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The synthesis of organoantimony(III) difluorides containing Y,C,Y pincer type ligands using organotin(IV) fluorinating agents

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Abstract

The organoantimony(III) difluorides containing Y,C,Y-chelating, so called pincer, ligands ([2,6-$(YCH_2)_2C_6H_3$]SbF_2; Y = MeO, *t*-BuO and Me_2N) were prepared by the reaction of corresponding dichlorides ([2,6-$(YCH_2)_2C_6H_3$]$SbCl_2$; Y = MeO, *t*-BuO and Me_2N) with two equivalents of organotin(IV) fluorinating agents Me_3SnF or 2-$(Me_2NCH_2)C_6H_4Sn(n\text{-}Bu_2)F$, respectively. The structure of organonantimony fluorides was determined both in solution by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy and in the solid state using X-ray diffraction.

Keywords: Antimony; Fluorine; Tin; Chelating ligand; X-ray structure

1. Introduction

Organometallic fluorides represent an area attracting considerable interest and results obtained have been reviewed several times [1–4]. Although the chemistry of main group organometallic fluorides is extensively explored by many groups, examples of organometallic fluorides containing heavier pnictogens in particular organoantimony and organobismuth are scarce [1]. Most organoantimony and organobismuth fluorides reported to date contain pentavalent central atoms [1]. These compounds were usually prepared by halide-exchange reactions using KF and AgF [5–10] or by oxidation of trivalent precursors with XeF_2 [11–14].

Synthesis and structural characterization of trivalent organoantimony and organobismuth fluorides remain rare and most examples constitute diorgano-compounds of the type R_2MF (R = carbon bound group, M = Sb, Bi). Organoantimony(III) fluorides were prepared by a halide-exchange reaction (Fig. 1A) [15] or by a conversion between SbF_3 and organolithium compounds [16,17] (Fig. 1B and C). The structure of Ph_2SbF was determined by X-ray diffraction (XRD) in the solid state, where this compound forms infinite chains through fluorine bridges (Fig. 1B) [16]. Among bismuth congeners, C,N,C-chelated compounds (Fig. 1A) represent the only examples of characterized organobismuth(III) fluorides to date; one of these compounds was studied by XRD in the solid state, forming a dimeric structure *via* hydrogen bonds between fluorine atoms and a coordinated water molecule [18]. Formation of organobismuth(III) fluorides (Fig. 1D) was also proposed by Suzuki et al., but these compounds could not be isolated in a pure form [19,20].

There are no references to monorgano-derivatives RMF_2 containing two metal–fluorine terminal bonds. Some unsuccessful attempts to prepare N,C,N-chelated organobismuth difluoride have been reported recently [21].

We report here on the synthesis, solution and solid state structure (XRD) of the first organoantimony(III) difluorides **4**, **5** and **6** containing Y,C,Y-chelating, so called pincer, ligands [2,6-$(YCH_2)_2C_6H_3$]SbF_2; Y = MeO (**4**), *t*-BuO (**5**), Me_2N (**6**) (Fig. 1E). Compounds **4–6** were prepared from corresponding

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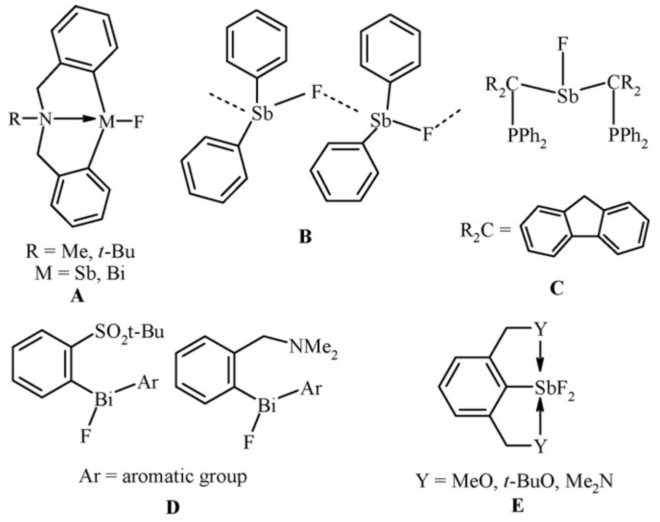


