# Thermally Induced Elimination Reactions in Xerosols Derived from (Fluoroorgano)tin Compounds: A New Efficient Way To Prepare F-Doped Tin Dioxide Materials

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Trialkynyl(fluoroorgano)tins(IV) $(C_4H_9-C\equiv C)_3-SnR_F$ (**1**) ($R_F = -(CH_2)_2-CF_3$, $-o\text{-}FC_6H_4$) have been synthesized in three steps from tricyclohexyltin hydride or chloride and were characterized by multinuclear $^1H$, $^{13}C$, $^{19}F$, and $^{119}Sn$ NMR spectroscopy. Hydrolysis of **1** yielded oxo-hydroxoorganotin oligomers soluble in acetonitrile and alcohols, where each tin atom bears a fluorinated organic group. Thermally induced $\beta$- or $\gamma$-elimination reactions, evidenced by TG/MS measurements, allowed the insertion of fluorine into the oxide network and the removal of the undesirable organics. Densification at 550 °C gave crystalline particles of $SnO_2$ cassiterite containing the required amount of doping fluorine (4 at. %) and exhibiting an electronic resistivity (0.3 Ω·cm) lower than that previously reported (2−10 Ω·cm) for similar tin oxide materials. $\beta$- or $\gamma$-elimination processes in organotin compounds appear to be a suitable method of preparation of highly conductive nanocrystalline F-doped $SnO_2$ materials by the sol−gel route with low contaminating carbon content.

## Introduction

Chemically or thermally induced $\beta$- and $\gamma$-elimination reactions are usually undesirable processes in organotin chemistry when the metal is linked to an organic group bearing heteroatoms such as oxygen or halogens.[1] Most studies have focused on the organic products released by the reactions. It is indeed an efficient method to prepare alkenes of controlled stereochemistry[2] and cyclopropanes.[3] However, very few works have been devoted to highlight the organometallic counterpart. To our knowledge, it has only been used to generate organotin catalysts for silicone curing or polyurethane formation.[4] On the other hand, doped tin dioxide materials find widespread applications in various fields. As thin films, they are present in modern electronic devices such as I.R. reflectors, electronic displays, and solar cells.[5] Doped $SnO_2$ powders are used in preparation of transparent electrodes[6] and as antistatic coatings in paints or photographic films.[7] It has been shown that fluorine is the most efficient doping agent leading to the highest electronic conductivity and I.R. reflectivity,[5,8] but to our knowledge, no study has been conducted on the preparation of F-doped $SnO_2$ powders.

Among the different preparations described, the sol−gel process is well-suited to prepare oxide materials with very specific shapes and properties.[9] This method consists of hydrolysis and condensation reactions of molecular precursors preforming an oxide network that is densified by thermal treatment. The route that involves the use of alkoxide precursors appears to be the more versatile one,[10] but very few papers report on F-doped $SnO_2$ materials obtained by the sol−gel process.[11] We recently described alkoxyfluorodi($\beta$-diketonate)tin complexes, including the Sn−F bond, which are sol−gel precursors of conductive F-doped $SnO_2$ powders.[11b−c] However, the use of strong chelating $\beta$-diketonate ligands, necessary to obtain stable sols,[12]

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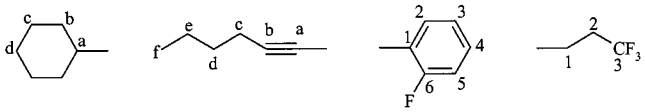
induced the presence of contaminating carbon in the final materials.[11c] An alternative to the route described above consists of the use of tin compounds with an organic group linked to the metal to provide good solubility of the hydrolyzed product and a source of tin−fluorine bond by thermal elimination. It should be a promising way both to introduce fluorine in tin oxide and to avoid polluting ligands.

Thus, the aim of this work was to prepare organotin compounds with three hydrolyzable groups and a $\beta$- or $\gamma$-fluorinated organic group capable of giving a fluorine−tin bond by an elimination reaction. Alkynyl substituents were selected as hydrolyzable groups for the ease of purification of the corresponding organotin by column chromatography on Florisil[13] instead of distillation at high temperature for liquid trialkoxytin derivatives, which could induce premature decomposition of the fluorinated chain. Tetraorganotins including $\beta$-substituted fluoroalkyl groups are known to be unstable at room temperature[14] whereas the decomposition temperature is higher (150−200 °C) when the chain is perfluorinated.[15] According to the literature, mono-[16] or polyfluorophenyltriorganotins[17] and 3,3,3-trifluoropropyltin compounds[18] seems to be more stable than the previous derivatives. Consequently, we hereafter describe the synthesis and the hydrolytic and thermolytic behaviors of new molecular precursors $(C_4H_9{-}C{\equiv}C)_3SnR_F$ (**1**) ($R_F$ = *o*-$FC_6H_4$, $-(CH_2)_2CF_3$) of F-doped $SnO_2$ materials.

## Experimental Section

**General Procedures, Starting Materials, and Instrumentation.** Diethyl ether, *n*-pentane, THF, and toluene were distilled from sodium benzophenone ketyl prior to use. Dichloromethane and *n*-hexane were distilled over $CaH_2$. Propan-2-ol was distilled over $CaSO_4$. All solvents were stored over activated 4-Å molecular sieves under an atmosphere of nitrogen in a glass storage vessel fitted with a high-vacuum PTFE stopcock. 3,3,3-Trifluoroprop-1-ene (Aldrich) and 1-bromo-2-fluorobenzene (Fluorochem) were used as purchased. Tricyclohexyltin chloride[19] and tricyclohexyltin hydride[20] were synthesized according to the literature methods.

