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# The First Organosilver(III) Fluoride, [PPh<sub>4</sub>][(CF<sub>3</sub>)<sub>3</sub>AgF]

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Dedicated to Dr. Milagros Tomás on the occasion of her 65th birthday

**Abstract:** Organosilver(III) fluoride complexes have been assigned a key role in different fluorination processes. To the best of our knowledge, however, none of them seem to have been isolated or even detected thus far. Here we report on the successful synthesis of the trifluoromethyl derivative [PPh<sub>4</sub>][(CF<sub>3</sub>)<sub>3</sub>AgF], which has been isolated in high yield. The thermodynamic stability of the Ag–F bond is shown by calculation and demonstrated by multistage mass spectrometry (MS<sup>n</sup>) under collision-induced dissociation (CID) conditions. Nevertheless, the substantial elongation found in the Ag–F bond (X-ray) is correlated with a marked nucleophilic character of the terminal F ligand. This Ag–F bond is, in fact, quite reactive: it suffers hydrolysis and is also solvolysed by thiols.

Silver-mediated fluorination of organic molecules is attracting much current interest in chemical synthesis owing to an advantageous combination of activity and selectivity.<sup>[1]</sup> The binary fluoride AgF<sub>2</sub> is known to behave as a strong fluorinating agent towards organic substrates.<sup>[2,3]</sup> Moreover, along with the monovalent binary fluoride AgF,<sup>[1,4]</sup> there is a number of Ag(I)mediated processes operating in the presence of electrophilic fluorinating reagents, where organometallic Ag(II) and mainly Ag(III) fluorides bearing both the Ag-C and Ag-F functionalities have been recently invoked as key intermediates (Scheme 1).<sup>[5,6]</sup> The fact that fluoride forms labile bonds with coinage metals makes this kind of compound very attractive from the reactivity point of view, but at the same time, difficult to isolate. As a matter of fact, no organosilver(III) fluoride seems to have been isolated or even detected to date.<sup>[7]</sup> This is in sharp contrast with the field of organogold fluorides, which emerged in the early years of the present century and is rapidly developing.<sup>[8]</sup> It is also worth noting that Ag(III) is the highest oxidation state currently available for silver.<sup>[9,10]</sup>

The only well-established organosilver fluorides of molecular nature reported to date,<sup>[11]</sup> namely (SIDipp)AgF and [{(SIDipp)Ag}<sub>2</sub>( $\mu$ -F)][BF<sub>4</sub>], contain silver(I) centres stabilized by NHC-ligands.<sup>[12]</sup> The lack of precedents in silver(III) chemistry can be ascribed to the unavailability of suitable synthetic methods, which is probably related to the higher lability of silver compared to gold. The substantially faster reaction kinetics usually achieved with silver together with its much lower price makes this 4d coinage metal a very attractive, promising and

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competitive system.<sup>[13]</sup> Interestingly, the importance of Ag(III) intermediates in silver-catalyzed C–X, C–C, C–N, and C–O cross-couplings was recently demonstrated.<sup>[14]</sup> The handful of organosilver(III) compounds currently known are only stabilized by either macrocyclic ligands<sup>[15]</sup> or by fluorinated methyl groups.<sup>[16]</sup> In fact, the non-fluorinated complexes [(CH<sub>3</sub>)<sub>3</sub>AgI]<sup>-</sup> and [(CH<sub>3</sub>)<sub>4</sub>Ag]<sup>-</sup> were found to be unstable.<sup>[17]</sup> On the other hand, aside from the paramagnetic phase Cs<sub>2</sub>KAgF<sub>6</sub>,<sup>[18]</sup> the known silver(III) fluorides are restricted to the binary compound AgF<sub>3</sub> and a number of salts of its diamagnetic [AgF<sub>4</sub>]<sup>-</sup> complex anion.<sup>[19]</sup> We report now on the synthesis and structural characterization of an organosilver(III) fluoride, which is, as far as we know, the first compound to incorporate both the Ag(III)–C and Ag(III)–F functionalities.



Scheme 1. Selected silver-mediated fluorination processes in which fluoride intermediates of high-valent silver have been invoked: a) Ref. [5a], b) Ref. [5b], c) Ref. [5c], d) Ref. [6].