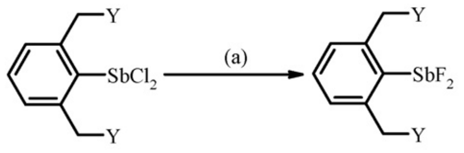
Fig. 1. Some organoantimony(III) and organobistmuth(III) fluorides.

dichlorides **1–3** ([2,6-$(YCH_2)_2C_6H_3$]$SbCl_2$; Y = MeO (**1**), *t*-BuO (**2**), Me_2N (**3**)) [22,23], using Me_3SnF [24] or 2-$(Me_2NCH_2)C_6H_4Sn(n\text{-}Bu)_2F$ [25–28] as organotin(IV) fluorinating agents. The structure of compounds **4–6** was determined both in the solution by ^1H, ^{13}C and ^{19}F NMR spectroscopy and in the solid state using X-ray diffraction techniques.

2. Results and discussion

2.1. Synthesis of 4–6

Two different fluorinating agents Me_3SnF or 2-$(Me_2NCH_2)C_6H_4Sn(n\text{-}Bu)_2F$ were employed for the preparation of organoantimony difluorides **4** and **5** starting from corresponding dichlorides **1** and **2** [22] (Scheme 1). The reagents, Me_3SnF and 2-$(Me_2NCH_2)C_6H_4Sn(n\text{-}Bu)_2F$ were converted to the corresponding chlorides within 1 week in toluene yielding organoantimony difluorides **4** and **5** in reasonable yields after appropriate workup (see Section 4). In the case of compound **6**, using Me_3SnF as the fluorinating agent failed and even after prolonged reaction time (14 days, 100 °C, toluene) only approximately 15% conversion was observed (based on ^1H NMR measurement). The successful formation of **6** was achieved by the reaction of the dichloride **3** with 2 eq. of 2-$(Me_2NCH_2)C_6H_4Sn(n\text{-}Bu)_2F$, although more forcing reaction conditions were required in comparison to the synthesis of O,C,O-chelated analogues (6 days, 100 °C, toluene, Scheme 1). Compound **6** was obtained in low yield (30%) as a result of the very similar solubilities of **6** and 2-$(Me_2NCH_2)C_6H_4Sn(n\text{-}Bu)_2Cl$, that made crystallization of **6** rather difficult [29]. Compounds **4–6** were isolated as colourless crystalline solids that are sparingly soluble in aliphatic hydrocarbons, but readily soluble in aromatics, chlorinated solvents and THF. All compounds are stable in the solid state at ambient temperature for at least several weeks.



Y= MeO, (**1**)
Y= *t*-BuO, (**2**)
Y= Me_2N, (**3**)

Y= MeO, (**4**)
Y= *t*-BuO, (**5**)
Y= Me_2N, (**6**)

(a) 2 eq. Me_3SnF (- 2 eq. Me_3SnCl) or 2 eq. 2-$(Me_2NCH_2)C_6H_4Sn(n\text{-}Bu)_2F$ (- 2 eq. 2-$(Me_2NCH_2)C_6H_4Sn(n\text{-}Bu)_2Cl$)

Scheme 1. Preparation of Y,C,Y-chelated fluorides 4–**6**.