Solution NMR analyses were performed on a Bruker AC-250 spectrometer or a Bruker DPX-200 spectrometer. $^1$H NMR spectra were recorded at 250 MHz (solvent $CDCl_3$) while $^{13}$C NMR spectra were obtained at 62.9 MHz (solvent $CDCl_3$). Chemical shifts were referenced using the *protio* impurities (at 7.24 and 77 ppm in $^1$H and $^{13}$C RMN, respectively) of the deuterated solvent. $^{119}$Sn NMR spectra were recorded at 74.6 MHz (solvent $CDCl_3$, reference $Me_4Sn$) and $^{19}$F NMR spectra at 188.3 MHz (solvent $CDCl_3$, reference $CFCl_3$). For NMR data, the multiplicity, coupling constants in Hz, and integration are given in parentheses. Tin−carbon coupling constants (Hz) are given in brackets. CP-MAS $^{119}$Sn NMR measurements were carried out on a Brucker DPX 400 ($B_0$ = 9.4 T, $\omega_0/2$ = 149.1514 MHz) NMR spectrometer. A standard $ZrO_2$ rotor (4 mm) was used. The spectra were obtained by using conventional Hartmann−Hahn cross-polarization with contact times of 25 ms, acquisition times of 17 ms, and recycle delays of 10 s. Exponential multiplication of 100 Hz was applied before Fourier transformation. Infrared spectra (KBr pellets or disks) were recorded in the absorption mode using a FTIR Perkin−Elmer spectrophotometer. Mass spectrometry data were collected with a VG Autospec-Q working in the electronic impact mode. Elemental analyses were performed in the Center of Chemical Analysis of the CNRS (Vernaison, France). The water content was determined by the classical Karl−Fischer method with short time contact to avoid the titration of surface hydroxyl functions. Gel permeation chromatography (GPC) data were collected on a Waters system (510-type pump and 410-type refractometer, eluent THF at 1 mL min$^{-1}$, TSK GMHXL column porosity 1500−10$^7$ Å). Average molecular weights were calculated using a third-order 12-points calibration curve obtained from polystyrene standards. The accuracy of the mass determination was checked with 3,3,3-trifluoropropyltricyclohexyltin.




**3,3,3-Trifluoropropyltricyclohexyltin (3a).** In a sealed tube, a mixture of tricyclohexyltin hydride (3.85 g, 10.4 mmol), 3,3,3-trifluoroprop-1-ene (4 g, 41.6 mmol), and AIBN (0.15 g, 0.9 mmol) was heated to 110 °C for 8 h. After cooling to room temperature, the white solids formed were dissolved in petroleum ether (200 mL) and the resulting solution was filtered. After solvent removal, the residue was recrystallized from absolute ethanol (100 mL) to give 4.09 g of white plates **3a** (yield: 85%): mp 163−165 °C.

$^1$H NMR ($CDCl_3$): $\delta$ 0.81 (part AA′ of a AA′$M_3$XX′ system, 2 H, $H_1$), 1.14−1.79 (m, 33 H, $H_{a,b,c,d}$), 2.10 (part XX′ of a AA′$M_3$XX′ system, 2 H, $H_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ −3 (q, $^3J_{C-F}$ = 2, [229], $C_1$), 26.5 ([336], $C_a$), 27.5 ($C_d$), 29.6 ([54], $C_c$), 31.9 (q, $^2J_{C-F}$ = 29, [11], $C_2$), 32.7 ([16], $C_b$), 127.7 (q, $^1J_{C-F}$ = 278, [66], $C_3$). MS-EI (*m*/*z*): 466 [M$^+$]; 383 [M$^+$ − $C_6H_{11}$]; 369 [M$^+$ − $C_3H_4F_3$]; 301 [MH$^+$ − $2C_6H_{11}$]; 218 [MH$^+$ − $3C_6H_{11}$]; 203 [M$^+$ − $2C_6H_{11}$ − $C_3H_4F_3$]. Anal. Calcd for $C_{21}H_{37}F_3Sn$: C, 54.22; H, 8.02; F, 12.25; Sn, 25.51. Found: C, 53.53; H, 8.07; F, 12.08; Sn, 26.72.

**2-Fluorophenyltricyclohexyltin (3b).** In a three-necked flask under nitrogen, 15 mL (37.5 mmol) of 2.5 M butyllithium in hexane was slowly added to a solution of 1-bromo-2-fluorobenzene (7 g, 40 mmol) in dry diethyl ether (165 mL) at −80 °C. After this mixture was stirred at this temperature for 1 h, a solution of tricyclohexyltin chloride (19.3 g, 48 mmol) in 100 mL of THF was slowly added and the temperature was held at −80 °C for 3 h. After hydrolysis with a saturated solution of $NH_4Cl$, the mixture was extracted with petroleum ether (250 mL) and the organic phase was treated with a saturated solution of KF to remove unreacted tricyclohexyltin chloride. After filtration, the organic layer was washed with water (2 × 100 mL), dried over magnesium sulfate, and concentrated under vacuum. The obtained solids were recrystallized from absolute ethanol (850 mL) to give 12.05 g (26 mmol; yield: 85%) of white crystals **3b**. mp 184−185 °C.

$^1$H NMR ($CDCl_3$): $\delta$ 1.2−2.2 (m, 33 H, $H_{a,b,c,d}$), 7.1 (m, 1 H, $H_5$), 7.2 (m, 1 H, $H_3$), 7.4 (m, 1 H, $H_4$), 7.5 (m, 1 H, $H_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 27.6 ([3], $C_d$), 27.9 ([354], $C_a$), 29.8 ([60], $C_c$), 32.7 ([16], $C_b$), 114.7 (d, $^2J_{C-F}$ = 29, [15], $C_5$), 124.4 (d, $^4J_{C-F}$ = 3, [30], $C_3$), 126.4 (d, $^2J_{C-F}$ = 48, [266], $C_1$), 130.5 (d, $^3J_{C-F}$ = 8, $C_4$), 138.3 (d, $^3J_{C-F}$ = 16, [14], $C_2$), 167.6 (d, $^1J_{C-F}$ = 235, [10], $C_6$). MS-EI (*m*/*z*): 464 [M$^+$]; 381 [M$^+$ − $C_6H_{11}$]; 299 [MH$^+$ − $2C_6H_{11}$]; 215 [M$^+$ − $3C_6H_{11}$]; 196 [M$^+$ − $3C_6H_{11}$ − F]. Anal. Calcd for $C_{24}H_{37}FSn$: C, 62.22; H, 8.05; F, 4.10; Sn, 25.62. Found: C, 61.84; H, 7.90; F, 4.23; Sn, 24.65.

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**3,3,3-Trifluoropropyltrichlorotin (2a).** To a solution of **3a** (15.32 g, 32.9 mmol) in 45 mL of dry dichloromethane was added slowly tin tetrachloride (8.57 g, 32.9 mmol) under nitrogen. The reaction mixture was then refluxed overnight. After evaporation of the solvent, the residue was extracted for 4 h with a 1:1 mixture of acetonitrile:*n*-pentane (220 mL). The phases were separated under nitrogen and the acetonitrile solution was extracted with *n*-pentane (3× 40 mL). All pentane phases were then washed with acetonitrile (3× 40 mL) and the acetonitrile phases were gathered. Evaporation of the acetonitrile gave the trichloride, which was distilled in a Kugelrohr apparatus (bp 40 °C (0.2 mmHg)). A colorless oil (6.93 g, 19 mmol) was thus obtained (yield: 58%).

