Intramolecular Nucleophilic Substitution in a C_6F_5 Moiety Assisted by Antimony

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Antimony tris-amides — $(Et_2N)_{3-n}Sb[N(C_6F_5)(2\text{-}C_5H_4N)]_n$ [n = 1 (**3**), 2 (**4**) or 3 (**5**)] — have been prepared by treatment of $Sb(NEt_2)_3$ (**1**) with stoichiometric amounts of (2-$C_5H_4N)(C_6F_5)NH$ (**2**). In contrast to amide **5**, compounds **3** and **4** are unexpectedly unstable and react further to give the bis-amido antimony fluorides [(2-Et_2N-C_6F_4)(2-C_5H_4N)N]-Sb(F)[$N(C_2H_5)_2$] (**6**) and [(2-Et_2N-C_6F_4)(2-C_5H_4N)N]Sb(F)-[$N(C_6F_5)$(2-C_5H_4N)] (**7**). The structure of **7** was confirmed by X-ray diffraction studies. DFT calculations, which reproduce the principal features of compound **7**'s geometry, have been used to explain the possible reaction pathway of this *ortho*-directed metathetical fluoride-amide exchange.

Introduction

During the past 50 years there has been a continuing interest in the chemistry of polyfluoro aromatic compounds. The main reason for this is that the unique properties of these derivatives suggest their possible use in various technological fields.[1,2] One of the most urgent aims of organofluorine chemistry is the preparation of polyfluorinated compounds with desired structures. As is well-known, organofluorine ligands have found widespread application in recent years for the stabilization of low-valent transition metal or main group species or for achieving unusual molecular geometries.[1,2] There is also a strong interest in activation of the C−F bond in polyfluoro organic compounds due to the possible utilization of these activation processes in organic synthesis.[3] A variety of methods for activating C−F bonds with transition metal centers have been published in the last two decades. Several catalytic systems based on transition metals have been used for the replacement of an F atom in polyfluoro aryl moieties, mostly by oxidative addition reactions.[3−5] Although only a few examples of early transition metal complexes (TMCs) useful for C−F bond activation have been found, most of the reported processes involving TMCs occur with late transition metals. As a common example of *intramolecular* oxidative addition of a C−F bond to a transition-metal center the reaction of C_6F_5−CH=N−(C_6H_4-*o*-NH_2) or similar Schiff bases with different TMCs [$W(CO)_3(PrCN)_3$, $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) etc.], which give stable products of metal insertion into a C−F bond, should be noted.[4,6,7] Two different mechanisms have been suggested by Roundhill and co-workers for aromatic nucleophilic substitution of the *ortho*-F atom in *trans*-[PtMe(THF)($PPh_2C_6F_5$)$_2$] by hydroxide or alkoxide ion, one of which is an intramolecular process.[8]

Nucleophilic substitution reactions of an aryl carbon-fluorine bond assisted by main group element compounds (alkali, alkaline earth metals and silicon derivatives) have been investigated to a considerable extent.[3,4,9−11] However, to the best of our knowledge, most of the mechanistically studied examples have been ascribed to *intermolecular* processes, although suppositions about *intramolecular* origins have been made for exclusively *ortho*-directed fluorine-atom substitution for C_6F_5X species (X containing carbon or sulfur multiple bonds to oxygen or nitrogen atoms) in reactions with Li or Mg reagents, such as ArLi, AlkMgHal, ArMgHal or ArN(R)MgHal.[11,12]

As part of our program to investigate the structure and the chemical behavior of hypervalent main-group-element compounds with intramolecular transannular interactions[13−15] we herein report the reaction of $Sb(NEt_2)_3$ (**1**) with C_6F_5NH(2-C_5H_4N) (**2**, LH), which leads to the antimony tris-amides **3**−**5** with one, two or three C_6F_5-(2-pyridyl)-amine groups, respectively. Compounds **3** and **4** are unexpectedly unstable and they react further to give bis-amido antimony fluorides **6** and **7**, respectively, after 21 days in almost quantitative yield. To the best of our knowledge no such intramolecular rearrangements have been reported previously. Schrock et al. have found that a