Based on our previous experience, the CF<sub>3</sub> group was selected here to stabilize Ag(III).<sup>[16a]</sup> Access to the (CF<sub>3</sub>)<sub>3</sub>Ag fragment, however, was not so easy. The only reported procedure leading to an isolable compound of this organosilver(III) moiety, namely [N(PPh<sub>3</sub>)<sub>2</sub>][(CF<sub>3</sub>)<sub>3</sub>AgCl], relied on the intriguing precursor  $(CF_3)_3Ag \cdot NCMe$ ,<sup>[20]</sup> which was itself obtained in about 8% estimated yield.<sup>[16b]</sup> A better synthetic method was obviously needed. While working with the homologous gold system, we had previously found that the photoinduced oxidative addition of CF<sub>3</sub>I to the linear organogold(I) complex [CF<sub>3</sub>AuCF<sub>3</sub>]<sup>-</sup> cleanly afforded the square-planar organogold(III) derivative [(CF<sub>3</sub>)<sub>3</sub>Aul]<sup>-</sup> in high yield and under mild conditions.<sup>[21]</sup> In contrast, no reaction was observed by treating the organosilver(I) complex  $[CF_3AgCF_3]$  with  $CF_3I$  under various conditions (Scheme 2). This is also at variance with the recently reported oxidative addition of CH<sub>3</sub>I to the non-fluorinated complex [CH<sub>3</sub>AgCH<sub>3</sub>]<sup>-</sup>, which resulted in the highly unstable [(CH<sub>3</sub>)<sub>3</sub>AgI]<sup>-</sup>. The latter compound was detected (NMR and MS) but not isolated.  $\ensuremath{^{[17]}}$ 

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**Scheme 2.** Synthetic procedures to prepare complexes **1** and **2** in pure form. Full details are given in the Experimental Section (see Supporting Information). The cation is  $[PPh_4]^*$  in every case.

After much trial, a convenient method to prepare [PPh<sub>4</sub>][(CF<sub>3</sub>)<sub>3</sub>AgCl] (1) was found, which involved chlorination of the linear organosilver(I) complex [CF<sub>3</sub>AgCF<sub>3</sub>]<sup>-</sup> at low temperature (Scheme 2). A mixture of the desired species 1 and the stoichiometrically required [PPh<sub>4</sub>][AgCl<sub>2</sub>] was thereby obtained, which could be cleanly separated making use of the low solubility of the latter in DME (see Experimental). Once obtained and isolated, compound 1 was successfully transformed into the fluoro-complex [PPh<sub>4</sub>][(CF<sub>3</sub>)<sub>3</sub>AgF] (2) by treatment with AgF (Scheme 2). It is worth noting that all previous attempts to obtain or even detect this fluoro-complex using reasonable procedures and careful experimental conditions had failed.<sup>[16b,16d]</sup>

In solution, compound 2 has a very rich and characteristic  $^{19}\mathrm{F}$  NMR spectrum (Figure S3), where all the ligands provide information relating to their respective environments. The spectral pattern is best resolved at low temperature. The less shielded signal ( $\delta_F = -24.43$  ppm) corresponds to the CF<sub>3</sub> group located *trans* to the F ligand and the signal appearing at  $\delta_F$  = -37.60 ppm is assigned to the mutually trans CF<sub>3</sub> groups. These signals are more than 13 ppm apart, which denotes very different chemical and magnetic environments for each inequivalent CF<sub>3</sub> group. Finally, the terminal F ligand is highly shielded and gives rise to a complex upfield signal at  $\delta_F$  = -236.22 ppm.<sup>[22,23]</sup> All of these signals are mutually coupled and belong to the same spin system. Furthermore, they all show additional coupling to the <sup>107/109</sup>Ag nuclei of the central atom. Each pair of  ${}^{n}J({}^{107}Ag,F)$  and  ${}^{n}J({}^{109}Ag,F)$  coupling constants shows the appropriate relationship required by the ratio of the corresponding gyromagnetic constants:  $\gamma(^{109}Ag)/\gamma(^{107}Ag) \approx 1.15$ . The experimental spectrum has been satisfactorily simulated (Figure S4) with the parameters given in Table S2. The J(<sup>107/109</sup>Ag,F) value (60.8 / 69.9 Hz) is much lower than that observed in the inorganic complex anion [AgF<sub>4</sub>] (370.4 / 425.8 Hz)<sup>[23]</sup> suggesting that the Ag-F bond in compound 2 might be elongated (see below).

The crystal structure of **2**, as established by X-ray diffraction methods, consists of tetrahedral  $[PPh_4]^{*}$  and square-planar  $[(CF_3)_3AgF]^{-}$  (Figure 1) ions connected by a network of  $C(sp^2)-H\cdots F$ –Ag hydrogen bonds (Figure S16). A minimum  $H\cdots F$  distance of 221 pm and an associated C–H $\cdots$ F angle of 155.7° denote fairly strong interactions.  $^{[24]}$  This can contribute to the elongated Ag–F bond observed in the anion (198.41(10) pm) when compared to that found in the purely inorganic salt K[AgF\_4] (188.9(3) pm).  $^{[25]}$  Moreover, the presence of these noteworthy hydrogen bonds can be taken as evidence of substantial