$^1$H NMR ($CDCl_3$): $\delta$ 2.34 (part AA′ of a AA′$M_3$XX′ system, 2 H, $H_1$), 2.69 (part XX′ of a AA′$M_3$XX′ system, 2H, $H_2$). $^{13}$C-{$^1$H} NMR ($CDCl_3$): $\delta$ 22.2 (q, $^3J_{C-F}$ = 3, [771], $C_1$), 29.1 (q, $^2J_{C-F}$ = 31, [46], $C_2$), 126 (q, $^1J_{C-F}$ = 277, $C_3$). MS-EI (*m*/*z*): 287 [$M^+$ − Cl]; 267 [$M^+$ − Cl − F]; 225 [$M^+$ − $C_3H_4F_3$]; 155 [$M^+$ − 2Cl − $C_3H_4F_3$].

**2-Fluorophenyltrichlorotin (2b).** The same procedure as that used for **2b** was followed with a solution of 16.96 g (37 mmol) of **3b** in 140 mL of *n*-pentane and 10.71 g (41 mmol) of tin tetrachloride. The desired product was purified by distillation in a Kugelrohr apparatus (bp 100 °C (0.05 mmHg)) to yield 7.43 g (23 mmol) of a colorless oil (yield: 63%).

$^1$H NMR ($CDCl_3$): $\delta$ 7.7 (m, 1 H), 7.8 (m, 1 H), 8.0−8.1 (m, 2 H). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 116.4 (d, $^2J_{C-F}$ = 23, [57], $C_5$), 121.9 (d, $^2J_{C-F}$ = 34, $C_1$), 126.2 (d, $^4J_{C-F}$ = 3, [53], $C_3$), 134.7 (d, $^3J_{C-F}$ = 8, [37], $C_2$), 135.7 (d, $^3J_{C-F}$ = 16, [15], $C_4$), 164.4 (d, $^1J_{C-F}$ = 244, [13], $C_6$). MS-EI (*m*/*z*): 320[$M^+$]; 285 [$M^+$ − Cl]; 250 [$M^+$ − 3Cl]; 190 [$M^+$ − Cl − $C_6H_4F$]; 155 [$M^+$ − 2Cl − $C_6H_4F$].

**(3,3,3-Trifluoropropyl)trihex-1-ynyltin (1a).** In a three-necked flask under nitrogen, 8 mL (20 mmol) of 2.5 M butyllithium in hexane was slowly added at 0 °C to a solution of 1.83 g (22.3 mmol) of hex-1-yne in THF/toluene: 1/1 (16 mL). After the reaction mixture was stirred at room temperature for 20 min, it was cooled to −80 °C and 2 g (6.2 mmol) of **2a** dissolved in THF/toluene: 1/1 (20 mL) was added dropwise. The mixture was allowed to return to room temperature and was then heated at 60 °C overnight. After filtration over dried $MgSO_4$ under nitrogen and evaporation of the solvent, the crude product was purified by column chromatography on Florisil (eluent: $CH_2Cl_2$). A yellow liquid was isolated (2 g, 4.8 mmol). Yield: 77%.

$^1$H NMR ($CDCl_3$): $\delta$ 0.90 (t, [7], 9 H, $H_f$), 1.2−1.5 (m, 14 H, $H_1$, and $H_{e,d}$), 2.25 (t, [7], 6 H, $H_c$), 2.35 (m, 2 H, $H_2$). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 5.8 (q, $^3J_{C-F}$ = 3, [636], $C_1$), 13.5 ($C_f$), 19.7 ([15], $C_c$), 21.9 ($C_e$), 29.9 (q, $^2J_{C-F}$ = 31, [46], $C_2$), 30.5 ($C_d$), 75.9 ([893], $C_a$), 113 ([181], $C_b$), 127.3 (q, $^1J_{C-F}$ = 277, $C_3$). IR (KBr disks) $\nu$ ($cm^{-1}$) = 2963, 2937, 2875, 2162, 1595, 1467, 1440, 1430, 1320, 1264, 1206, 1173, 1113, 1064, 1025, 985, 952, 882, 830, 705. MS-EI (*m*/*z*): 379 [$M^+$ − $C_6H_9$]; 363 [$M^+$ − $C_3H_4F_3$].

**2-Fluorophenyltrihex-1-ynyltin (1b).** In a three-necked flask under nitrogen, 8 mL (20 mmol) of 2.5 M butyllithium in hexane was slowly added at 0 °C to a solution of 1.83 g (22.3 mmol) of hex-1-yne in THF (20 mL). After the solution was stirred at room temperature for 20 min, the resulting solution was transferred via cannula to a funnel and was added dropwise at −80 °C to 2.38 g (7.4 mmol) of **2b** dissolved in THF/toluene: 1/1 (60 mL). The mixture was allowed to return to room temperature and was then heated at 60 °C overnight. The same purification procedure as that used for **1a** was followed. A yellow liquid was thus obtained (2 g, 4.6 mmol). Yield: 62%.

$^1$H NMR ($CDCl_3$): $\delta$ 0.88 (t, [7], 9H, $H_f$), 1.4−1.6 (m, 12 H, $H_{e,d}$), 2.27 (t, [7], 6H, $H_c$), 7.07 (m, 1 H), 7.19 (m, 1 H), 7.42 (m, 1 H), 7.60 (m, 1 H). $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ 13.5 ($C_f$), 19.8 ([16], $C_c$), 21.8 ($C_e$), 30.4 ([9], $C_d$), 75.9 ([600], $C_a$), 112.7 ([200], $C_b$), 114.9 (d, $^2J_{C-F}$ = 25, [21], $C_5$), 121.5 (d, $^2J_{C-F}$ = 38, $C_1$), 124.6 (d, $^4J_{C-F}$ = 3, [63], $C_3$), 132.3 (d, $^3J_{C-F}$ = 8, $C_2$), 136.7 (d, $^3J_{C-F}$ = 12, [31], $C_4$), 166.5 (d, $^1J_{C-F}$ = 240, $C_6$). IR (KBr disks) $\nu$ ($cm^{-1}$) = 2959, 2933, 2872, 2162, 1595, 1576, 1545, 1468, 1439, 1390, 1325, 1260, 1211, 1107, 1060, 1018, 970, 945, 855, 818, 762, 550, 537. MS-EI (*m*/*z*): 458[$M^+$]; 377 [$M^+$ − $C_6H_9$]; 363 [$M^+$ − $C_6H_4F$]; 296 [$M^+$ − $2C_6H_9$]; 282 [$M^+$ − $C_6H_9$ − $C_6H_4F$]; 215 [$M^+$ − $3C_6H_9$]; 201 [$M^+$ − $2C_6H_9$ − $C_6H_4F$].

**Hydrolysis Experiments.** To stirred **1** or $Sn(C_6H_9)_4$, a mixture of $H_2O$/propan-2-ol was slowly added to reach a hydrolysis ratio *h* equal to 8. After the mixture was stirred for 15 min at room temperature, the solvent and the volatile hydrolysis products were removed. The resulting powders were washed with dried *n*-hexane until the washing residue was colorless.