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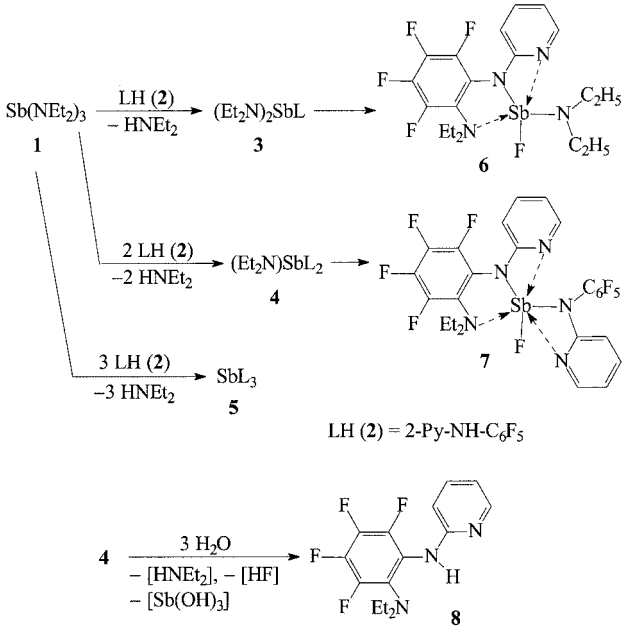
similar nucleophilic substitution product formed (23% yield) in the reaction of $Mo(NMe_2)_4$ with $(C_6F_5NHCH_2CH_2)_2NMe$. However, they were unable to determine whether this was due to an intra- or intermolecular process.[16] The structure of **7** was confirmed by X-ray diffraction studies. DFT calculations, which reproduce the principal features of the geometry of compound **7**, have been used to distinguish possible reaction pathways.

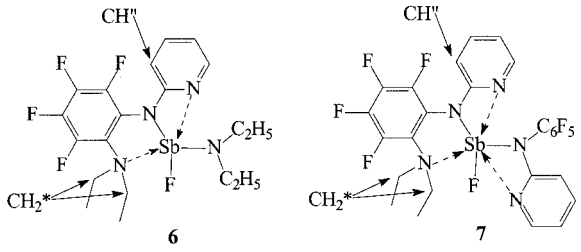
Results and Discussion

Treatment of $Sb(NEt_2)_3$ (**1**) with two or three equivalents of ligand LH (**2**) in toluene afforded amides **4** or **5**, respectively (Scheme 1). Compound **4** is unstable in toluene solution as well as in C_6D_6 solution and reacts further to give fluoride **7** after 21 days at room temperature. The reaction of **1** with one equivalent of LH led to reaction mixture **A**, consisting of **3** (as a major component) and **4** as well as starting material **1**, after 12 hours. Unfortunately, it was impossible to prepare compound **3** in a pure form. However, NMR spectroscopy data unambiguously confirm its structure. As for **4**, compound **3** (reaction mixture **A**) is unstable in solution and reacts further to give fluoride **6** after 21 days at room temperature. After recrystallization in order to remove traces of compound **7** partially formed from **4**, fluoride **6** was obtained as a pure solid. At the same time only compound **5** has been found in the reaction of **1** with three equivalents of LH (**2**) and no traces of fluorides **6** or **7** have been detected during this process. Hydrolysis of **6** after standard workup led, with moderate yield, to free amine **8**, which is difficult to access by other methods.



Scheme 1

The ^1H, ^{13}C, and ^{19}F NMR spectra of **3**–**8** are consistent with the proposed structural formula. In particular, the presence of the NEt_2 group, which is probably coordinated to the Sb atom, adjacent to the C_6F_4 ring in fluorides **6** and **7** stops the rotation of the $C_6F_4NEt_2$ group and the Py group of this ligand about the C–N bonds in C_6D_6 solution. This immobility results in the presence of two different signals for the $N(CH_2)_2$ carbon atoms of the NEt_2 group adjacent to the C_6F_4 ring (marked with an asterisk below) in the ^{13}C NMR spectra of **6** and **7**, a broadening of the $N(CH_2)_2$ signal in the ^1H NMR spectra of **6** and **7** (broad singlet instead of a quadruplet) as well as the presence of two different signals for the protons and carbons of CH_2''.