nucleophilic character at the terminal F atom. Another factor contributing to the Ag–F bond elongation is of intrinsic character, namely the high *trans* influence of the CF<sub>3</sub> group.<sup>[26]</sup> The involved Ag–C distance (203.6(2) pm) is, in turn, substantially shorter than that corresponding to the mutually *trans* CF<sub>3</sub> groups (Ag–C 209.8(2) pm av.). The latter value exactly coincides with the mean value observed in the homoleptic derivative [PPh<sub>4</sub>][(CF<sub>3</sub>)<sub>4</sub>Ag].<sup>[16a]</sup> There is also excellent agreement between the structure of the [(CF<sub>3</sub>)<sub>3</sub>AgF]<sup>-</sup> anion experimentally found in crystals of **2** and that calculated in the gas phase by theoretical methods (DFT/M06). Our current results (Figure S17) are also in good agreement with previous calculations by Preiss and Krossing.<sup>[27]</sup>



**Figure 1.** Displacement-ellipsoid diagram (50% probability) of the  $[(CF_3)_3AgF]^$ anion as found in single crystals of **2**. Only the most populated set of the rotationally disordered F atoms found in every  $CF_3$  group is shown. Selected bond lengths [pm] and angles [°] with estimated standard deviations: Ag–F(10) 198.41(10), Ag–C(1) 210.02(18), Ag–C(2) 203.61(19), Ag–C(3) 209.63(18), C(1)–Ag–C(2) 90.50(8), C(1)–Ag–C(3) 177.42(7), C(1)–Ag–F(10) 89.22(6), C(2)–Ag–C(3) 89.35(8), C(2)–Ag–F(10) 179.46(7), C(3)–Ag–F(10) 90.91(6). A view of the C(sp<sup>2</sup>)–H···F–Ag hydrogen bonds is shown in Figure S16.

We wanted also to evaluate the thermodynamic strength of the Ag-F bond. With this purpose in mind, the most relevant decomposition paths that might be reasonably expected to operate on the [(CF<sub>3</sub>)<sub>3</sub>AgF]<sup>-</sup> anion at the unimolecular level were mapped by calculation (DFT/M06). The results are shown in Scheme S1 and summarized in Scheme 3. Non-reductive ionic dissociation of  $F^-$  is highly endergonic:  $\Delta G^0 = 74.5$  kcal/mol. This value is the reverse of the FIA corresponding to the (CF<sub>3</sub>)<sub>3</sub>Ag fragment, which thus appears as a molecular Lewis acid of considerable strength.<sup>[28]</sup> The overall thermodynamic balance for the concerted reductive elimination of CF<sub>4</sub> or C<sub>2</sub>F<sub>6</sub> is strongly favoured ( $\Delta G^0 < -52$  kcal/mol). These concerted processes, however, involve high activation barriers ( $\Delta G^* \sim 40$  kcal/mol) that might well hinder the occurrence of these single-step twoelectron reductions in favour of less energetically demanding paths. Radical dissociation of CF3 was found to be less endergonic in general and to exhibit significant stereochemical dependence. Thus, the energy required for radical dissociation of the CF<sub>3</sub> group *trans* to F is still rather high ( $\Delta G^0$  = 35.3 kcal/mol), in keeping with the short experimental Ag-C bond length: 203.61(19) pm. In contrast, dissociation of any of the mutually trans CF3 groups is substantially less endergonic  $(\Delta G^0 = 24.8 \text{ kcal/mol})$ , which nicely correlates with the appreciably longer Ag-C bonds found in this case (209.8(2) pm av.). Dissociation of a second CF3' from the resulting open-shell,

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T-shaped  $[(CF_3)_2AgF]^-$  transient species should be energetically inexpensive  $(\Delta G^0 = 1.1 \text{ kcal/mol})$ . Thus, following our calculations, we conclude that this two-step radical process should be the preferred decomposition path.



**Scheme 3.** Most relevant unimolecular fragmentation processes in  $[(CF_3)_3AgF]^-$  with calculated  $\Delta G^0$  ( $\Delta G^+$ ) values (kcal/mol). Dissociation of F at the first stage is less favored. There is no experimental evidence for  $CF_2$  extrusion. An unabridged mapping is given in Scheme S1.