*$X_1$*. **1a**: 1.82 g, 4 mmol. $H_2O$: 0.57 g, 32 mmol. Propan-2-ol: 5.77 g. After the solution was dried at 70 °C in vacuo, 1 g of a white powder was recovered.

Anal. Calcd for $(C_3H_4F_3)(C_3H_7O)_{0.1}Sn(OH)_{0.2}O_{1.35}\cdot 0.9H_2O$: C, 15.1; H, 2.6; F, 21.7; Sn, 45.1; $H_2O$, 6.2. Found: C, 15.2; H, 2.2; F, 21.6; Sn, 44.2; $H_2O$, 6.1.

*$X_2$*. **1b**: 2.10 g, 4.6 mmol. $H_2O$: 0.66 g, 36.63 mmol. Propan-2-ol: 6.62 g. After the solution was dried at 70 °C in vacuo, 0.83 g of a white powder was recovered.

Anal. Calcd for $(C_6H_4F)(C_3H_7O)_{0.1}Sn(OH)_{0.2}O_{1.35}\cdot 0.9H_2O$: C, 29.0; H, 2.6; F, 7.3; Sn, 45.5; $H_2O$, 6.2. Found: C, 28.9; H, 2.5; F, 6.8; Sn, 45.0; $H_2O$, 6.0.

**Thermolysis Experiments and Electrical Measurements.** Thermal analyses were carried out on a Netzsch STA simultaneous analyzer. Thermogravimetry (TG) and derivative thermogravimetry (DTG) analyses were recorded in the range 50−650 °C under helium at a heating rate of 10 °C $min^{-1}$. Mass analyses were performed on a Thermostar Balzers Instruments quadrupole spectrometer. Powder samples were placed in alumina crucibles. Electron impact mass spectra (70 eV) were continuously recorded and stored, with scans from 3 to 300 amu. Each scan was recorded in 0.5 s with a delay time of 0.1 s. The coupled configuration (TG/MS) allowed us (i) to identify the evolved gaseous species from the total ion current as a function of *m*/*z* curves obtained from a recorded scan and (ii) to follow the ion current of a single proper *m*/*z* value that may represent the evolution, as a function of the temperature, of a particular molecular species.

The elimination reactions were also characterized as follows. In a Schlenk tube, 500 mg of xerosol $X_1$ was heated at 300 °C for 2 h under nitrogen. The gases released were trapped in a graduated flask filled with water. After cooling to room temperature, 10 mL of thermolysis products was recovered. The gas collected was then analyzed by gas chromatography (Hewlett-Packard 5890 chromatograph; column DBXLB; 30 m, $d$ = 0.25 mm) coupled to mass spectrometry (VG autospec-Q; EI mode). Two main products were identified:

(1) 3,3,3-Trifluoroprop-1-ene (EI, *m*/*z*): 95 ($M^+$ − H); 77 ($M^+$ − F); 69 ($CF_3^+$); 51 ($CF_2H^+$); 27 ($C_2H_3^+$).

(2) 1,1-Difluorocyclopropane (EI, *m*/*z*): 77 ($M^+$ − H); 59 ($M^+$ − F); 51 ($MH^+$ − $C_2H_4$); 27 ($C_2H_3^+$).

Xerosols $X_1$ and $X_2$ were calcined in air at 550 °C for 15 min. Crystallinity of the powders was determined by powder X-ray diffraction using a Philips $\theta-2\theta$ PW1820 diffractometer. The sample resistivity was estimated by compacting under pressure (10 ton) a given amount of powder (200 mg) between two stainless steel cylinders. The resistance $R_s$ of the pelletized materials (13-mm diameter, 0.42-mm thickness) was measured with a Rhopoint M210 Milli-ohmeter, under pressure (0.5 ton), using the previous cylinders as contacts. The sample resistivity $\rho_s$ was deduced from $R_s$ by the simple formula $\rho_s = SR_s/e$ where $S$ and $e$ are the surface and the thickness of the sample, respectively.

## Results and Discussion

**Synthesis and Characterization of the Precursors.** Compounds **1** were obtained by treatment of the corresponding trichloroorganotins **2** with 3 equiv of hex-1-ynyllithium,[13,21] as presented in Scheme 1. In the case of the aromatic compound, hex-1-ynyllithium had to be

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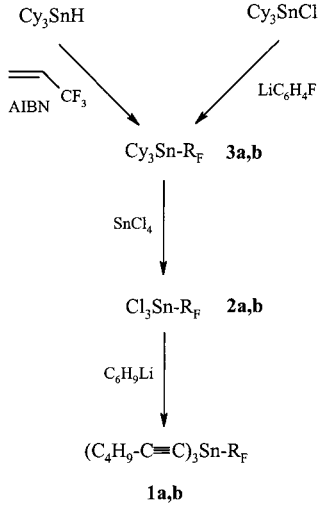
**Scheme 1. Synthetic Pathway toward Trialkynyl(fluoroorgano)tin(IV) 1**




slowly added to **2b**, the reverse procedure leading to decomposition products. Purification by column chromatography on Florisil gave analytically pure products in good yields (55−75%).

As far as compounds **2** are concerned, the synthesis of 3,3,3-trifluoropropyltin trichloride was already reported in the literature.[18a] However, it was isolated from a redistribution reaction between tin tetrachloride and tetrakis(3,3,3-trifluoropropyl)tin with the concomitant formation of an equimolar amount of tris(3,3,3-trifluoropropyl)tin chloride as the byproduct. As this method leads to the waste of the fluorinated chains, monoorganotins **2** were more conveniently prepared[22] from functional tricyclohexyltins **3** and tin tetrachloride. Purification by distillation under high vacuum produced the desired products in good yields (55−65%).

Derivatives **3** were obtained by hydrostannation of 3,3,3-trifluoroprop-1-ene by tricyclohexyltin hydride, either in the presence of a radical initiator or under UV irradiation, or by coupling of 2-fluorophenyllithium with tricyclohexyltin chloride. In the latter case, the substitution reaction must be conducted at −80 °C to avoid elimination processes producing benzyne. The addition product of **3b** on benzyne was indeed isolated in experiments driven at −30 °C or above. After recrystallization in absolute ethanol, tetraorganotins **3** were obtained in high yields (65−85%).