Single crystals of **7** were obtained as a toluene solvate from toluene solution (–30 °C). The molecular structure is presented in Figure 1; selected bond length and angles are summarized in Table 1. The primary coordination environment of the Sb atom is formed by the nitrogen atoms N(1) and N(14) and the F(1) atom, and may be treated as a trigonal pyramid. The $Sb-N_{cov}$ distances [2.103(2), 2.089(2) Å] are similar to those found for the closely related diamide $ClSb[N(SiMe_3)\{2\text{-}(6\text{-}Mepy)\}]_2$ (6-MepyH = 6-methylpyridine) [2.074(3)–2.127(8) Å][17] and somewhat shorter than in the tris-amide $Sb[N(SiMe_3)\{2\text{-}(6\text{-}Mepy)\}]_3$ [2.159(3)–2.167(3) Å].[18] The Sb(1)–F(1) distance [1.931(1) Å] is slightly shorter than those in the monofluoride $FSb(1,2\text{-}O_2C_6H_4)\cdot$1,10-phenanthroline [1.965(7) Å][19] and the difluoride $F_2Sb[OC(OCH_3)(2\text{-pyridyl})_2]$ [1.967(4) Å],[20] but slightly longer than those in $[SbF_3\cdot\{3\text{-}NH_2C(O)\text{-pyridine}\}_2]$ [1.911(8), 1.986(6) Å].[21] Internal coordination of both $N_{Pyridine}$ atoms and the N atom of the Et_2N group to antimony leads to a six-coordinate antimony in a

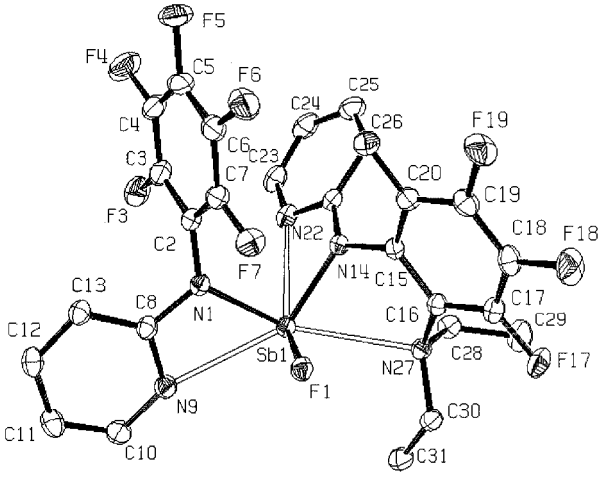


Figure 1. Molecular structure of **7**; hydrogen atoms and solvate toluene molecule are omitted for clarity

Table 1. Most important bond lengths (Å) for **7** (X-ray data) and for **4**, **ts** and **7** (calculated data)

Compound	N(1)−Sb(1)	N(9)−Sb(1)	N(14)−Sb(1)	N(22)−Sb(1)	N(27)−Sb(1)	F(1)−Sb(1)	N(27)−C(16)	F(1)−C(16)
7 (X-ray data)	2.103(2)	2.780	2.089(2)	2.664	2.848	1.931(1)	1.429(2)	3.006
	N(20)−Sb(1)	N(22)−Sb(1)	N(2)−Sb(1)	N(4)−Sb(1)	N(38)−Sb(1)	F(16)−Sb(1)	N(38)−C(11)	F(16)−C(11)
4 (calcd. data)	2.163	2.679	2.172	2.647	3.070	1.984	1.428	3.135
ts (calcd. data)	2.160	2.768	2.126	2.563	2.326	2.802	1.714	1.560
7 (calcd. data)	2.197	2.763	2.201	2.685	2.057	3.364	3.290	1.349

strongly distorted octahedral environment, with the N(22) and F(1) atoms in axial positions and the four nitrogen atoms N(1), N(9), N(14), and N(27) in equatorial sites. It should be noted that the axial transannular Sb(1)−N(22) bond is considerably shorter than the equatorial transannular N(27)−Sb(1) and N(9)−Sb(1) bonds. The $Sb-N_{Pyridyl}$ bond lengths [Sb(1)−N(22), N(9)−Sb(1)] are similar to the values reported for an Sb compound contained pyridine moieties (2.371−2.837 Å).[22,23] The $Sb-NEt_2$ transannular bond length is similar to analogous $Sb-NMe_2$ contacts reported previously [2.766(4)−3.04(2) Å][24−26] and shorter than those in the hexacoordinate complex [Sb(2-$Me_2NCH_2C_6H_4)_3$] [3.03(2)−3.04(2) Å].[26] Finally, there is no short intramolecular contact between Sb and any of the F atoms (the sum of the van der Waals radii of Sb and F is 3.66 Å).[27]