2.2. Structure of 4–6

One set of expected signals was observed in the ^{13}C NMR spectra of **4–6** and the splitting of the signal of the *ipso*-carbon to the symmetrical triplet proves unambiguously the presence of two equally bound fluorine atoms with $^2J(^{19}F,^{13}C) = 7$ Hz for **4–6**. In ^{19}F NMR spectra one signal was detected with chemical shift $\delta(^{19}F) = -156.3$ for **4**, -148.1 for **5**, and $\delta(^{19}F) = -153.3$ ppm for **6**. These values are comparable to those found for other terminal (Sb–F) fluorine atoms in some pentavalent organoantimony derivatives [9].

^1H NMR spectra of **4** and **5** revealed one set of relatively sharp signals for both benzylic CH_2O and OR (R = Me for **4**, *t*-Bu for **5**) groups at room temperature indicating fast fluxional process of coordination/de-coordination of ligands arms [22]. However, the VT-^1H NMR showed splitting of the signal of the CH_2O groups to an AX pattern at lower temperatures (220 K) in $CDCl_3$ (signals of OR groups remain intact even at 220 K), these findings are indicative for *cis* coordination of both ligands arms at low temperature in solution of **4** and **5** [22]. ^1H NMR spectrum of compound **6** at 300 K in C_6D_6 revealed an AX pattern for CH_2N groups and two signals for non-equivalent

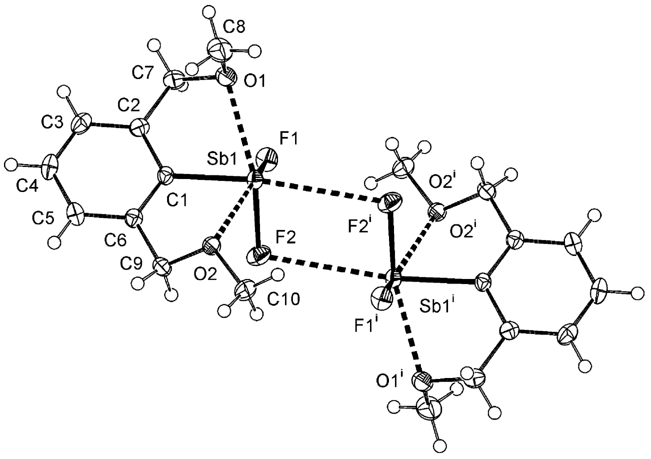


Fig. 2. ORTEP drawing (50% probability atomic displacement ellipsoids) of molecular structure of 4 (symmetry code: (i) 1-x,-y,2-z). Selected bond lengths (Å) and angles (deg): Sb(1)–C(1) 2.150(3), Sb(1)–F(1) 1.948(2), Sb(1)–F(2) 1.957(2), Sb(1)–O(1) 2.597(2), Sb(1)–O(2) 2.606(2), F(1)–Sb(1)–F(2) 82.99(8), C(1)–Sb(1)–F(1) 95.98(10), C(1)–Sb(1)–F(2) 94.37(10), O(1)–Sb(1)–O(2) 124.47(6), C(1)–Sb(1)–O(1) 71.72(9), C(1)–Sb(1)–O(2) 69.34(9), O(1)–Sb(1)–F(1) 71.09(7), O(2)–Sb(1)–F(2) 72.27(7).

