synthesis

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ABSTRACT: *Silver(I) fluoride is a versatile tool in desulfuration-fluorination reactions with thiuram disulfides and thioureas. Reactions of AgF and trimethyl(perfluoroorgano)- and trimethyl(alkynyl)-silanes offer a convenient approach to the corresponding organosilver derivatives, which are excellent reagents for oxidative organylations of group 12–16 elements. Reactions of AgF and elements of groups 13–16 open a convenient access to the corresponding fluorides.* © 2002 Wiley Periodicals, Inc. Heteroatom Chem 13:561–566, 2002; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10102

INTRODUCTION

Among silver(I) halides two characteristic features of AgF are striking—its extremely good solubility in water (1800 g/l at 25°C) and the fact that it is the only silver halide that forms hydrates. In contrast, the heavier halides are almost insoluble in water. This is attributed to the ionic character of the silver–fluorine bond, which has been calculated to be 70% ionic while those of the heavier halides exhibit values of only 30% for AgCl, 23% for AgBr, and 11% for AgI [1].

Some general remarks have to be made on the quality of AgF for synthetic purposes. Silver(I) fluoride should be yellow or orange. Impurities by bronze Ag_2F and brown AgF_2 sometimes give AgF a darker color. However, AgF is obtained in sufficient purity from several commercial sources and can be used as received.

For the reactions described in this paper, the choice of the solvent was essential. Solvents without "acidic" protons were suitable. Because of the extremely low solubility of AgF in nonpolar solvents such as alkanes, halogenated alkanes, aromatics (benzene, toluene), and ethers ($(C_2H_5)_2O$, THF, 1,2-dimethoxyethane (DME)), the palette of solvents was restricted to nitriles (CH_3CN, C_2H_5CN, C_3H_7CN), DMF, pyridine, *N*-methylimidazol, and *N*-methylmorpholine. Of these solvents, propionitrile was the solvent of choice because of its minimum side reactions, good availability, and convenient handling.

RESULTS

Desulfuration-Fluorinations with Silver(I) Fluoride

Several methods are known to convert a C=S moiety into a C—F unit [2]. In all these, either toxic materials or a combination of reagents are involved. Reactions of AgF and thiuramdisulfides display the advantage of a selective approach to either thiocarbamoyl fluorides ($R_2NC(S)F$) or trifluoromethylamines (R_2NCF_3). Thiuramdisulfides can easily be converted into the corresponding thiocarbamoyl fluoride and the silver dithiocarbamate ($AgSC(S)NR_2$) in 1:1 reactions. Stoichiometries of AgF and $[R_2NC(S)S]_2$ of 3:1 and 6:1 offer direct approaches to diorgano(trifluoromethyl)amines, as indicated in Scheme 1 [3]. Trifluoromethylamines are also formed in separate reactions of $R_2NC(S)F$ or $AgSC(S)NR_2$ with AgF.