In order to get a better understanding of the driving forces of this unusual *ortho*-directed methatetic fluoride-amide rearrangement of **4** to **7** (Figure 2−4) we carried out DFT calculations on compounds **4** and **7** up to the PBE level of theory. The most important calculated geometric parameters of these compounds are listed in Table 1. Taking into consideration that no X-ray derived structure of **4** is available, the calculated geometric data for this molecule are of particular interest. The primary coordination environment of the Sb atom in **4** may be treated as a trigonal pyramid. The $Sb-N_{Py}$ distances are significantly smaller than the sum of the van der Waals radii of antimony and nitrogen (3.74 Å).[27] Consequently, the Sb atom can be regarded as [3+2]-coordinated in **4**; the presence of an additional short contact between the Sb atom and one fluorine atom of the C_6F_5 group (3.36 Å) should be noted. Such steric proximity may be one of reasons for the easy rearrangement.

The DFT calculations predict that the geometry of **7** is significantly more stable (30.25 kcal mol^{-1}) than that of **4**. The relative energies and reaction barriers calculated at various computational levels are listed in Table 2. Taking into consideration the calculated structure of compound **4** (steric proximity of Sb atom and one fluorine atom of the C_6F_5 group) and the absence of *meta*- or *para*-substitution products a concerted reaction pathway may be proposed for the nucleophilic process. We have calculated the transition-state geometry (**ts**) of this process (Figure 3). A considerable shortening of the Et_2N-C distances accompanied by an elongation of the C−F bond was found in **ts** in comparison with that in **4**. An analogous alteration is observed for the Sb−F and $Sb-NEt_2$ distances. The considerable shift of the F atom from the plane of the phenyl ring in the **ts** geometry should be noted. The computed barrier of gas-phase interconversion of **4** into **7** is low (27.70 kcal mol^{-1}). According to the literature the calculated activation barrier of insertion reactions of $Pd(PH_3)_2$ into the C−F bond of different fluoroarenes ($F-C_6H_3XY$, X,Y = H, CN, NO_2) lies within the range 21.8−41.2 kcal mol^{-1} (RB3LYP/DZVP level of theory).[28] The use of the COSMO solvation model does not drastically change these results. The computational investigation of a single-step mechanism for the

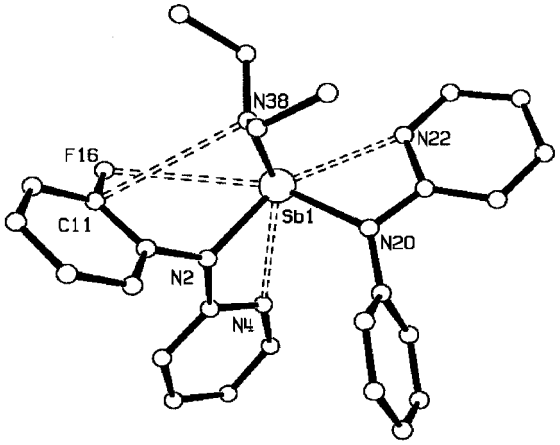


Figure 2. DFT calculated structure of **4**; hydrogen and fluorine atoms (except F16) are omitted for clarity

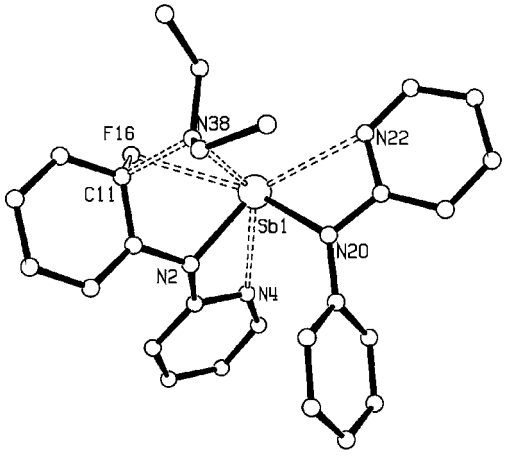


Figure 3. DFT calculated structure of **ts**; hydrogen and fluorine atoms (except F16) are omitted for clarity

