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# Oxidative perfluoroorganylation methods in group 12–16 chemistry The reactions of haloperfluoroorganics and In and InBr, a convenient new route to $AgR_f$ ($R_f = CF_3$, $C_6F_5$) and reactions of $AgR_f$ with group 12–16 elements

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## Abstract

Perfluoroiodo organics $R_fI$ ($R_f = n\text{-}C_nF_{2n+1}$ ($n = 1, 2, 3, 4, 6$), $i\text{-}C_3F_7$, $C_6F_5$) and $C_6F_5Br$ react with elemental indium in polyethers or THF to give spectroscopic evidence for compounds of the general composition $In^{II}R_fX$ ($X = I$, Br). All isolation attempts led to decomposition into $In^{III}(R_f)_2I$ and $In^{I}I$. In contrast, the reaction of In, $0.5Br_2$ and $C_6F_5Br$ in THF selectively and quantitatively yielded $In(C_6F_5)Br_2{\cdot}2THF$ which was structurally characterized. The reaction of $In(C_6F_5)Br_2{\cdot}2THF$ and acetylacetone (Hacac) quantitatively gave the distorted octahedral molecule $In(acac)Br_2{\cdot}2THF$. Perfluoroorganosilver(I) compounds $Ag(R_f)$ ($R_f = CF_3$, $C_6F_5$) are conveniently and selectively prepared from AgF and $Me_3SiR_f$ in several nitrile solvents. $[PNP][Ag^{I}(CF_3)_2]$ ([PNP] = bis(triphenylphosphoranyliden)ammo-PNP]$[Ag^{I}(CF_3)Cl]$ is formed which is characterized by single crystal structure analysis. Besides its properties as a nucleophilic perfluoroorganylating reagent, $AgR_f$ exhibits to be an excellent oxidative perfluoroorganylation reagent in reactions with various elements of groups 12–16 to give the corresponding perfluoroorgano element compounds in moderate to excellent yields leaving elemental silver.

*Keywords:* Indium; Silicon; Silver; Perfluoroalkyl; Pentafluorophenyl; Oxidation; Group 12–16 elements

## 1. Introduction

While perfluoroiodo organics have been used mainly in ‘‘high-temperature’’ reactions since the early beginning of perfluoroalkylelement chemistry [1], less is known about the synthetic use at lower temperature and especially in group 13 chemistry.

All known perfluoroalkyl indium compounds were accessible exclusively via halide exchange reactions using perfluoroorgano cadmium compounds [2], while pentafluoro-phenyl derivatives have been prepared via oxidative routes using $C_6F_5I$, $Hg(C_6F_5)_2$ and $Tl(C_6F_5)_2Br$ [3–5].

Perfluoroorganosilver(I) compounds, $AgR_f$ ($R_f = C_nF_{2n+1}$ ($n = 2, 3, 4$) [6] $i\text{-}C_3F_7$ [6–8], $t\text{-}C_4F_9$ [8] $C_6F_5$ [9–12]) are known for some time; however, the knowledge of $AgCF_3$ is limited because of its tendency to decompose into elemental silver and $Ag^{I}[Ag^{III}(CF_3)_4]$ in the presence of metal ions stemming from the starting material $Cd(CF_3)_2{\cdot}2D$ ($D =$ unidentate donor) or $Bi(CF_3)_3$ [6,13,14].

The use of perfluoroorgano silver derivatives in halide substitution reactions is documented [6–12]. Less is known about their oxidative properties compared with the corresponding mercury derivatives $Hg(R_f)_2$, especially $Hg(C_6F_5)_2$.