Compounds **1**−**3** were characterized by multinuclear NMR studies (Table 1). $^{119}$Sn NMR chemical shift values are in good agreement with those expected.[22,23] Resonances of trialkynides **1** are thus more shielded than those of tricyclohexylorganotins **3**, signals of trichlorides **2** showing the most pronounced downfield shift. Likewise, compounds bearing the *o*-fluorophenyl group exhibit more shielded resonances than the analogues including the 3,3,3-trifluoropropyl chain. In the $^{119}$Sn NMR spectra, the key feature is the hyperfine structure

**Table 1. $^{119}$Sn and $^{19}$F NMR Data of Compounds 1, 2, and 3**

| | $\delta$ $^{119}$Sn (ppm)[a] | $\delta$ $^{19}$F (ppm) | $J_{^{119}Sn-^{19}F}$ (Hz)[b] |
|---|---|---|---|
| **3a** | −67(s) | −70 | unresolved |
| **3b** | −87(d) | −92 | 112 |
| **2a** | −16(s) | −68 | unresolved |
| **2b** | −63(d) | −93 | 138 |
| **1a** | −244(q) | −69 | 7 |
| **1b** | −291(d) | −93 | 127 |

[a] s, singlet; d, doublet; q, quartet. [b] Determined from $^{119}$Sn NMR spectra.

due to $^{3,4}J$ ($^{119}$Sn−$^{19}$F) couplings observed for most compounds studied. Only a few examples of $^{119}$Sn−$^{19}$F couplings through more than one bond were described.[18b,24] In the 3,3,3-trifluoropropyl series, an unusual long-range coupling constant $^4J$ was measured for **1a**, with a value slightly larger than those already reported for similar analogues.[18b] Also, $^3J$($^{119}$Sn−$^{19}$F) coupling constants larger than 100 Hz were determined in the *o*-fluorophenyl series, with values 1 order of magnitude higher than those reported through saturated squeleton[24a,b] and similar to $^3J$($^{119}$Sn−$^1$H) coupling measured in phenyltin derivatives.[23] The $^{19}$F NMR chemical shifts of **1**−**3a** are equal to the one of trifluoropropane.[25] In contrast, those of **1**−**3b** are more than 10 ppm deshielded compared to the $\delta$ values tabulated for *o*-substituted benzene.[26]

Intramolecular coordination of tin by a heteroatom, such as oxygen, located on a substituent of the metal atom, has been demonstrated in the case of trichlorostannyl ester and alcohols.[22,27] However, the same phenomenon with fluorine is not well-documented. In the case of the 3,3,3-trifluoropropyl group, the NMR data are not consistent with a coordination of the tin atom by fluorine groups as already underlined by Williams et al.[18b] This type of interaction cannot be completely excluded in the *o*-fluorophenyl series because a strong shift of the $^{19}$F chemical shift was observed.

**Hydrolytic Behavior and Characterization of the Xerosols.** Compounds **1** were hydrolyzed in propan-2-ol according to the conditions settled in the case of functional trialkynyltins.[13] After evaporation of the solvent and the volatile hydrolysis products, two xerosols $X_1$ and $X_2$ highly soluble in polar or coordinating solvents such as acetonitrile, tetrahydrofuran, and alcohols were obtained. Indeed, the lower functionnality of **1** compared to tin molecules with hydroxyl groups or ligands[11b,12] allowed condensed species exhibiting remarkable solubility properties to be prepared. To establish the nature of the condensed species formed, the IR, NMR, and TGA data of the as-prepared xerosols were collected.

In Figure 1 is shown the IR spectrum of $X_1$, which indicates the tin−alkynyl bond cleavage and the concomitant formation of Sn−OH and Sn−O−Sn bonds. Indeed, the strong −C≡C− stretching vibration at 2162

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(27) Biesemans, M.; Willem, R.; Damoun, S.; Geerlings, P.; Lahcini, M.; Jaumier, P.; Jousseaume, B. *Organometallics* **1996**, *15*, 2237.

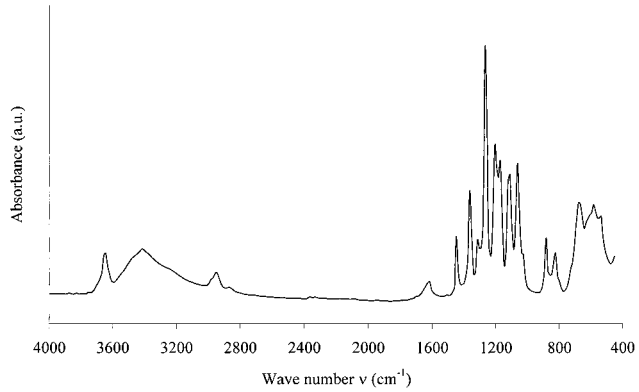


**Figure 1.** FTIR spectrum of xerosol $X_1$ after drying.

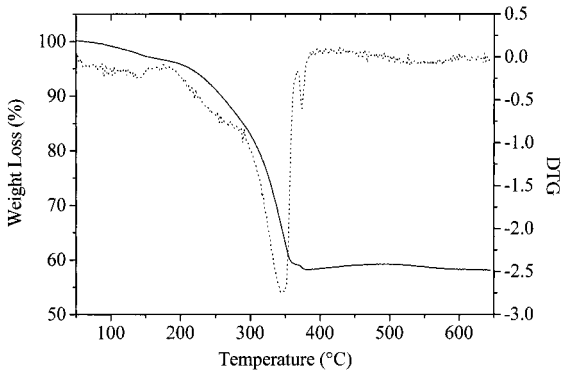


**Figure 2.** TGA plot of xerosol $X_1$ between 50 and 650 °C recorded at 5 °C $min^{-1}$.

$cm^{-1}$ observed in the starting material **1a** disappeared completely and broad bands are found in the Sn−O stretching region (700 and 500 $cm^{-1}$).[28] Stretching modes at 3650 $cm^{-1}$ (sharp) and 3415 $cm^{-1}$ (very broad) are consistent with the presence of isolated and hydrogen-bonded surface hydroxyl groups, respectively, the corresponding deformation modes being centered at 1620 $cm^{-1}$.[29] Moreover, the peaks related to the C−H bond stretching centered at 2951 $cm^{-1}$, to the bending of the C−H bond in $CH_2$ at 1442 and 1361 $cm^{-1}$, and to the C−F bond stretching in $CF_3$ in the 1300−1150-$cm^{-1}$ region accounts for the presence of the 3,3,3-trifluoropropyl chain. The fluorinated group therefore seems to remain unaffected by the hydrolysis−condensation process. This was confirmed by the solution $^{19}F$ NMR spectrum recorded in $CD_3CN$, which exhibits broadened resonances around −69 ppm in the same chemical shift range as that for **1a,** and by elemental analysis, which yields the following atomic ratios F/Sn = 3.05 and C/Sn = 3.4. As shown in the next section, the slight excess of carbon found is likely due to the small amount of propan-2-oxy groups remaining in $X_1$. Consequently, according to the microanalysis, the following formula $(C_3H_4F_3)(C_3H_7O)_{0.1}Sn(OH)_{0.2}O_{1.35}\cdot 0.9H_2O$ may be proposed for xerosol $X_1$. This formula is in rather good agreement with the TG results. Indeed, TG−DTG of the xerosol carried out in air showed a mass loss occurring in three successive steps of 5.1, 34.2, and 2.1%, centered at 110, 295, and 420 °C, respectively, to give a final residue of 58.6% (expected: 57.3%).