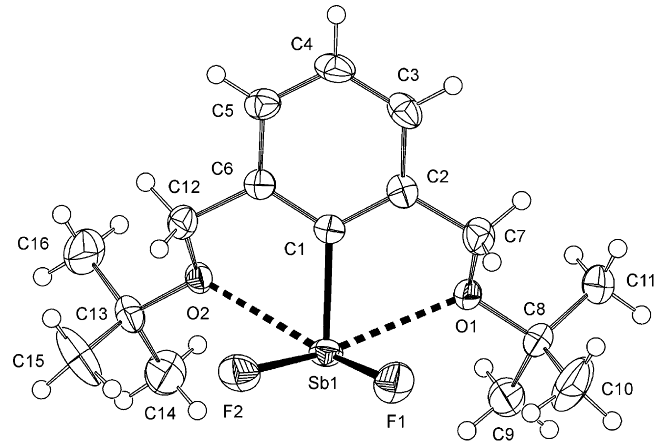


Fig. 3. ORTEP drawing (50% probability atomic displacement ellipsoids) of molecular structure of 5. Selected bond lengths (Å) and angles (deg): Sb(1)–C(1) 2.127(2), Sb(1)–F(1) 1.952(2), Sb(1)–F(2) 1.968(2), Sb(1)–O(1) 2.640(2), Sb(1)–O(2) 2.678(2), F(1)–Sb(1)–F(2) 83.96(7), C(1)–Sb(1)–F(1) 94.45(8), C(1)–Sb(1)–F(2) 93.33(7), O(1)–Sb(1)–O(2) 118.50(4), C(1)–Sb(1)–O(1) 69.60(6), C(1)–Sb(1)–O(2) 68.84(6), O(1)–Sb(1)–F(1) 73.55(5), O(2)–Sb(1)–F(2) 74.15(5).

Me_2N groups (1:1 ratio). These findings again indicate *cis* coordination of nitrogen donor atoms to the central antimony atom in solution of **6** at low temperatures [30] (i.e. structure similar to this found for all compounds in the solid state structure *vide infra*).

Molecular structures of **4–6** were determined by single crystal X-ray diffraction and are depicted in Figs. 2–4 together with selected structural parameters.

Both oxygen donor atoms are coordinated to the central metal through weak intramolecular interactions in **4** with bonding lengths Sb1–O1 2.597(2) and Sb1–O2 2.606(2) Å (Σ_{cov}(Sb,O) 2.14 Å [31]). These values indicate a further attenuation of this coordination, when compared with corresponding dichloride and diiodide $[2,6\text{-}(MeOCH_2)C_6H_3]SbX_2$ (Sb–O bond lengths 2.523(2), 2.577(2) Å, X = Cl; 2.293(2), 2.279(2) Å, X = I) [22]. The bond distances Sb1–F1 1.948(2) and Sb1–F2 1.957(2) Å are comparable to those found for Sb–F terminal bonds in other organoantimony fluorides [9,32]. The overall coordination polyhedron around the central atom can be best described as a strongly distorted square pyramid with axial carbon C1 and the basal plane formed with both F1, F2 and oxygens atoms O1, O2 (Σ of angles describing SbO_2F_2 girdle is 350.8°) [33]. Both donor oxygen atoms and fluorine atoms are coordinated mutually in *cis* fashion with angles O1–Sb1–O2 124.47(6)° and F1–Sb1–F2 83.96(7)°. Closer inspection of the molecular structure of **4** revealed very weak intermolecular contacts $Sb1–F2\cdots Sb1^i$ (Fig. 2) resulting to formation a weakly bound dimeric units ($F2\cdots Sb1^i$ 3.287 Å, Σ_{vdW}(Sb,F) 3.7 Å [31]). These Sb–F···Sb bridges are considerably weaker than those found in Ph_2SbF (F···Sb 2.221 Å) [16] most probably as a result of the presence of coordinated pendant arms on the ligand.