## 2. Results

### 2.1. Reactions of indium metal and halogenoperfluoroorganics and consecutive reactions

Perfluoroiodo organics $R_fI$ ($R_f = n\text{-}C_nF_{2n+1}$ ($n = 1, 2, 3, 4, 6$), $i\text{-}C_3F_7$, $C_6F_5$) and $C_6F_5Br$ and indium metal react in the stoichiometry 1:1 in polyethers such as glyme, diglyme, tetraglyme or THF at ambient temperature to give compounds of the general composition $In^{II}R_fX$ ($X = I$, Br ($R_f = C_6F_5$)). The reactions proceed selectively giving colorless to pale yellow solutions.

$$R_fI + In \xrightarrow[\text{r.t.}]{\text{solvent}} [In^{II}(R_f)I]_2$$

solvent: polyther, THF

$$R_f : n\text{-}C_nF_{2n+1} \quad (n = 1, 2, 3, 4, 6), \quad i\text{-}C_3F_7, C_6F_5$$

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The reactions were most intensively studied for $R_f$ being $i$-$C_3F_7$ and especially $C_6F_5$. Mass spectra of highly concentrated solutions of $[In^{II}(R_f)I]_2$ are dominated by the peaks of highest mass as well as intensity being assigned to $[In_2(R_f)_2I]^+$, $[In_2(R_f)I_2]^+$ and $[In(R_f)_2]^+$. These results show that primarily indium(II) species are formed during oxidative addition of perfluoroiodo organics to indium metal.

Isolation of crude products was successful when carefully dried argon was passed over highly concentrated solutions to blow out the solvent. Attempted precipitations by adding solvents, such as *n*-pentane, toluene or dichloromethane or by reducing the solvent volume in vacuo lead to a rapid disproportionation giving $In^{III}(R_f)_2I$ and $In^II$ as the major products.

The reactions of In, $0.5X_2$ and $C_6F_5X$ ($X = Br, I$) in THF selectively and quantitatively yield $In(C_6F_5)X_2 \cdot 2THF$. $In(C_6F_5)Br_2 \cdot 2THF$ was also quantitatively formed starting from $In^IBr$ and $C_6F_5Br$, while no reaction occurs starting from $In^II$ and $C_6F_5I$. In contrast to the bromo compound, $In(C_6F_5)I_2 \cdot 2THF$ undergoes dismutation reactions in solution. $^{19}F$ NMR signals of $In(C_6F_5)_3$ and $In(C_6F_5)_2I$ are detected beside those of $In(C_6F_5)I_2$.

$$C_6F_5X + In + 0.5X_2 \xrightarrow{THF} In(C_6F_5)X_2 \cdot 2THF$$

$$C_6F_5Br + In^IBr \xrightarrow{THF} In(C_6F_5)Br_2 \cdot 2THF$$

$In(C_6F_5)Br_2 \cdot 2THF$ is a colorless to pale lemon solid with a characteristic smell, melting at 68–69°C. It crystallizes in the monoclinic space group $P2_1/c$ ($a = 1694.3$ ppm; $b = 1421.5$ ppm; $c = 813.4$ ppm; $\beta = 100.3°$; $Z = 4$).

The molecular structure (Fig. 1) exhibits distorted trigonal bipyramidal geometry. The $C_6F_5$ group and the bromine atoms occupy equatorial sites, while the linear O–In–O (176.6°) unit only slightly deviates from the 180° angle [15].

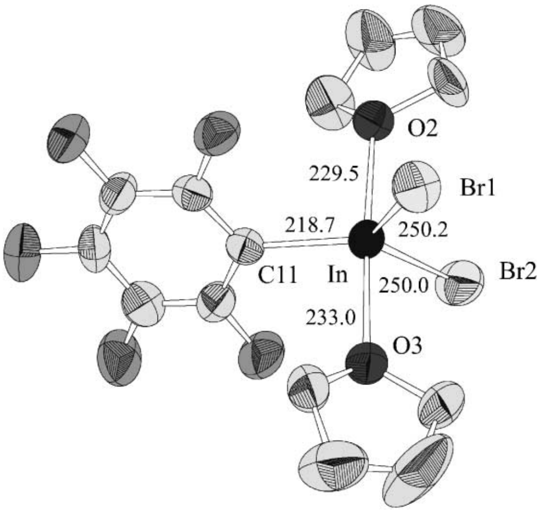


Fig. 1. Molecular structure of $In(C_6F_5)Br_2 \cdot 2THF$.