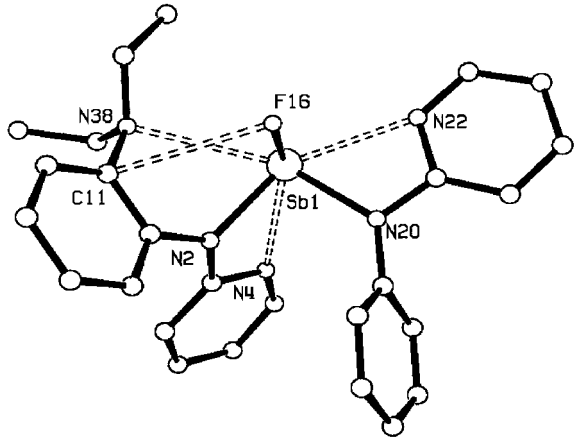


Figure 4. DFT calculated structure of **7**; hydrogen and fluorine atoms (except F16) are omitted for clarity

aromatic nucleophilic substitution of halobenzenes and halonitrobenzenes with halide anions for the reaction $C_6H_5X + X^- \rightarrow C_6H_5X + X^-$ (X = Cl, Br, I) gave similar values for the activation barrier (24.0−24.5 kcal mol^{-1}) at the MP2/6-31+G(d) + ZPE(HF/6-31+G(d) level.[29]

Table 2. Relative energies (kcal·mol^{-1}) of compounds **4** and **7** as well as the transition state (**ts**) of the rearrangement **4** → **7** (activation barrier in square brackets) calculated at various computational levels

	PBE	PBE-ZPE	RI-MP2//PBE
4	30.25	29.26	29.78
ts	57.95 [27.70]	57.18 [27.92]	62.37 [32.59]
7	0	0	0

Conclusion

This paper reports the syntheses of antimony tris-amides $(Et_2N)_{3-n}Sb[N(C_6F_5)(2\text{-}C_5H_4N)]_n$ [n = 1 (**3**), 2 (**4**) or 3 (**5**)] upon reaction of antimony tris-diethylamide (**1**) with stoichiometric amounts of $HN(C_6F_5)(2\text{-}C_5H_4N)$ (**2**). Compounds **3** and **4** are unstable in solution and rearrange to the corresponding fluorides $[(2\text{-}Et_2N\text{-}C_6F_4)(2\text{-}C_5H_4N)N]Sb(F)[N(C_2H_5)_2]$ (**6**) and $[(2\text{-}Et_2N\text{-}C_6F_4)(2\text{-}C_5H_4N)N]Sb(F)[N(C_6F_5)(2\text{-}C_5H_4N)]$ (**7**). A concerted mechanism of nucleophilic substitution has been proposed for this rearrangement according to density functional calculations. Hydrolysis of **6** provides a new entry to the tridentate amine $[(2\text{-}Et_2N\text{-}C_6F_4)(2\text{-}C_5H_4N)NH$.

Experimental Section

General Remarks: All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. Starting materials $Sb(NEt_2)_3$ [30] and $C_6F_5NH(2\text{-}C_5H_4N)$[31] were prepared according to the literature. C_6D_6 was obtained from Deutero GmbH and dried over sodium. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker AC200 FT NMR and Bruker AC300 FT NMR spectrometers (in C_6D_6 at 23 °C). Chemical shifts in the ^1H and ^{13}C NMR spectra are given in ppm relative to internal $SiMe_4$; ^{19}F NMR experiments are referenced to $CFCl_3$ as an external standard. Mass spectra (EI-MS) were recorded on a Varian CH-7a device using electron-impact ionization at 70 eV; mass spectra (FD-MS) were recorded on an HP-5989B device; all assignments were made with reference to the most abundant isotopes. Elemental analyses were carried out by the Fachbereich Chemie of the Philipps University Marburg (Heraeus Rapid Analyzer). In this work, the nonempirical generalized gradient approximation (GGA) for the exchange-correlation functional of Perdew et al. (PBE) was employed and single point RI-MP2//PBE calculations were used.[32−36] All calculations were performed using the program "PRIRODA" developed by Laikov, which implements an economical computational procedure.[37] The all-electron large orbital basis sets of contracted Gaussian-type functions of the size (5s1p):[3s1p] for H, (11s6p2d):[4s3p2d] for C, (11s6p2d):[4s3p2d] for N, (11s6p2d):[4s3p2d] for F and (22s19p12d):[7s6p4d] for Sb were used for DFT-PBE. The all-electron basis set of contracted Gaussian-type functions of the size Sb {17,18,19,20,21,22/13,14,15,16,17/9,10,11}, N {8,9,10/5,6/2}, C {8,9,10/5,6/2}, H {5,6/2}, F {8,9,10/5,6/2} were used for RI-MP2. The frozen-core approximation was used in the RI-MP2 calculations. Full geometry optimization was performed by DFT-PBE for a number of structures followed by vibrational-frequency calculation using analytical first and second derivatives. Each structure was characterized by the vibrational analysis. The transition state has only one imaginary normal mode and equilibrium geometry states have only real normal modes. An IRC (intrinsic reaction coordinate) calculation was run starting from the transition-state geometry in both directions and verified the initial and final structures linked to the transition state. Transition-state normal modes were animated using MOLDEN.[38] Coordinates and normal modes for **1**, **2**, and **ts** in MOLDEN format are available from the author upon request. The present theoretical method has previously given very useful results in antimony chemistry.[8]