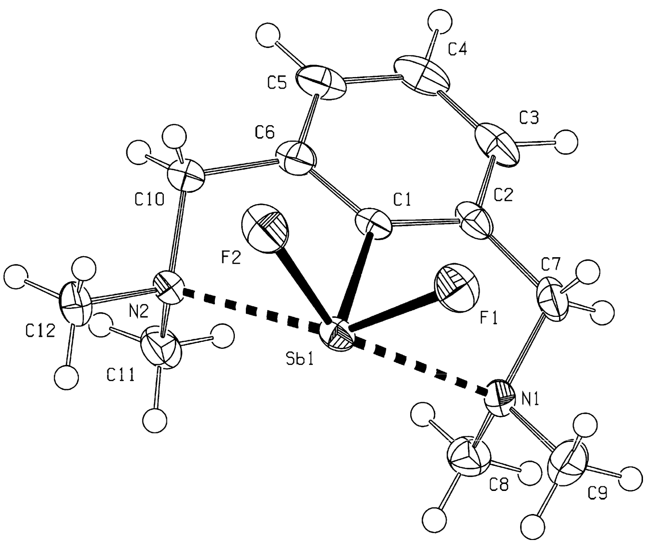


Fig. 4. ORTEP drawing (50% probability atomic displacement ellipsoids) of molecular structure of 6. Selected bond lengths (Å) and angles (deg): Sb(1)–C(1) 2.130(3), Sb(1)–F(1) 1.975(2), Sb(1)–F(2) 1.984(2), Sb(1)–N(1) 2.560(3), Sb(1)–N(2) 2.588(3), F(1)–Sb(1)–F(2) 81.20(8), C(1)–Sb(1)–F(1) 91.55(10), C(1)–Sb(1)–F(2) 93.57(11), N(1)–Sb(1)–N(2) 120.37(9), C(1)–Sb(1)–N(1) 71.60(10), C(1)–Sb(1)–N(2) 70.88(10), N(1)–Sb(1)–F(1) 74.13(9), N(2)–Sb(1)–F(2) 75.00(9).

The molecular structure of **5** resembles closely that of **4** (Fig. 3) and the coordination of both oxygen donor atoms O1 and O2 (Sb1–O1 2.640(2) and Sb1–O2 2.678(2) Å) leads to a strongly distorted square-pyramidal array around the central Sb1 atom similarly to **4** [33]. As a consequence of the presence of bulky *t*-Bu groups the intramolecular Sb–O interactions are weaker in **5** compared to **4**, also formation of Sb–F···Sb bridges is excluded and difluoride **5** remains monomeric in the solid state.

Two symmetrically independent molecules of **6** are present in the unit cell, differing only marginally in structural parameters and only one of these molecules is shown in Fig. 4 and discussed here.

Analogously to compounds **4** and **5**, the coordination of the central antimony atom is a strongly distorted square pyramid [33] as a result of present Sb–N intramolecular interactions (Sb(1)–N(1) 2.560(3), Sb(1)–N(2) 2.588(3) Å; Σ_{vdW}(Sb,N) 3.74 Å [31]), where the fluorine atoms are placed mutually in *cis* positions F(1)–Sb(1)–F(2) 81.20(8)° and the apical position is occupied by the *ipso*-C1 carbon of the ligand. Similarly to O,C,O-chelated fluorides also in **6** the strength of Sb–N intramolecular interactions is significantly weaker compared with the parent $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]SbCl_2$ **3** (Sb–N bond lengths 2.491(9) and 2.422(8) Å). Compound **6** is monomeric in the solid state without any significant intermolecular contact.

Trivalent organobismuth fluorides can be still regarded as a chemical rarity and their synthesis remains a challenge, so that after success with O,C,O-chelated organoantimony(III) compounds we turned our attention to fluorination of organobismuth congener $[2,6\text{-}(t\text{-}BuOCH_2)_2C_6H_3]BiCl_2$ (**7**). Although we used various fluorinating systems including KF (organic solvent/water), Me_3SnF, AgF (CH_3CN or water/toluene) and $2\text{-}(Me_2NCH_2)C_6H_4Sn(n\text{-}Bu)_2F$ desired organobismuth difluoride could not be isolated.

3. Concluding remarks

Organotin(IV) fluorides are useful reagents for halide-exchange reactions leading to organoantimony difluorides **4–6**. The structure of these compounds are very similar independent of the ligand used (O,C,O type in **4** and **5** and N,C,N type in **6**). In all cases the present intramolecular Sb–O or Sb–N interactions are significantly attenuated in comparison with compounds containing heavier halogen atoms (Cl, I). It should be also noted, that using of organotin(IV) compounds, in preparation of desired organobismuth difluoride failed.