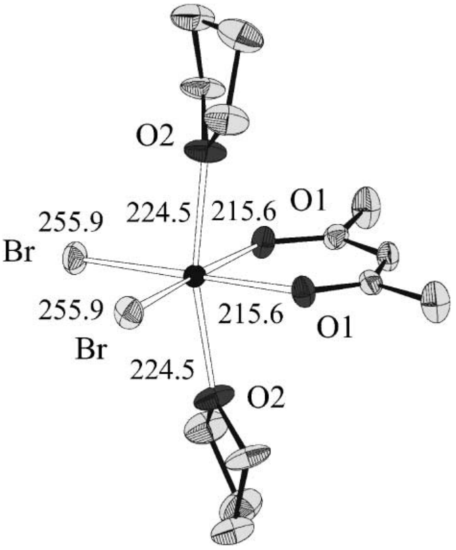


Fig. 2. Molecular structure of $In(acac)Br_2 \cdot 2THF$.

The reaction of $In(C_6F_5)Br_2 \cdot 2THF$ and acetylacetone (Hacac) in aqueous THF quantitatively gives $In(acac)Br_2 \cdot 2THF$ and $C_6F_5H$ [15].

$$In(C_6F_5)Br_2 \cdot 2THF + Hacac \xrightarrow{THF} In(acac)Br_2 \cdot 2THF + C_6F_5H$$

$In(acac)Br_2 \cdot 2THF$ is a colorless solid melting at 81–82°C. Crystals are orthorhomboedric (space group $Pbcn$, $a = 1314.9$ ppm; $b = 928.5$ ppm; $c = 1468.4$ ppm) and exhibit four molecules per unit cell. The molecular structure (Fig. 2) is distorted octahedral with the chelating acac ligand and the *cis*-bromine atoms in equatorial positions and the THF molecules occupying axial sites (cf. [16–18]). The linearity of the O–In–O moiety is more distorted compared with $In(C_6F_5)Br_2 \cdot 2THF$ being 166.20°.

Synthetic approaches to prepare gallium, tin, bismuth and tellurium compounds from the addition of haloperfluoroorganics to the corresponding elements under comparable conditions remained less successful.

### 2.2. Reactions of $Me_3SiR_f$ and AgF

The reactions of $Me_3SiR_f$ and AgF proceed selectively and almost quantitatively at room temperature in solvents such as RCN (R = Me, Et, *n*-Pr, *n*-Bu), DMF, *N*-methylimidazole and pyridine to give the corresponding perfluoroorgano silver(I) species in approximately quantitative yields ($^{19}F$ NMR).

$$Me_3SiR_f + AgF \xrightarrow[r.t.]{} AgR_f + Me_3SiF$$

According to the low solubility of AgF in O-donor solvents, no reactions were observed in ethers, such as THF, glyme, polyglymes and $Et_2O$. None or less than 1% formation of salts with the anion $[Ag^{III}(CF_3)_4]^-$ was observed even after stirring reaction mixtures for 14 days at ambient temperature due to the absence of less noble metal ions [6,13,14,19] which in other synthetic approaches catalyze a decay of $AgCF_3$/$Ag[Ag(CF_3)_2]$ into elemental silver and $Ag^{I}[Ag^{III}(CF_3)_4]$. By-products formed are up to 4% $CH_3CF_3$ and up to 9% $(CH_3)_2SiF_2$. Equilibria as described in [6] were observed in all cases.

In the same manner, the reaction of $Me_3SiC_6F_5$ and AgF proceeds selectively and quantitatively within a few minutes to give $AgC_6F_5$.