Diethylaminobis[*N*-pentafluorophenyl-*N*-(2-pyridyl)amino]stibane, $[Et_2NSb\{N(C_6F_5)(2\text{-}C_5H_4N)\}_2]$ (4): A solution of amine **2** (1.09 g, 4.2 mmol) in toluene (20 mL) was added dropwise at −78 °C to a stirred solution of the stibane **1** (0.70 g, 2.1 mmol) in toluene (15 mL). The reaction mixture was stirred for 12 h at room temperature and all volatiles were removed under reduced pressure to give **4** as a yellow oil (yield 1.43 g, 97%). ^1H NMR (C_6D_6, 300.130 MHz): δ = 0.74 (t, 6 H, CH_3), 2.98 (q, 4 H, NCH_2), 5.69 (m, 2 H), 6.18 (m, 2 H), 6.85 (m, 2 H), 7.73 (m, 2 H) (hydrogen atoms of pyridyl group) ppm. ^{13}C NMR (C_6D_6, 75.47 MHz): δ = 15.22 (CH_3), 43.82 (NCH_2), 107.00, 114.11, 138.93, 145.79, 160.76 (carbon atoms of pyridyl groups) ppm; the signals of the carbon atoms of C_6F_5 were not detected. ^{19}F NMR (C_6D_6, 200.13 MHz): δ = −164.45 (br. t, 4 F), −159.58 (br. t, 2 F), −143.95 (br. d, 4 F) ppm. FD-MS: *m*/*z* (%) = 711 (100) [M^+].

Bis(diethylamino)[*N*-pentafluorophenyl-*N*-(2-pyridyl)amino]stibane, $[(Et_2N)_2Sb\{N(C_6F_5)(2\text{-}C_5H_4N)\}]$ (3): Following the same experimental procedure as for **4** using **1** (0.67 g, 2.0 mmol), **2** (0.52 g, 2.0 mmol), and toluene (20 mL). Isolated as a yellow oil (reaction mixture **A**, 1.01 g; according to ^1H NMR spectroscopy the ratio **1**:**3**:**4** was approximately 1:2:1). Data for **3**: ^1H NMR (C_6D_6, 200.130 MHz): δ = 0.92 (t, 12 H, CH_3), 3.00 (q, 8 H, CH_2), 5.80

(m, 1 H), 6.30 (m, 1 H), 7.00 (m, 1 H), 7.91 (m, 1 H) (hydrogen atoms of pyridyl group) ppm. ^{13}C NMR (C_6D_6, 50.32 MHz): δ = 16.23 (CH_3), 42.91 (CH_2), 106.79, 114.10, 138.54, 147.05, 161.00 (carbon atoms of pyridyl groups) ppm; the signals of the carbon atoms of C_6F_5 were not detected. ^{19}F NMR (C_6D_6, 188.28 MHz): δ = −164.04 (br. t, 2 F), −159.12 (t, 1 F), −145.46 (br. d, 2 F) ppm. FD-MS: *m*/*z* (%) = 524 (3) [M^+].