4. Experimental

4.1. General experimental procedures

All manipulations were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures and distilled prior to use. ^{1}H (500.13 MHz), ^{13}C (125.76 MHz) and ^{19}F NMR (470.53 MHz) spectra were recorded on Bruker 500 Avance spectrometer. δ values are given in ppm and coupling constants (*J*) in Hz. Appropriate chemical shifts in ^{1}H and ^{13}C NMR spectra were calibrated on the residual signals of the solvents (CDCl$_3$: $\delta(^1H) = 7.27$ ppm and $\delta(^{13}C) = 77.23$ ppm, C$_6$D$_6$ $\delta(^1H) = 7.16$ ppm and $\delta(^{13}C) = 128.39$ ppm). ^{19}F NMR chemical shifts were related according to the external standard CCl$_3$F $\delta(^{19}F) = 0.0$ ppm. Positive-ion and negative-ion electrospray ionization (ESI) mass spectra were measured on an ion trap analyzer Esquire 3000 (Bruker Daltonics, Bremen, Germany) in the range *m/z* 50–1000. The samples were dissolved in acetonitrile and analyzed by direct infusion at the flow rate 5 μL min^{-1}. The ion source temperature was 300 °C, the tuning parameter compound stability was 100% for measuring of positive ions and 20% for measuring of negative, the flow rate and the pressure of nitrogen were 4 L min^{-1} and 10 psi, respectively. The ions observed in the full scan both positive- and negative-ion ESI mass spectra (listed below, designation L means Y,C,Y-chelating ligand) correspond with the structures of studied molecules. The molar masses were determined based on the mass spectrometric results. Designation (L) in MS experimental part means Y,C,Y-chelating ligand.

4.1.1. X-ray structure determination

Colourless single crystals of **4** and **5** were obtained by crystallization from CH$_2$Cl$_2$/*n*-hexane (1:5) solution at −30 °C. Single crystals of **6** were obtained by slow evaporation of saturated toluene/*n*-hexane (1:5) solution. The crystal of compounds of **4–6** were mounted on glass fibre with epoxy cement and measured on four-circle diffractometer Nonius-KappaCCD with CCD area detector by monochromatized Mo Kα radiation (λ = 0.71073 Å) at 150(1) K. The crystallographic details are summarized in Table 1, Gaussian absorption corrections [34] based on crystal shape were applied. The structures were solved by the direct method (SIR92 [35]) and

Table 1
Crystal data and structure refinement of **4–6**

	4	**5**	**6**
Empirical formula	$C_{10}H_{13}F_2O_2Sb$	$C_{16}H_{25}F_2O_2Sb$	$C_{12}H_{19}F_2N_2Sb$
Colour	Colourless	Colourless	Colourless
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbca*	*P*2$_1$/*n*	*P*-1
a (Å)	14.5001(1)	10.4409(2)	9.3050(9)
b (Å)	10.3301(2)	11.3352(3)	10.7790(10)
C (Å)	14.8829(2)	15.3227(3)	14.1150(7)
α (°)	–	–	84.757(6)
β (°)	–	102.8521(12)	86.085(6)
γ (°)	–	–	79.594(8)
Z	8	4	4
μ (mm^{-1})	2.480	1.581	1.997
D_x (Mg m^{-3})	1.936	1.537	1.684
Crystal size (mm)	0.4 × 0.25 × 0.05	0.27 × 0.15 × 0.1	0.58 × 0.45 × 0.21
Crystal shape	Plate	Irregular	Plate
θ range (deg)	1–27.5	1–27.5	1–27.5
T_{min}, T_{max}	0.371, 0.867[a]	0.679, 0.831[a]	0.531, 0.784[a]
No. of reflections measured	37220	28342	22898
No. of unique reflections; R_{int}	2544, 0.041	4061, 0.050	6261, 0.084
No. of observed ref. $[I > 2\sigma(I)]$	2277	3573	5397
No. of parameters	139	197	307
S[b] all data	1.042	1.040	1.153
Final *R*[a] indices $[I > 2\sigma(I)]$	0.026	0.025	0.032
*wR*2[a] indices (all data)	0.064	0.062	0.072
w_1/w_2[c]	0.0240/7.5275	0.0354/1.0657	0.0168/2.2614
$\Delta\rho$, max., min., [e Å^{-3}]	2.373, −1.248	1.019, −0.585	1.268, −1.338

[a] Correction by SORTAV program.