$AgCF_3$ could not be isolated from the reaction mixtures but trapped by addition of [PNP]Br or [PNP]Cl. The isolated product, $[PNP][Ag(CF_3)_2]$, decomposes at 98°C [11] and is characterized by its $^{109}$Ag, $^{19}$F HMQC-spectrum exhibiting the expected multiplicity, $^{19}$F and $^{109}$Ag chemical shifts (−25.6 and 556 ppm, respectively) as well as the coupling constants ($^{1}J(^{19}F, ^{13}C) = -371$ Hz, $^{1}J(^{109}Ag, ^{13}C) = +280$ Hz and $^{2}J(^{109}Ag, ^{19}F) = 100$ Hz). Using excess [PNP]Cl, the salt $[PNP][Ag(CF_3)Cl]$ is formed.

$$AgCF_3 + [PNP]Cl \longrightarrow [PNP][Ag(CF_3)Cl]$$

It crystallizes in the triclinic space group $P$-1 ($a = 972.4$ ppm; $b = 1098.3$ ppm; $c = 1710.8$ ppm; $\alpha = 105.7°$; $\beta = 93.9°$; $\gamma = 102.2°$). The geometry of the anion is shown in Fig. 3.

## 2.3. Synthetic properties of $AgR_f$

Besides its known properties as an effective nucleophilic halide substitution reagent (Scheme 1), $AgR_f$ exhibits excellent properties as an oxidative perfluoroorganylating reagent as shown in Tables 1 and 2. All reactions have been carried out starting with $AgCF_3$ and $AgC_6F_5$ freshly prepared from $Me_3SiR_f$ and AgF as described above. Similar results have been obtained using $Ag(i\text{-}C_3F_7)$ — prepared via the route starting from AgF and hexafluoropropene [7,8] — and tellurium, zinc, cadmium or mercury.

$$nAgR_f + E \xrightarrow{EtCN} E(R_f)_n + nAg$$

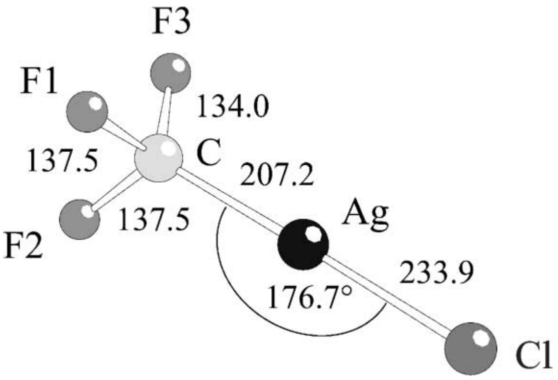


Fig. 3. Structure of the anion $[Ag(CF_3)Cl]^-$.

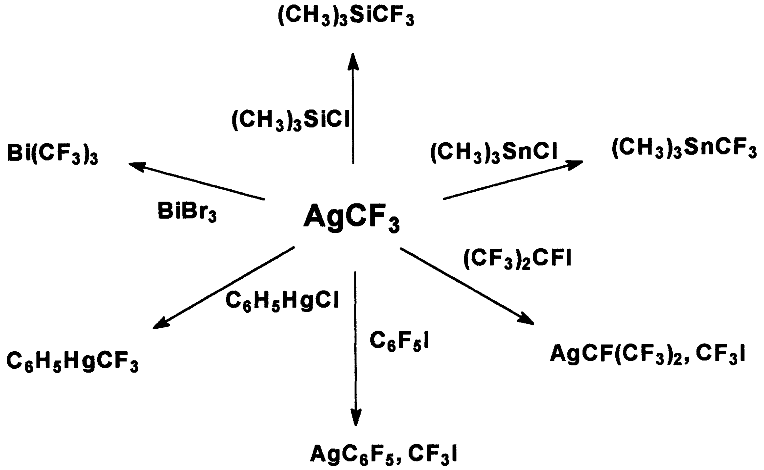
These results clearly demonstrate that $AgR_f$ is a versatile tool to prepare perfluoroorgano group 12–16 compounds directly from the elements without the use of halides or alkyl derivatives in better than common yields with formation of conveniently disposable elemental silver even at moderate temperatures.