Tris[*N*-pentafluorophenyl-*N*-(2-pyridyl)amino]stibane, [Sb{N-(C_6F_5)(2-C_5H_4N)}$_3$] (5): Following the same experimental procedure as for **4** using **1** (0.56 g, 1.7 mmol), **2** (1.29 g, 5.0 mmol), and toluene (20 mL); yellow crystals (1.27 g, 83%) were obtained. ^{1}H NMR (C_6D_6, 200.13 MHz): δ = 5.56 (m, 3 H), 6.04 (m, 3 H), 6.77 (m, 3 H), 7.68 (m, 3 H) (hydrogen atoms of pyridyl group) ppm. ^{13}C NMR (C_6D_6, 50.32 MHz): δ = 107.05, 113.92, 139.53, 145.46, 160.42 (carbon atoms of pyridyl groups) ppm; the signals of the carbon atoms of C_6F_5 were not detected. ^{19}F NMR (C_6D_6, 188.28 MHz): δ = −164.53 (br. s, 6 F), −160.83 (br. t, 3 F), 144.51 (br. s, 6 F) ppm. EI-MS: *m*/*z* (%) = 898 (52) [M^+], 639 (39) [M^+ − N(C_5H_4N)(C_6F_5)]. $C_{33}H_{12}F_{15}N_6Sb$ (899.25): calcd. C 44.08, H 1.35, N 9.35; found C 43.87, H 1.31, N 9.15.

Diethylamino[*N*-(2-diethylamino-3,4,5,6-tetrafluorophenyl)-*N*-(2-pyridyl)amino]fluorostibane, [(Et_2N)Sb(F){N(C_6F_5)(2-C_5H_4N)}] (6): A solution of amide **3** (from reaction mixture **A**, 0.55 g, 1.1 mmol) in toluene (5 mL) was stirred for 21 days at room temperature and all volatiles were then removed under reduced pressure. Recrystallization of the residue from toluene/*n*-pentane (−30 °C) gave colorless crystals of **6** (yield 0.36 g, 66%). ^{1}H NMR (C_6D_6, 200.13 MHz): δ = 0.83 (br. s, 6 H, CH_3 of *o*-$Et_2NC_6F_4$ group), 1.03 (t, 6 H, CH_3 of Et_2NSb group), 2.95 (br. s, 4 H, CH_2 of *o*-$Et_2NC_6F_4$ group), 3.23 (q, 4 H, CH_2 of $SbNCH_2$), 5.79 and 5.80 (2 m, 1 H, CH′′), 6.17 (m, 1 H,), 6.96 (m, 1 H), 7.62 (m, 1 H) (hydrogen atoms of pyridyl group) ppm. ^{13}C NMR (C_6D_6, 50.32 MHz): δ = 12.13 (CH_3 of *o*-$Et_2NC_6F_4$ group), 16.38 (CH_3 of Et_2NSb group), 43.56 ($SbNCH_2$), 46.19 and 46.25 (CH_2 of *o*-$Et_2NC_6F_4$ group), 106.55 and 106.58 (CH′′), 112.96, 139.45, 145.42, 167.72 (carbon atoms of pyridyl groups) ppm; the signals of the carbon atoms of C_6F_5 were not detected. ^{19}F NMR (C_6D_6, 188.28 MHz): δ = −162.04 (br. t, 1 F), −161.42 (br. t, 1 F), −160.04 (br. s, 1 F, F−Sb), −148.02 (br. d, 1 F), −146.01 (br. d, 1 F) ppm. FD-MS: *m*/*z* (%) = 524 (13) [M^+], 505 (23) [M^+ − F], 452 [M^+ − NEt_2]. $C_{19}H_{24}F_5N_4Sb$ (525.17): calcd. C 43.45, H 4.61, N 10.67; found C 42.63, H 4.74, N 10.29.