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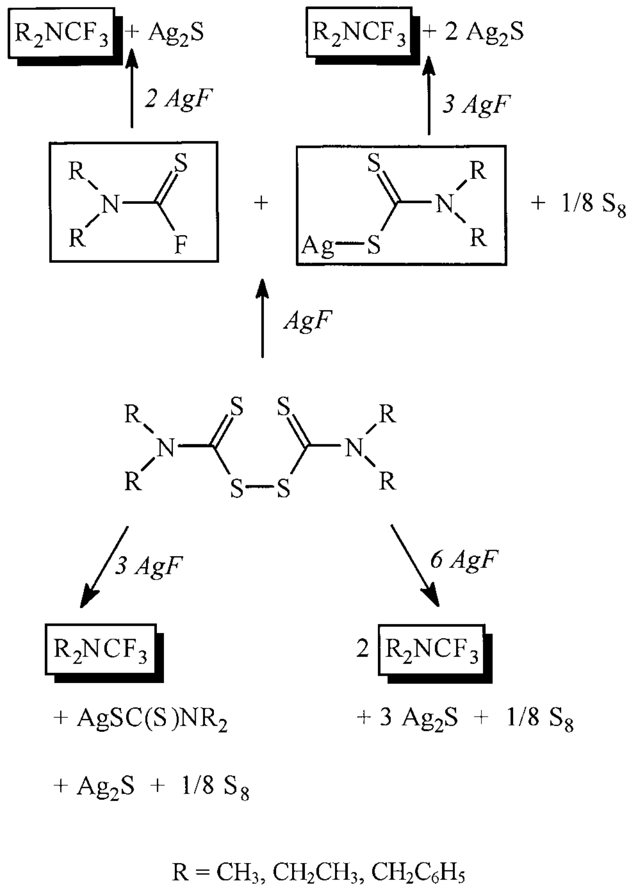
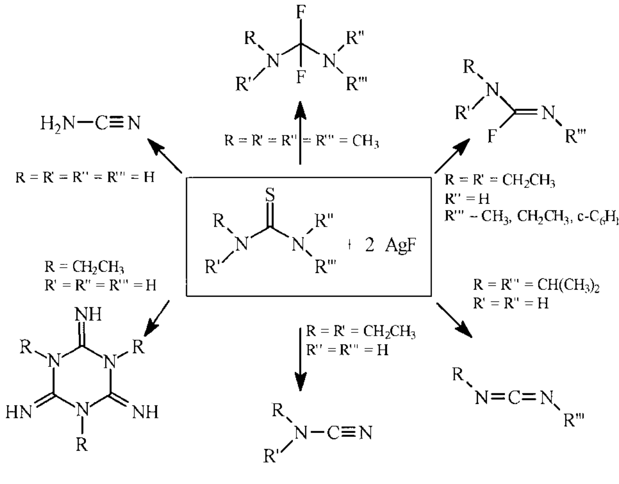


SCHEME 1 Desulfuration-fluorination reactions of AgF and thiuramdisulfides.

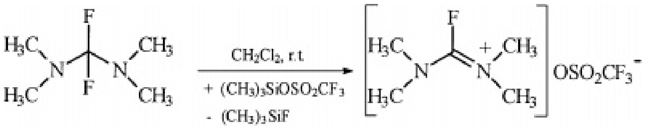
Investigations on desulfuration-fluorination reactions have been extended to differently substituted thioureas (Scheme 2) [4].

The reaction of tetramethylthiourea, $(CH_3)_2NC(S)N(CH_3)_2$, and AgF in propionitrile at room temperature selectively gave bis(dimethylamino)difluoromethane, $[(CH_3)_2N]_2CF_2$, and Ag_2S in approximately quantitative yield.



SCHEME 2 Desulfuration-fluorination reactions of AgF and thioureas.

Bis(dimethylamino)difluormethane can be regarded as a "liquid fluoride source" [5], as has been demonstrated in its reaction with $(CH_3)_3SiOSO_2CF_3$ to give tetramethylfluoroformamidinium trifluoromethanesulfonate, $\{[(CH_3)_2N]_2CF\}OSO_2CF_3$.



The situation becomes more complicated in reactions with trialkylthioureas. In principle, sulfur is substituted by two fluorine atoms but the corresponding dialkylamino(monoalkylamino)difluoromethane, $(R_2N)(R'NH)CF_2$, forms an equilibrium with the HF-adduct of the fluoroformamidine. HF is intercepted by addition of the pyridine-borontrifluoride adduct to give the fluoroformamidine in pure form.

Reactions with *N,N'*-dialkylthioureas proceed via different (not yet analyzed) fluorine-containing intermediates to yield finally dialkylcarbodiimides, RN=C=NR, while reactions with *N,N*-dialkylthioureas exclusively yield dialkylcyanamides, $R_2NC{\equiv}N$. Reactions with monoalkylthioureas give cyclic trialkyl-[1,3,5]-triazinetrione triimine whereas thiourea is selectively converted into cyanamide, $H_2NC{\equiv}N$. Further investigations in this field are in progress.