As far as $X_2$ is concerned, the atomic ratios F/Sn = 0.95 and C/Sn = 6.3 were found by elemental analysis and a broad resonance around −93 ppm, close to the one of the precursor **1b**, was obtained by $^{19}F$ NMR spectroscopy. As for $X_1$, bands characteristic of Sn−OH and Sn−O−Sn stretching vibrations were detected by IR spectroscopy but, also, these of the *o*-fluorophenyl group at 3065 $cm^{-1}$ ($\nu$(C−H)), at 1594, 1577, 1469, and 1437 $cm^{-1}$ ($\nu$(C═C)), at 1208 $cm^{-1}$ ($\nu$(C−F)), at 1107 and 1054 $cm^{-1}$ ($\delta_{In-plane}$(C−H)), and at 756 $cm^{-1}$ ($\delta_{Out-of-plane}$-(C−H)). Consequently, taking into account that the small excess of carbon is probably due to propan-2-oxy groups, the following formula $(C_6H_4F)(C_3H_7O)_{0.1}Sn(OH)_{0.2}O_{1.35}\cdot 0.9H_2O$ can be proposed for $X_2$. The TG−DTG of $X_2$ carried out in air exhibited a continuous mass loss of 39.8% centered at 242 °C, to give a final residue of 60.2%, close to the one expected (57.9%).

To determine the coordination of the tin atom, solution $^{119}Sn$ NMR analyses were tentatively made, but the species formed gave no resonance. The latter could be ill-defined oligomeric or polymeric entities, which are not observed by solution $^{119}Sn$ NMR because of their long reorientation times.[30] CP-MAS $^{119}Sn$ NMR measurements were therefore performed on $X_1$. The spectrum, which is poorly resolved, exhibits two isotropic chemical shifts associated with their pattern of spinning sidebands. The major one is located around − 370 ppm and the minor at − 430 ppm, values falling into the region of five- or six-coordinate monoalkyltin atoms. Thus, the oxo-hydroxobutyltin cluster $\{(BuSn)_{12}O_{14}(OH)_6\}(OH)_2$ is characterized in solid-state $^{119}Sn$ NMR by two resonances at −280 and −450 ppm, which were ascribed to five- and six-coordinate tins, respectively.[31]

On the basis of GPC investigations, the average molecular weight of the species obtained was estimated to be 900 and 700 (±10% error) for xerosols $X_1$ and $X_2$, respectively. These values would indicate that these species would contain around three or four tin atoms. In summary, within experimental uncertainties, all the results are consistent with the formation of oxo-hydroxoorganotin entities, each tin atom being linked to a 3,3,3-trifluoropropyl or a *o*-fluorophenyl group.

**Xerosol Pyrolysis.** To study the conversion of the xerosols into densified powders, the pyrolysis of $X_1$ and $X_2$ was followed under helium flow by thermogravimetry coupled to mass spectrometry, an efficient technique to draw the reactions involved during the pyrolysis and the nature of the organics in sol−gel materials.[32]

Under these conditions, the TG analysis of $X_1$ shows a continuous mass loss from 50 to 650 °C (Figure 2). Four mass losses, the second being the most conspicuous, were observed on TG traces and the main molecules detected by MS measurements were water ($m/z$ = 18), hydrofluoric acid ($m/z$ = 20), carbon dioxide ($m/z$ = 44), propan-2-ol ($m/z$ = 60), 1,1-difluorocyclopropane ($m/z$ = 77), and 3,3,3-trifluoroprop-1-ene ($m/z$ = 96) (Table 2).

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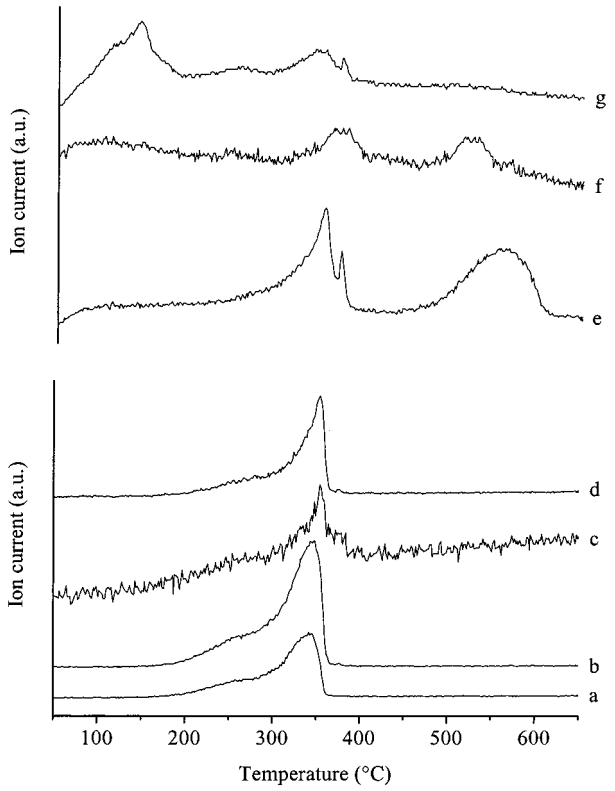



**Figure 3.** Xerosol $X_1$ *m*/*z* curves as a function of temperature. (a) 96 ($CF_3CHCH_2$); (b) 77 ($CF_2CH_2CH_2$); (c) 60 ($CH_3CHOHCH_3$); (d) 59; (e) 44 ($CO_2$); (f) 20 (HF); (g) 18 ($H_2O$).

**Table 2. TGA Coupled with MS Data for Xerosol $X_1$**

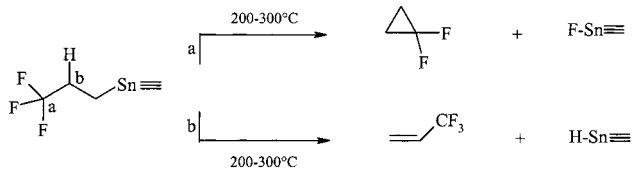
| pyrolysis step | sampling temperature (°C) | mass loss intensity (%) | species detected |
|---|---|---|---|
| I | 140 | 4 | $H_2O$ |
| II | 345 | 36.1 | $H_2O$, HF, $CO_2$, $C_3H_7OH$, $C_3H_4F_2$, $C_3H_3F_3$ |
| III | 375 | 0.7 | HF, $CO_2$, $CF_3OH$ |
| IV | 530 | 1.8 | HF, $CO_2$ |

In addition, no significant amount of ion fragment *m*/*z* = 81 was detected, confirming that most of the alkynide groups were removed upon hydrolysis.