[*N*-(2-Diethylamino-3,4,5,6-tetrafluorophenyl)-*N*-(2-pyridyl)amino]-[*N*-(pentafluorophenyl)-*N*-(2-pyridyl)amino]fluorostibane, [{(2-Et_2N-C_6F_4)(2-C_5H_4N)N}Sb(F){N(C_6F_5)(2-C_5H_4N)}] (7): A solution of amide **4** (1.23 g, 1.7 mmol) in toluene (5 mL) was stirred for 21 days at room temperature. Storage at −30 °C overnight resulted in colorless crystals of **7** (yield 0.87 g, 71%). ^{1}H NMR (C_6D_6, 300.130 MHz): δ = 0.74 (br. t, 6 H, CH_3), 2.82 (br. s, 4 H, NCH_2), 5.60 and 5.62 (2 m, 1 H, CH′′), 5.77 (m, 1 H), 6.02 (m, 1 H), 6.31 (m, 1 H), 6.77 (m, 1 H), 6.99 (m, 1 H), 7.66 (m, 1 H), 7.99 (m, 1 H) (hydrogen atoms of pyridyl group) ppm. ^{13}C NMR (C_6D_6, 75.47 MHz): δ = 11.61 (CH_3), 46.20 and 46.30 (NCH_2), 106.26 and 106.35 (CH′′), 106.81, 113.66, 114.16, 139.11, 139.97, 144.56, 146.43, 160.73, 161.23 (carbon atoms of pyridyl groups) ppm; the signals of the carbon atoms of C_6F_5 were not detected. ^{19}F NMR (C_6D_6, 188.28 MHz): δ = −164.45 (br. s, 2 F), −160.64 (br. t, 1 F), −160.07 (br. t, 1 F), −159.18 (br. t, 1 F), −154.72 (br. s, 1 F, F−Sb), −147.20 (br. d, 1 F), −146.85 (br. d, 1 F), −143.96 (br. t, 2 F) ppm. FD-MS: *m*/*z* (%) = 711 (45) [M^+]. $C_{26}H_{18}F_{10}N_5Sb$ (712.20): calcd. C 43.85, H 2.55, N 9.83; found C 43.47, H 2.64, N, 9.08.

***N*-(2-Diethylamino-3,4,5,6-tetrafluorophenyl)-*N*-(2-pyridyl)amine, HN(C_6F_5)(2-C_5H_4N) (8):** Water (2 mL) was added to a solution of stibane **6** (0.55 g, 1.1 mmol) in toluene (10 mL). The organic layer was separated, dried over Na_2SO_4 and all volatiles were removed under reduced pressure. Recrystallization of the residue from *n*-heptane gave colorless crystals of **8** (yield 0.10 g, 61%). ^{1}H NMR (C_6D_6, 200.13 MHz): δ = 0.65 (t, 6 H, CH_3), 2.66 and 2.67 (2 q, 4 H, NCH_2), 5.25 (br. s, 1 H, NH), 6.25 and 6.27 (2 m, 1 H), 6.39 (m, 1 H), 7.03 (m, 1 H), 8.14 (m, 1 H) (hydrogen atoms of pyridyl group) ppm. ^{19}F NMR (C_6D_6, 188.28 MHz): δ = −166.09 (br. t, 1 F), −160.77 (br. t, 1 F), −148.91 (br. d, 1 F), −141.88 (br. d, 1 F) ppm. $C_{15}H_{15}F_4N_3$ (313.29): calcd. C 57.51, H 4.83, N 13.41; found C 57.23, H 4.69, N 12.94.

X-ray Crystallographic Study. Crystal Data for 2: $C_{33}H_{26}F_{10}N_5Sb$, M_r = 804.34, triclinic, *a* = 8.5318(5), *b* = 11.6819(7), *c* = 16.680(1) Å, *α* = 83.687(5), *β* = 77.456(5), *γ* = 83.518(5)°, *V* = 1606.2(2) Å^3, space group $P\bar{1}$, *Z* = 2, D_c = 1.663 g·cm^{-3}, *F*(000) = 800, *μ*(Mo-K_α) = 0.950 mm^{-1}. Colourless crystal of approximate dimensions 0.45 × 0.27 × 0.18 mm^3 was used for data collection. Total of 23604 reflections (6418 unique, R_{int} = 0.0366) were measured on a Stoe IPDS-2 diffractometer (graphite-monochromatized Mo-K_α radiation, *λ* = 0.71073 Å) at 193(2) K. Data were collected in the range 1.76 < *θ* < 26.19° (−10 ≤ *h* ≤ 10, −14 ≤ *k* ≤ 14, −20 ≤ *l* ≤ 20). Absorption correction based on measurements of equivalent reflections resulted in transmission factors 0.6607/0.9884. The structure was solved by direct methods (SHELXS-86)[39] and refined by full-matrix least-squares on F^2 (SHELXL-97)[40] with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms (except methyl hydrogens of solvate toluene) were refined isotropically. All other H atoms were refined by using a riding model. The final residuals were: R_1 = 0.0232 for 5935 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0619 for all data with 535 parameters. Goof = 1.030, max. Δ*ρ* = 0.370 e·Å^{-3}.
CCDC-225205 (for **2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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