Reactions with Trimethylsilyl Derivatives

The interactions of trimethyl(perfluoroorgano)silanes and silver(I) fluoride offer a new, convenient access to perfluoroorganosilver(I) compounds. In these reactions, the fluoride source itself, AgF, becomes the center to which the perfluoroorgano group is transferred. These reactions have been most intensively studied with the trifluoromethyl [6] and the pentafluorophenyl group [6,7]. Propionitrile has been the solvent of choice although other N-donor solvents are also suitable.

$$(CH_3)_3SiCF_3 + AgF \xrightarrow[\text{r.t., 5 min}]{CH_3CH_2CN} AgCF_3 + (CH_3)_3SiF$$

Trifluoromethylsilver equilibrates with silver[bis(trifluoromethyl)argentate(I)] and a second not yet characterized species [8]. These reactions offer the advantage that the formation of tetrakis(trifluoromethyl)argentate(III), $[Ag(CF_3)_4]^-$, which is formed in ligand exchange reactions of different silver salts and $Cd(CF_3)_2$ complexes [8,9] or $Bi(CF_3)_3$, is nearly completely suppressed.

Addition of [PNP]Cl to solutions of $AgCF_3$ selectively yielded the argentates $[PNP][Ag(CF_3)_2]$ and $[PNP][Ag(CF_3)Cl]$, ($[PNP]^+ = Ph_3P{=}N{-}PPh_3{}^+$).

$$2AgCF_3 + [PNP]Cl \xrightarrow[\text{r.t.}]{CH_3CH_2CN} [PNP][Ag(CF_3)_2] + AgCl$$

$$AgCF_3 + [PNP]Cl \xrightarrow[\text{r.t.}]{CH_3CH_2CN} [PNP][Ag(CF_3)Cl]$$

Both compounds were obtained as colorless, light-sensitive crystalline solids. While the composition of the anion $[Ag(CF_3)_2]^-$ could only be proved by NMR spectroscopy (Fig. 1), single crystal structure analysis of $[PNP][Ag(CF_3)Cl]$ exhibited the expected composition and anion geometry (Fig. 2).

Besides having excellent properties as a trifluoromethylating reagent in nucleophilic halide substitutions, $AgCF_3$ opened the possibility of synthesizing trifluoromethyl element compounds of groups 12–16 elements directly from the elements via oxidative