The first weight loss at 140 °C is mainly assignable to the release of $H_2O$, probably trapped into the porosity of the xerosol, despite the drying step at 70 °C under vacuum (Figure 3g). The second contribution to the release of water occurs at 345 °C and probably comes from the condensation of Sn−OH moieties with the formation of oxo bridges, as was proposed in the case of gels prepared from modified zirconium *n*-butoxide.[32b]

The large mass loss at 345 °C mainly corresponds to the elimination of the fluorinated chain as evidenced by the 96 *m*/*z*, 77 *m*/*z*, and 59 *m*/*z* ions versus temperature profiles (Figure 3a, b, and d). The two first ion fragments are characteristic of 3,3,3-trifluoroprop-1-ene and the two last are consistent with the formation of 1,1-difluorocyclopropane. The formation of the former product can be rationalized by postulating a $\beta$-elimination of hydrogen, leading to the creation of Sn−H bonds, which could rapidly decompose into Sn−O bonds in the presence of water at such temperature. On the other hand, $\gamma$-elimination of fluorine induces the formation of Sn−F bonds and 1,1-difluorocyclopropane (Scheme 2). With the aim to assess this interpretation, xerosol $X_1$

**Scheme 2. Thermolysis Products of Xerosol $X_1$ Treated at 300 °C**




was thermolyzed for 2 h at 300 °C and the nature of the released gases was checked by gas chromatography coupled to mass spectrometry. As expected, two main products were detected, 3,3,3-trifluoroprop-1-ene and 1,1-difluorocyclopropane in about a 2/3 molar ratio. At this stage, it can be concluded that $\gamma$-elimination of fluorine does take place and starts from 200 °C according to Figure 3b. It must also be underlined that although this elimination was not the only reaction, it took place at a sufficient rate for introducing a suitable amount of fluorine imparting low resistivity to tin dioxide materials. In addition, propan-2-ol was released from 200 to 350 °C as shown by the 60 *m*/*z* ion versus temperature profile (Figure 3c). This rather high-temperature process is in favor of the presence of propan-2-oxy groups in the xerosol, which validates the chemical formula proposed for $X_1$ (see above). The origin of such tin substituents can be rationalized by postulating an alcoholysis reaction occurring between propan-2-ol and Sn−alkynyl bonds during the hydrolysis step.[13]

The minor, but well-defined, mass loss at 375 °C can be ascribed to the departure of carbon dioxide and hydrofluoric acid. Finally, residual carbon (as $CO_2$) and fluorine (as HF) releases are responsible for the last mass loss around 530 °C (Figure 3e,f).

According to Figure 3e, fluorine loss occurs as hydrofluoric acid in two steps, around 350 and 530 °C, respectively. The former is associated with the decomposition of the fluoroorganic chain whereas the latter is probably due to the hydrolysis of the Sn−F bonds, generated by the $\gamma$-elimination reaction, in the presence of traces of water as was recently pointed out for xerosols prepared from alkoxyfluorodi($\beta$-diketonate)tin complexes.[33] In this respect, it is worthwhile to note that this process is catalytic because it gives rise to Sn−OH groups, which react via an oxolation reaction to form water again. Detection of fluorine after the complete removal of the organic chain is therefore in favor of the creation of Sn−F bonds via a $\gamma$-elimination reaction.

The thermolytic behavior of $X_2$ is noticeably different from the previous one. The TG analysis of $X_2$ indeed indicates a continuous loss from 50 to 650 °C, with a maximum at 290 °C, without different stages being clearly distinguished. MS measurements revealed the removal of water, carbon dioxide, propan-2-ol, benzyne (*m*/*z* = 76), and *o*-fluorobenzene (*m*/*z* = 96) but, surprisingly, neither fluorine nor hydrofluoric acid was detected. In Figure 4 is shown the 96, 76, and 60 ion fragment versus temperature profiles, allowing the TG/DTG data to be highlighted.

As for $X_1$, propan-2-oxy groups are likely present in $X_2$. The stricking feature is the loss of the fluorinated aromatic unit as fluorobenzene and benzyne, a process

(33) Gamard, A.; Babot, O.; Jousseaume, B.; Rascle, M.-C.; Toupance, T.; Campet, G. *Chem. Mater.*, in press.

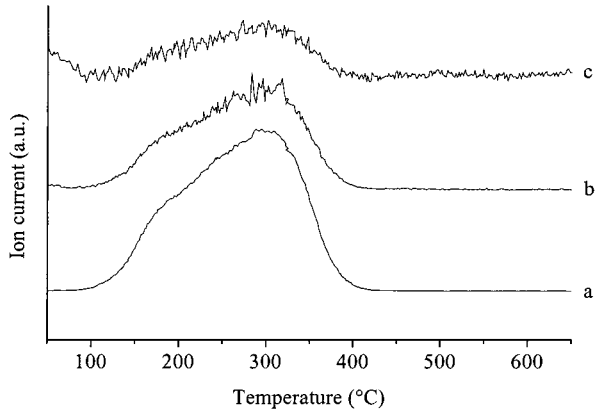



**Figure 4.** Selected *m/z* curves as a function of temperature for xerosol $X_2$. (a) 96 ($C_6H_5F$); (b) 76 ($C_6H_4$); (c) 60 ($CH_3$-$CHOHCH_3$).

starting from a relatively low temperature, i.e., 100 °C. Consequently, partial decomposition of the aromatic unit during the drying step could account for the slight lack of fluorine in $X_2$ pointed out by elemental analysis. In comparison with the behavior of $X_2$, these findings may be interpreted, on one hand, by the lower stability of the Sn−$C_{ar}$ bond susceptible to cleavage by the Sn−OH group and, on the other hand, by $\beta$-elimination reactions, which are known to occur at lower temperatures than $\gamma$-elimination. Thus, benzyne would come from $\beta$-fluoride elimination, even if, in contrast to $X_2$, TG/MS measurements did not provide clues about the creation of Sn−F bonds. It must also be remarked that pyrolysis of the organics takes place over a wide temperature range, i.e., from 100 to 350 °C, which is consistent with the rather slow reaction at low temperature.