[b] Definitions: $R(F) = \Sigma||F_o| - ||F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2)^2]^{1/2}$, $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{reflns} - N_{params})]^{1/2}$.

[c] Weighting scheme $w = [\sigma^2(F_o^2) + (w_1P) + w_2P]^{-1}$. $P = [\max(F_o^2, 0) + 2F_c^2]/3$. $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$ (summation is carried out only where more than one symmetry equivalent is averaged).

refined by a full matrix least squares procedure based on F^2 (SHELXL97 [36]). Hydrogen atoms were fixed into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom), for the methyl moiety multiple of 1.5 was chosen (C–H distances being 0.96 and 0.97 Å, respectively). The final difference maps displayed no peaks of chemical significance except of residual electron density in the area of Sb atoms (less than 1 Å from Sb).

CCDC 655917, 655918 and 658785 contain the supplementary crystallographic data for **4**, **5** and **6**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

4.2. Synthesis

Compounds **1–3** were prepared according to literature procedures [22,23]. Fluorinating agents 2-(Me_2NCH_2)C_6H_4 SnR_2F [25] and Me_3SnF [24] (sublimed before use) were prepared according to literature methods. KF (98%) and AgF (99%) were obtained from Sigma–Aldrich and used as delivered.

4.2.1. Synthesis of [2,6-($MeOCH_2$)$_2C_6H_3$]SbF_2 (4)

Method A. Two equivalents of Me_3SnF (117 mg, 0.64 mmol) were added to a stirred solution of **1** (114 mg, 0.32 mmol) in toluene (50 mL) at room temperature. The reaction mixture was stirred for 1 week, then the insoluble material was filtered off and solvent was evaporated in high *vacuo* to remove resulting Me_3SnCl. The remaining white solid was washed twice with 10 mL of *n*-hexane. Compound **4** was obtained as white crystals (76 mg). Yield 73%. M.p. 107–110 °C. Anal. Calc. for $C_{10}H_{13}F_2O_2Sb$: C, 36.96; H, 4.03. Found: C, 37.01; H, 4.05%. Positive-ion MS: *m/z* 607 [LSbOSbLF]$^+$; *m/z* 347 [M + Na]$^+$, 100%; *m/z* 305 [M-F]$^+$. Negative-ion MS: *m/z* 381 [$LSbF_5$]$^-$, 100%. ^{1}H NMR ($CDCl_3$, 300 K): 3.65 (s, 6H, CH_3O), 4.79 (s, 4H, OCH_2), 7.18 (d, 2H, Ar-H3,5), 7.29 (t, 1H, Ar-H4). ^{13}C NMR ($CDCl_3$, 300 K): 58.6 (s, CH_3O), 75.7 (s, OCH_2), 125.2 (s, Ar-C3,5), 129.8 (s, Ar-C4), 145.6 (s, Ar-C2,6), 155.9 (t, ^2J(^{19}F, ^{13}C) = 7, Ar-C1). ^{19}F NMR ($CDCl_3$, 300 K): −156.3.

Method B. Two equivalents of 2-(Me_2NCH_2)C_6H_4Sn(*n*-Bu)$_2$F (540 mg, 1.4 mmol) were added to a stirred solution of **1** (250 mg, 0.7 mmol) in toluene (50 mL) at room temperature. The reaction mixture was stirred for 1 week and the solvent was evaporated in *vacuo*. The resulting oily residue was washed twice with 30 mL of *n*-hexane (30 °C) to give **4** (160 mg). Yield 70%. All other data were consistent with those described above.