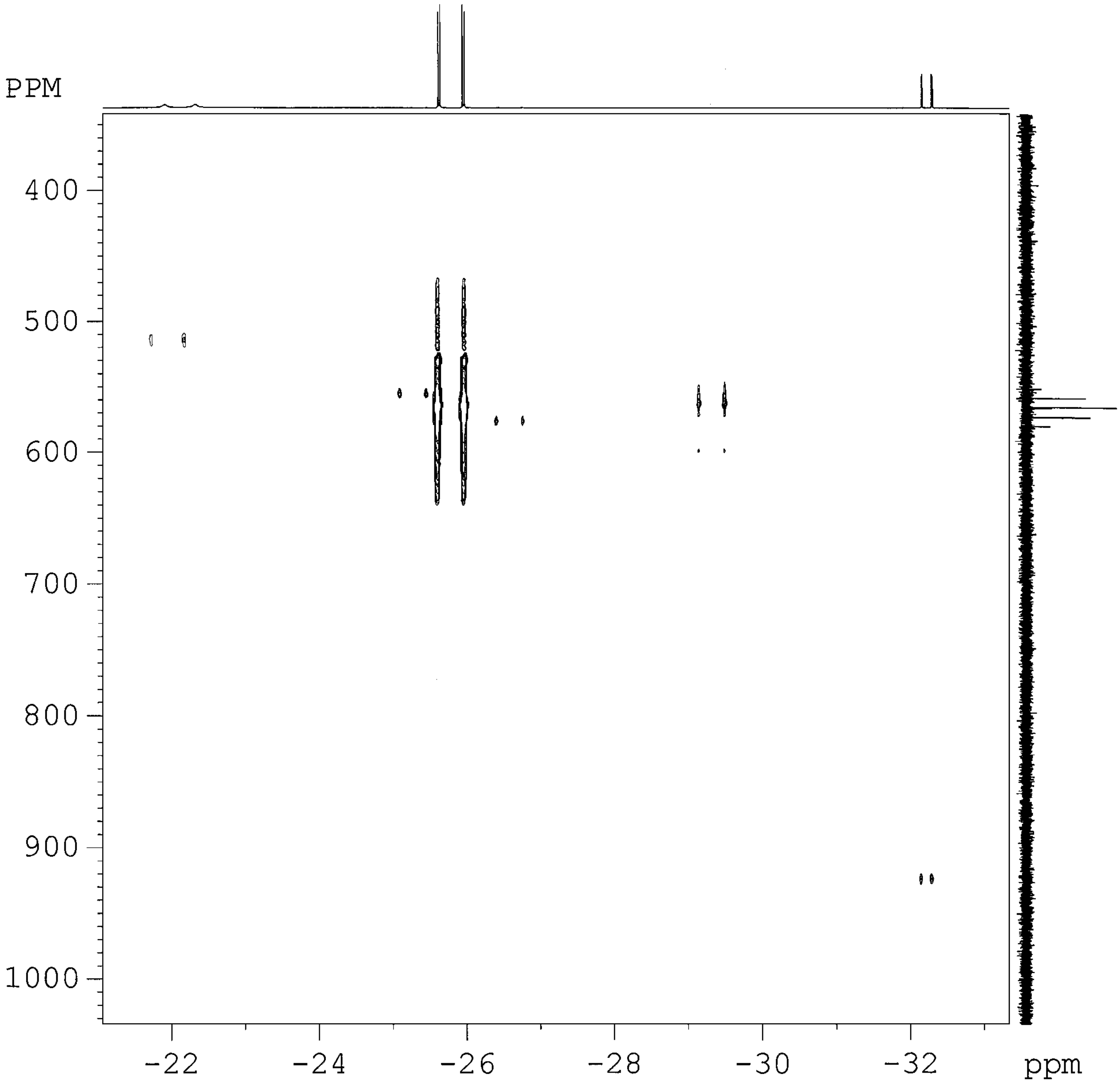


FIGURE 1 ^{109}Ag, ^{19}F HMQC spectrum of $[PNP][Ag(CF_3)_2]$ (horizontal trace: ^{19}F NMR spectrum; vertical trace: ^{109}Ag NMR spectrum; $\delta(^{19}F) = -25.6$; $\delta(^{109}Ag) = +556$; $^{1}J_{F,C} = 371$ Hz; $^{1}J_{Ag,C} = 280$ Hz; $^{2}J_{Ag,F} = 100$ Hz).

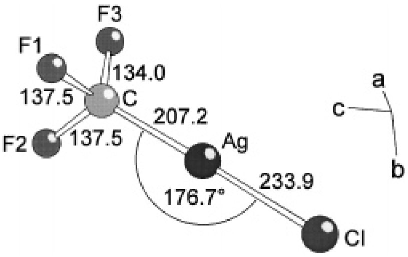


FIGURE 2 Structure of the anion $[Ag(CF_3)Cl]^-$ ([PNP][$Ag(CF_3)Cl$]): triclinic, P-1, $a = 972.4$ pm; $b = 1098.3$ pm; $c = 1710.8$ pm; $\alpha = 105.7^\circ$; $\beta = 93.9^\circ$; $\gamma = 102.2^\circ$).

trifluoromethylations.

$$n\mathrm{AgCF_3} + \mathrm{E} \xrightarrow{\mathrm{CH_3CH_2CN}} \mathrm{E(CF_3)}_n + n\mathrm{Ag}$$

Yields and conditions of these reactions are summarized in Table 1.