**Characterization of the Calcined Xerosols.** Crystallization of tin dioxide particles is a prerequisite to obtain highly conductive F-doped materials.[7,11b] In the case of powders prepared by the sol−gel route, thermal treatment below 400 °C gave poorly crystallized materials.[11b] With xerosols $X_1$ and $X_2$, annealing at 550 °C for 15 min led to the formation of crystalline materials. X-ray patterns of the resulting powders are characteristic of nanocrystalline particles of $SnO_2$ cassiterite (Figure 5).[34] The crystalline domains were estimated to be 7 nm by using the conventional Laue−Scherrer formula.[35] Transmission electron micrographs (TEM) show agglomerated nanoparticles with sizes in general agreement with the XRD determinations. It must also be noted that there was considerable distribution in size and that many particles exhibited irregular shapes.

Resistance measurements were then performed to estimate the conductivity of the materials (Table 3). Thermally treated xerosols $X_1$ and $X_2$ exhibited resistivity several orders of magnitude lower than that measured for commercial $SnO_2$ (Aldrich) powders, which can be explained by the migration of fluorine toward tin atoms in the materials through $\beta$- or $\gamma$-elimination

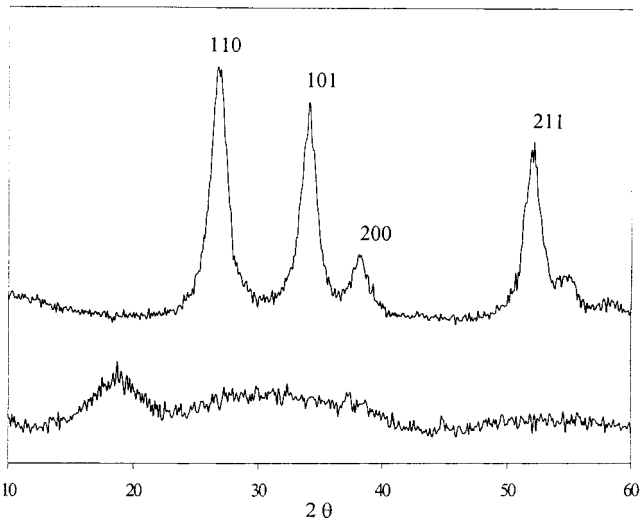



**Figure 5.** X-ray diffraction patterns of xerosol $X_1$ after thermal treatment at bottom (50 °C) and top (550 °C).

**Table 3. Resistivity $\rho$, Crystallite Size ($t$), and Composition of the Different $SnO_2$ and F:$SnO_2$ Materials Studied (All Materials Were Treated at 550 °C and the Atomic Ratios F/Sn and C/Sn Were Determined by Elemental Analysis)**

| precursor | xerosol | $\rho$ (Ω·cm) | $t$ (nm)[a] | F/Sn | C/Sn | ref |
|---|---|---|---|---|---|---|
| **1a** | $X_1$ | 0.3 | 7 | 0.05 | <0.03 | *b* |
| **1b** | $X_2$ | 10 | 7 | 0.04 | <0.03 | *b* |
| $SnF(OR)(acac)_2$ | *c* | 0.8 | 8 | 0.06 | 0.12 | 11c, 33 |
| $SnO_2$ (Aldrich) | | $2 \times 10^3$ | 50 | | | *b* |

[a] Determined according to ref 35. [b] This study. [c] The xerosol was obtained according to a procedure described in ref 11c.

reaction. Atomic F/Sn ratios of 0.05−0.04 found by elemental analysis were in the range of the best doping amount, leading to the highest conductivity.[36] Another stricking feature of these results was the low carbon amount of these powders, less than 4 times lower than that in materials prepared from alkoxyfluorodi($\beta$-diketonate)tin complexes.[11c] In this respect, these results corroborate the approach chosen, which involves a well-defined elimination reaction favoring the clean removal of the organics during the pyrolysis.

Xerosol $X_1$ treated at 550 °C gave rise to the lowest resistivity ever reported for F-doped $SnO_2$ powders.[11b−c] Besides, the resistivity of this highly conductive nanocrystalline F-doped $SnO_2$ powder was 1 order of magnitude lower than that described for Sb-doped $SnO_2$ powders.[7] The higher resistivity measured in the case of xerosol $X_2$ was quite unexpected because the chemical composition was close to the one described for xerosol $X_1$. It could be due to the differences between $X_1$ and $X_2$ found for the fluorine loss by TG/MS analyses.

## Conclusions

New trialkynyl(fluoroorgano)tin(IV) ($C_4H_9$−C≡C)$_3$−$SnR_F$ ($R_F$ = $C_3H_4F_3$, *o*-$FC_6H_4$) **1** compounds have been synthesized and characterized by multinuclear NMR spectroscopy. Hydrolysis−condensation processes removed the alkynide groups without affecting the Sn−$R_F$ bond and provided soluble oxo-hydroxo stannic

(34) Powder diffraction file; J.C.P.D.S. International Center for Diffraction Data: Swarthmore, PA, 1997; no. 41-1445.

(35) The mean particle size is deduced from the bandwidth of the different peaks. See ref 11b and also Eberhardt, J. P. *Structural and Chemical Analysis of Materials*; John-Wiley & Sons: New York, 1991; p 203.

(36) The best doping amount is comprised between 1 and 8 at. % F per Sn atom. See ref 8 and also Fantini, M.; Torriani, I. *Thin Solid Films* **1986**, *138*, 255.

oligomers endowed with fluorinated organic groups after solvent removal.

TG/MS measurements afforded some insights into the reactions occurring during the pyrolysis step of these oxide species: (1) the trifluoropropyl chain is released from 200 to 350 °C as 3,3,3-trifluoroprop-1-ene and 1,1-difluorocyclopropane; (2) the *o*-fluorophenyl unit thermolyzes from a lower temperature, 100 °C, as *o*-fluorobenzene and benzyne; (3) in the case of the 3,3,3-trifluoropropyl unit, hydrofluoric acid is emitted in two stages around 350 and 530 °C, respectively. These results demonstrate that thermolysis of the xerosols resulted in $\beta$- or $\gamma$-elimination reactions, leading to the insertion of fluorine in the tin dioxide network.

The sample thermally densified in air at 550 °C gave nanocrystalline particles of $SnO_2$ cassiterite including the required amount of doping fluorine and exhibiting electronic resistivity lower (0.3 Ω·cm) than that previously reported for similar tin oxide materials (2−10 Ω·cm). The approach developed in this paper, which exploits well-defined thermally induced elimination reactions, appears to be a suitable preparation method of highly conductive nanocrystalline F-doped $SnO_2$ materials by the sol−gel route with a low content of contaminating carbon. The solubility of the xerosol obtained after hydrolysis should allow one to prepare F-doped $SnO_2$ thin films by dip- or spin-coating techniques.

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