The unimolecular fragmentation of the anionic complex  $[(CF_3)_3AgF]^-$  has been experimentally determined by multistage mass spectrometry (MS<sup>*n*</sup>) under collision-induced dissociation (CID) conditions. A very simple pattern is observed (Figure S8) consisting exclusively of the mixed organosilver(I) fluoride complex  $[CF_3AgF]^-$ . This pattern confirms our proposed dissociation based on the energy profiles calculated for the different decomposition paths (Scheme 3). It further demonstrates that the Ag–F bond in compound **2** has marked thermodynamic stability, at least in comparison with the accompanying Ag–C bonds.<sup>[29,30]</sup>

In the solid state, compound **2** is appreciably less stable (dec. 145 °C; Figure S14) than the homoleptic compound [PPh<sub>4</sub>][(CF<sub>3</sub>)<sub>4</sub>Ag] (dec. 188 °C)<sup>[16a]</sup> and much less so than its gold homologue [PPh<sub>4</sub>][(CF<sub>3</sub>)<sub>3</sub>AuF] (mp 180 °C, dec. 267 °C).<sup>[21]</sup> Upon thermolysis of **2** in the solid state, no sign of CF<sub>4</sub> or C<sub>2</sub>F<sub>6</sub> was observed, which is against a concerted mechanism. Instead, formation of CF<sub>3</sub>H together with trifluoromethylation of the [PPh<sub>4</sub>]<sup>+</sup> cation (Figure S15) are in keeping with CF<sub>3</sub> generation, thus favouring the radical path.<sup>[31]</sup> Furthermore, predominant formation of the homoleptic [(CF<sub>3</sub>)<sub>4</sub>Ag]<sup>-</sup> derivative (Figure S15) gives unequivocal proof for intermolecular processes operating in the condensed phase, which are necessarily absent in the gas phase.

The structural evidence for substantial nucleophilicity at the terminal fluoride ligand in **2** together with the ease with which it suffers hydrolysis (Figures S5 and S6) prompted us to explore its reactivity towards thiols, RSH. Representative R substituents were selected (Scheme 4) and, in all cases, reaction takes place under formation of the corresponding thiolato complexes [(CF<sub>3</sub>)<sub>3</sub>AgSR]<sup>-</sup> (**3–6**). These compounds, which were detected, but not isolated (see Supporting Information), consistently undergo elimination of the corresponding trifluoromethyl thioethers RS–CF<sub>3</sub> in good-to-excellent yields and under very mild conditions. Elimination proceeds readily at room temperature with the alkyl groups *n*-decyl and benzyl; in the case of the aryl groups C<sub>6</sub>H<sub>5</sub> and C<sub>6</sub>F<sub>5</sub>, it was greatly accelerated

by gentle warming (40 °C). Trifluoromethylation of thiols (or thiolate anions) can be accomplished by various existing procedures, which include the use of  $CF_3|^{[32]}$  or convenient surrogates thereof,  $CF_3|\cdot D,^{[33]}$  as well as different electrophilic trifluoromethylating reagents.<sup>[34]</sup> It is worth noting, however, that with our system even the 'deactivated' thiol  $C_6F_5SH$  is efficiently trifluoromethylated. Moreover, the experimental detection of the intermediate Ag(III) thiolate compounds **3–6** is of certain interest. To the best of our knowledge, the only compound bearing Ag(III)–S bonds reported to date is the neutral complex ( $CF_3$ )<sub>2</sub>Ag(S<sub>2</sub>CNEt<sub>2</sub>), the stability of which is likely enhanced by the  $\kappa^2S$ -didentate ligand.<sup>[16b]</sup>



**Scheme 4.** Solvolysis of **2** with thiols, RSH, and evolution of the resulting thiolato complexes (**3–6**) into the corresponding trifluoromethyl thioethers RSCF<sub>3</sub> under the conditions indicated (full details given in the Experimental Section). The cation is  $[PPh_4]^+$  in every case.

In summary, an unprecedented organosilver(III) fluoride complex, [PPh<sub>4</sub>][(CF<sub>3</sub>)<sub>3</sub>AgF] (**2**), has been prepared and isolated. This compound lends experimental support to several previous proposals on the existence of this interesting kind of chemical species operating in silver-mediated fluorination processes.<sup>[1,5]</sup> The Ag–F bond in **2** is strong, yet reactive. Although significantly elongated (Figure 1), it withstands harsh CID conditions in the gas phase, which gives proof of its strength. On the other hand, it suffers solvolysis with thiols, RSH, giving rise to the corresponding thiolato complexes [(CF<sub>3</sub>)<sub>3</sub>AgSR]<sup>-</sup>, which readily eliminate the corresponding RSCF<sub>3</sub> thioethers. Further experiments aiming to exploit the nucleophilic character of this terminal fluoride ligand are in progress.

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**Keywords**: fluorides • high oxidation state • organosilver(III) • thiols • trifluoromethylation

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Strong yet reactive: The Ag-F bond in the unprecedented organosilver(III) fluoride complex [(CF<sub>3</sub>)<sub>3</sub>AgF]<sup>-</sup> readily undergoes solvolysis with thiols giving rise to thiolato complexes, which themselves furnish RSCF<sub>3</sub> molecules under very mild conditions.

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