Several pathways for the synthesis of AgC_6F_5 are mentioned in the literature [10]. All reactions give AgC_6F_5 in moderate yields after long reaction times and extensive working-up procedures. The synthesis according to

$$\mathrm{(CH_3)_3SiC_6F_5 + AgF} \xrightarrow[\text{r.t., 30 min}]{\mathrm{CH_3CH_2CN}} \mathrm{AgC_6F_5 + (CH_3)_3SiF}$$

has the advantage that AgC_6F_5 is selectively formed within 30 min at room temperature, with concomitant formation of volatile $(CH_3)_3SiF$ in nearly quantitative yield. After distilling off all volatile compounds in vacuo, AgC_6F_5 is obtained as the 1:1 adduct with propionitrile. It is a colorless, light-sensitive compound which loses propionitrile at 87–93°C to give donor-free AgC_6F_5, which is at ca. 270°C selectively decomposed into $(C_6F_5)_2$ and elemental silver.

TABLE 1 Transmetalations of Group 12–16 Elements and Trifluoromethylsilver

E	*T (°C)*	*Reaction Time*	*Product*	*Yield (%)*
Zn	0	4 h	$Zn(CF_3)_2 \cdot 2CH_3CH_2CN$	66
Cd	0	1 h	$Cd(CF_3)_2 \cdot 2CH_3CH_2CN$	75
	21	1 h	$Cd(C_2F_5)_2$, AgC_2F_5, C_2F_4, CF_3H, F-polymers	
	50	30 min	C_2F_4, CF_3H, F-polymers	
Hg	21	<5 min	$Hg(CF_3)_2$	85
Ga	21	72 h	$Ga[Ag(CF_3)_4]_3$	
In	21	48 h	$In(CF_3)_3 \cdot 2CH_3CH_2CN$	
Tl	21	96 h	$Tl^I[Ag^I(CF_3)_2]$ (85%), $Tl^I[Ag^{III}(CF_3)_4]$ (10%), $Ag[Tl^{III}(CF_3)_4]$ (5%)	
Sn	50	12 h	$Sn(CF_3)_4$	
Pb	50	24 h	$Pb(CF_3)_4$	
As	55	16 h	AsF_3 (total decomposition)	
Sb	65	24 h	$Sb(CF_3)_3$	
Bi	50	24 h	$Bi(CF_3)_3$	39
Se	50	16 h	$Se(CF_3)_2$, $Se_2(CF_3)_2$, $AgSeCF_3$	
Te	50	12 h	$Te(CF_3)_2 \cdot CH_3CH_2CN$	75

Although all arylsilver derivatives structurally characterized till date form tetrameric units in the solid state [11], $AgC_6F_5 \cdot CH_3CH_2CN$ crystallizes in infinite chains (Fig. 3) [7].

In the crystal structure of $AgC_6F_5 \cdot CH_3CH_2CN$, two crystallographically different Ag atoms are found. Both are located on special sites of the space group *C*2/*c*. One silver atom is in ideal linear coordination of two carbon atoms with a silver–carbon bond length of 213 pm. The carbon atoms belong to two C_6F_5 groups, which act as bridging ligands to the second silver atoms. Here, silver–carbon bonds are significantly longer (239 pm) compared to those of the linear unit because of additional bonds to two CH_3CH_2CN molecules, building up a strongly distorted tetrahedral geometry at this silver atom. The bridging functionality of the C_6F_5 groups leads to infinite chains according to $^1_\infty[\mathrm{Ag(2)(CH_3CH_2CN)_{2/1}(C_6F_5)_{2/2}Ag(1)(C_6F_5)_{2/2}}]$, which are oriented along the [001] direction of the unit cell.

In a manner similar to that described for the trifluoromethyl derivatives, AgC_6F_5 could be transferred into the corresponding argentate in reactions with [PNP]Br from which [PNP][$Ag(C_6F_5)_2$] was isolated as a colorless solid in 74% yield decomposing at 123–126°C.

$$\mathrm{2AgC_6F_5 + [PNP]Br} \xrightarrow[\text{r.t.}]{\mathrm{CH_3CH_2CN}} \mathrm{[PNP][Ag(C_6F_5)_2] + AgBr}$$

As expected, AgC_6F_5 showed excellent properties in oxidative transmetalations with a great number of group 12–16 elements, giving the corresponding pentafluorophenyl element compounds in moderate to excellent yields (Table 2).