## 2.4. Final remarks and conclusion

Oxidative additions of $R_fI$ to elemental indium in solution proceed via subvalent perfluoroorganoindium compounds. The reaction of $C_6F_5Br$ and InBr (or In and $0.5Br_2$) is a convenient route to $In(C_6F_5)Br_2\cdot 2THF$ which is used as a starting material for further investigations.

The reactions of AgF and $Me_3SiR_f$ open a new and convenient access to $AgR_f$ derivatives which are excellent tools in nucleophilic halide substitutions as well as oxidative additions.

These results offer a new access to highly reactive perfluoroorganylation reagents rather than a spoil of noble metals in synthesis since silver and silver halides can easily be recycled.



Scheme 1. Substitution reactions of $AgCF_3$.

Table 1
Conditions and products of transmetalations of group 12–16 elements and trifluoromethylsilver

| Element | Temperature (°C) | Reaction time (h) | Products | Yield (%) |
|---|---|---|---|---|
| Zn | 0 | 4 | $Zn(CF_3)_2 \cdot 2EtCN$ | 66 |
| Cd | 0 | 1 | $Cd(CF_3)_2 \cdot 2EtCN$ | 75 |
|  | 21 | 1 | $Cd(C_2F_5)_2$, $AgC_2F_5$, $C_2F_4$, $CF_3H$, F-polymers |  |
|  | 50 | 0.5 | $C_2F_4$, $CF_3H$, F-polymers |  |
| Hg | 21 | <0.12 | $Hg(CF_3)_2$ | 85 |
| Ga | 21 | 72 | $Ga[Ag^{III}(CF_3)_4]$ |  |
| In | 21 | 48 | $In(CF_3)_3 \cdot 2EtCN$ |  |
| Tl | 21 | 96 | $Tl^I[Ag^I(CF_3)_2]$ (85%), $Tl^I[Ag^{III}(CF_3)_4]$ (10%), $Ag[Tl^{III}(CF_3)_4]$ (5%) |  |
| Sn | 50 | 12 | $Sn(CF_3)_4$ |  |
| Pb | 50 | 24 | $Pb(CF_3)_4$ |  |
| As | 55 | 16 | $AsF_3$ (total decomposition) |  |
| Sb | 65 | 24 | $Sb(CF_3)_3$ |  |
| Bi | 65 | 24 | $Bi(CF_3)_3$ | 39 |
| Se | 50 | 16 | $Se(CF_3)_2$, $Se_2(CF_3)_2$, $AgSeCF_3$ |  |
| Te | 50 | 12 | $Te(CF_3)_2 \cdot EtCN$ | 75 |

Table 2
Conditions and products of transmetalations of group 12–16 elements and pentafluorophenylsilver

| Element | Temperature (°C) | Reaction time (h) | Product | Yield (%) |
|---|---|---|---|---|
| Zn | 21 | 4 | $Zn(C_6F_5)_2 \cdot 2EtCN$ | 77 |
| Cd | 21 | <0.12 | $Cd(C_6F_5)_2 \cdot 2EtCN$ | 62 |
| Hg | 21 | <0.12 | $Hg(C_6F_5)_2$ | 85 |
| Ga | 65 | 72 | $Ga(C_6F_5)_3 \cdot EtCN$ | 69 |
| In | 21 | 4 | $In(C_6F_5)_3 \cdot EtCN$ | 35 |
| Sn | 65 | 16 | $Sn(C_6F_5)_4$ | 92 |
| As | 21/65 | 48/8 | $As(C_6F_5)_3$ | 79 |
| Sb | 65 | 24 | $Sb(C_6F_5)_3$ | 88 |
| Bi | 50 | 24 | $Bi(C_6F_5)_3$ | 73 |
| Se | 50 | 16 | $Se(C_6F_5)_2$ | 73 |
| Te | 50 | 12 | $Te(C_6F_5)_2$ | 30 |

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