4.2.2. Synthesis of [2,6-(t-$BuOCH_2$)$_2C_6H_3$]SbF_2 (5).

Compound **5** was obtained analogously to compound **4**.

Method A. Me_3SnF (80 mg, 0.44 mmol), **2** (97 mg, 0.22 mmol)—gave **5** (61 mg). Yield 68%.

Method B. 2-((CH_3)$_2NCH_2$)C_6H_4Sn(*n*-Bu)$_2$F(227 mg, 0.59 mmol), **2** (130 mg, 0.29 mmol)—gave **5** (82 mg). Yield 68%.

Data for **5**: M.p. 131–133 °C. Anal. Calc. for $C_{16}H_{25}F_2O_2Sb$: C, 46.97; H, 6.16. Found: C, 47.01; H, 6.23%. Positive-ion MS: *m/z* 775 [LSbOSbLF]$^+$; *m/z* 389 [M-F]$^+$, 100%; *m/z* 333 [M-F-butene]$^+$; *m/z* 277 [M-F-2*butene]$^+$; *m/z* 257 [M-F-2*butene-HF]$^+$. Negative-ion MS: *m/z* 389 [LSbF]$^-$, 100%. ^{1}H NMR ($CDCl_3$, 300 K): 1.43 (s, 18H, (CH_3)$_3$CO), 4.79 (s, 4H, OCH_2), 7.19 (d, 2H, Ar-H3,5), 7.26 (t, 1H, Ar-H4). ^{13}C NMR ($CDCl_3$, 300 K): 28.4 (s, (CH_3)$_3$), 65.3 (s, OCH_2), 77.9 (s, CO), 125.0 (s, Ar-C3,5), 129.4 (s, Ar-C4), 146.8 (s, Ar-C2,6), 154.4 (t, ^2J(^{19}F, ^{13}C) = 7, Ar-C1). ^{19}F NMR ($CDCl_3$, 300 K): −148.1.

4.2.3. Synthesis of [2,6-(Me_2NCH_2)$_2C_6H_3$]SbF_2 (6)

Two equivalents of 2-(Me_2NCH_2)C_6H_4Sn(*n*-Bu)$_2$F (540 mg, 1.4 mmol) were added to a stirred solution of **3** (250 mg, 0.65 mmol) in toluene (50 mL) at room temperature, the resulting solution was heated to 100 °C for 6 days. Then the reaction mixture was evaporated and hexane (20 mL) was added, this mixture was stirred for 24 h. The white precipitate was filtered off, washed twice with pentane (10 mL) and dried *in vacuo*. Compound **6** was obtained as a white powder (68 mg). Yield 30%. M.p. 110–113 °C. Anal. Calc. for $C_{12}H_{19}F_2N_2Sb$: C, 41.06; H, 5.46. Found: C, 41.15; H, 5.52%. Positive-ion MS: *m/z* 661 [LSbOSbLF]$^+$,100%; *m/z* 389 [M + K]$^+$; *m/z* 331 [M-F]$^+$. ^{1}H NMR (C_6D_6, 300 K): 1.55 and 2.20 (s(br), 12H, (CH_3)$_2$N), 2.61 and 4.47 (AX pattern, 4H, NCH_2), 6.83 (d, 2H, Ar-H3,5), 7.04 (t, 1H, Ar-H4). ^{13}C NMR (C_6D_6, 300 K): 41.6 and 45.3 (s(br), (CH_3)$_2$N), 63.5 (s, NCH_2), 126.4 (s, Ar-C3,5), 130.0 (s, Ar-C4), 148.2 (s, Ar-C2,6), 157.2 (t, ^2J(^{19}F, ^{13}C) = 7, Ar-C1). ^{19}F NMR (C_6D_6, 300 K): −153.3.

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