It was also found that trimethyl(alkynyl)silanes react in a manner that is similar to the way trimethyl(perfluoroorgano)silanes react with AgF. These reactions were most intensively studied only with the phenylethynyl group.

$$\mathrm{AgF + (CH_3)_3SiC{\equiv}CC_6H_5} \xrightarrow[\text{r.t., 12 h } or \text{ 50°C, 1 h}]{\mathrm{CH_3CH_2CN}} \mathrm{AgC{\equiv}CC_6H_5 + (CH_3)_3SiF}$$

However, because of the polymeric nature of $[\mathrm{AgC{\equiv}CC_6H_5}]_\infty$ [12] transmetalations with selected elements required extended reaction times or higher temperatures compared with $AgCF_3$ and AgC_6F_5 (Table 3).

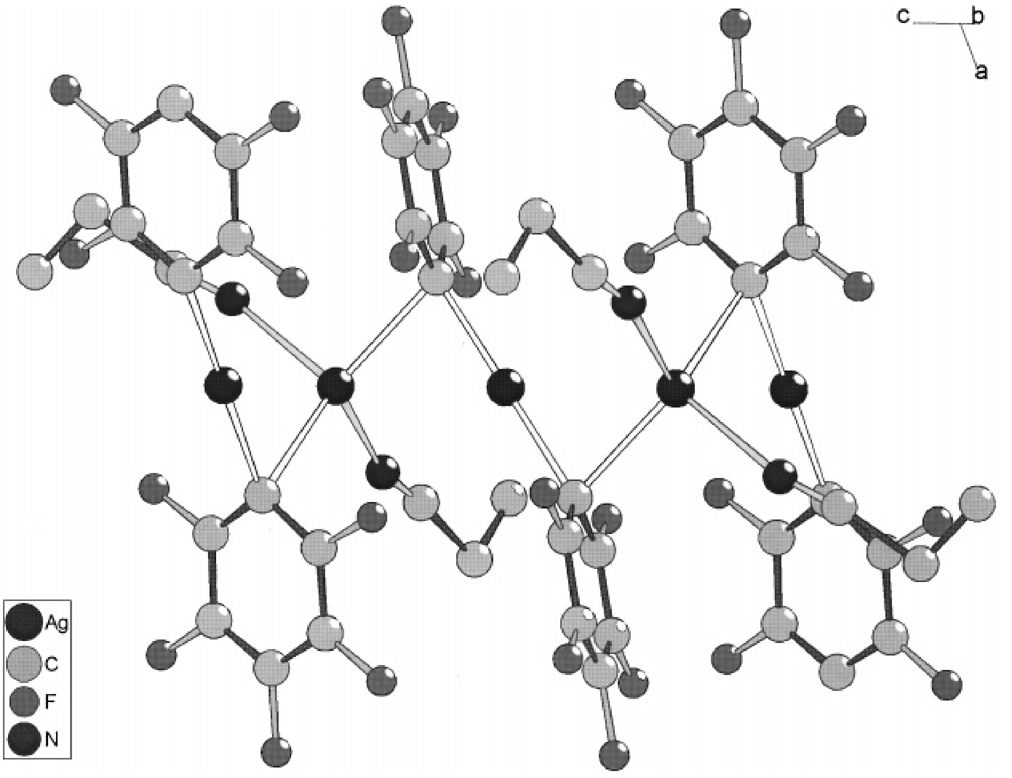


FIGURE 3 Section of the infinite chain $^{1}_{\infty}[Ag(CH_3CH_2CN)_{2/1}(C_6F_5)_{2/2}Ag(C_6F_5)_{2/2}]$ ($AgC_6F_5 \cdot CH_3CH_2CN$): monoclinic, C2/c (no. 15), $Z = 8$, $a = 2301.4$ pm; $b = 1078.8$ pm; $c = 948.0$ pm; $\beta = 113.2°$).

Reactions of Silver(I) Fluoride and Selected Elements

Silver fluoride itself exhibits the properties of a good oxidative fluorinating reagent for group 13–16 elements under mild to moderate conditions, a property that has been mentioned only once in literature [13].

TABLE 2 Transmetalations of Group 12–16 Elements and Pentafluorophenylsilver

E	*T* (°*C*)	*Reaction Time*	*Product*	*Yield (%)*
Zn	21	4 h	$Zn(C_6F_5)_2 \cdot 2CH_3CH_2CN$	77
Cd	21	<5 min	$Cd(C_6F_5)_2 \cdot 2CH_3CH_2CN$	62
Hg	21	<5 min	$Hg(C_6F_5)_2$	85
Ga	65	72 h	$Ga(C_6F_5)_3 \cdot CH_3CH_2CN$	69
In	21	48 h	$In(C_6F_5)_3 \cdot CH_3CH_2CN$	35
Sn	65	16 h	$Sn(C_6F_5)_4$	92
Pb	65	24 h	$Pb(C_6F_5)_4$	65[a]
As	21/65	48/8 h	$As(C_6F_5)_3$	79
Sb	65	24 h	$Sb(C_6F_5)_3$	88
Bi	50	24 h	$Bi(C_6F_5)_3$	73
Se	50	16 h	$Se(C_6F_5)_2$	73
Te	50	12 h	$Te(C_6F_5)_2$	60

[a] $AgC_6F_5 + Pb \xrightarrow[20–90°C]{CH_3CH_2CN} Pb[Ag(C_6F_5)_2]_2 + 2Ag$

$\xrightarrow[160°C]{1\ Torr} Pb(C_6F_5)_4 + 2Ag$

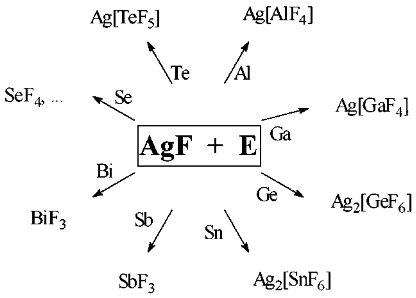
Reactions of excess AgF with the elements Al, Ga, Ge, Sn, and Te proceed selectively with formation of the corresponding fluoroelementates, whereas reactions with Sb and Bi gave only the corresponding trifluorides SbF_3 and BiF_3, respectively. The reaction with elemental selenium gave spectroscopic evidence for SeF_4 but several not yet identified byproducts were also formed (Scheme 3).

CONCLUSIONS

Silver(I) fluoride is a versatile reagent in desulfuration-fluorinations of thioureas and related compounds.

TABLE 3 Transmetalations of Group 12–16 Elements and Phenylethynylsilver

E	*T* (°*C*)	*Reaction Time*	*Product*	*Yield (%)*
Hg	21	75 min	$Hg(C{\equiv}CC_6H_5)_2$	88
As	50	7 d	$As(C{\equiv}CC_6H_5)_3$	74
Sb	50	7 d	$Sb(C{\equiv}CC_6H_5)_3$	72
Bi	50	21 d	$Bi(C{\equiv}CC_6H_5)_3$	0
Se	50	4 d	$Se(C{\equiv}CC_6H_5)_2$	54
Te	50	7 d	$Te(C{\equiv}CC_6H_5)_2$	65



SCHEME 3 Reactions of silver(I) fluoride and elements of groups 13–16.

Organosilver compounds with electron-withdrawing groups could easily be prepared from AgF and the corresponding trimethylsilyl derivatives.

Beside the expected and known properties of organosilver compounds as reactive species in nucleophilic halide substitutions, these compounds also exhibited excellent properties in oxidations of a variety of group 12–16 elements.

Silver(I) fluoride itself could be used as a fluorinating reagent for group 13–16 elements.

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