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Structure of *C*, *N*-chelated *n*Butyltin(IV) fluorides and their use as fluorinating agents of some chlorosilanes, chlorophosphine and metal halides

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Abstract

The tin atom in the solid-state structure of {2-[$(CH_3)_2NCH_2$]C_6H_4}$n$$Bu_2SnF$ is five coordinated with carbon atoms in equatorial and fluorine and nitrogen atoms in axial positions. The fluorination of {2-[$(CH_3)_2NCH_2$]C_6H_4}$n$$BuSnCl_2$ is described by NMR methods. The successful attempts to fluorinate various chlorosilanes, chlorophosphine and metal halides are also reported.

Keywords: Organotin(IV) fluorides; C,N-ligand; Structure

1. Introduction

One of the goals in the chemistry of tri- and diorganotin(IV) compounds is to prepare and structurally characterize monomeric organotin fluorides, which are of great interest due to their ability to undergo the metathetical halide for fluoride exchange reactions with different kinds of organometallic halides [1]. The structures of many tri- and a limited number of diorganotin fluorides have been determined and found to be either oligo- or polymeric with the "rod-like" or "zig-zag" F–Sn–F chains [2]. These compounds have relatively high melting points, and are rather insoluble in common organic solvents, which is a limitation in studies of their structure and reactivity. Only a small number of compounds containing bulky ligands, e.g., Sn[$C(SiMe_2Ph)_3$]-Me_2F [3], Sn[$C(SiMe_3)_3$]Ph_2F [3], Sn[C_6H_2 Me_3-2,4,6)$_3$]Me_2F [4] and Sn(CH_2SiMe_3)$_3$F [5], with a four-coordinated tin central atom, are monomeric with a Sn–F terminal single bond distance about 1.96 Å [6]. Recently, we have reported triorganotin(IV) fluorides of general formula $L^{CN}R_2SnF$, where L^{CN} is {2-[$(CH_3)_2NCH_2$]C_6H_4}$^-$ and R is alkyl (Me, *n*Bu, *t*Bu) or aryl (Ph) groups of different steric bulk and electronic properties [7]. The compounds have five-coordinated tin and are able to fluorinate titanocene dichloride essentialy quantitatively. In our latest reports on this field, we reported the di- [8] and monoorganotin(IV) [9] fluorides having the same ligand. These compounds are presumably tri- or tetranuclear species with rather low solubility in common organic solvents and we used them as a part of selective and sensitive carriers for fluoride ion recognition [10]. In this paper, we communicate on solid-state structure {2-[$(CH_3)_2NCH_2$]C_6H_4}$n$$Bu_2SnF$, earlier used as fluorinating agent [7], solution structure of {2-[$(CH_3)_2NCH_2$]C_6H_4}$n$$BuSnCl_2$ [11] and products of its fluorination. The attempts to fluorinate various chlorosilanes, chlorophosphine and metal halides are also reported.

2. Results and discussion

Both {2-[$(CH_3)_2NCH_2$]C_6H_4}$n$$Bu_2SnCl$ (**1**) and {2-[$(CH_3)_2$ NCH_2]C_6H_4}$n$$Bu_2SnF$ (**2**) were described in the previous papers

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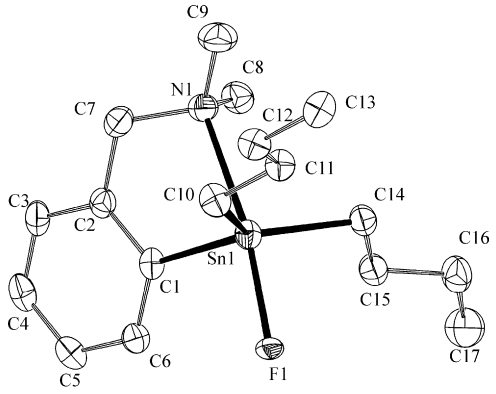


Fig. 1. The molecular structure (ORTEP 40% probability level) of {2-[$(CH_3)_2NCH_2$]C_6H_4}$n$$Bu_2$SnF (**2**), hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn–F 2.0804(16), Sn–C10 2.144(3), Sn–C14 2.143(3), Sn–C1 2.139(3), Sn–N 2.526(3), C10–Sn–C14 123.28(13), C10–Sn–C1 113.86(12), C14–Sn–C1 121.81(12), F–Sn–N 168.80(8), F–Sn–C1 94.52(10), C1–Sn–N 74.38(11), C10–Sn–N 92.57(12), C14–Sn–N 92.25(11), C3–C2–C7–N 30.6(2).

as a yellowish oil [7,11] which cannot be crystallized. The crystalline and sublimable material was obtained by changing slightly the preparation procedure, which facilitate easier handling with it (see Section 3).

2.1. Structure of **2**

Structure of **2** (Fig. 1) is similar to analogous chlorides and fluorides (Me or Ph instead of *n*Bu) [7,12,13], i.e. trigonal bipyramidal geometry of the tin atom with electronegative atoms (N, Cl (F)) in axial and carbon atoms in equatorial positions. The Sn–F distance (2.0804(16) Å) is the longest known for the terminal Sn–F bond which is caused by *trans* effect of nitrogen donor atom. The adjacent fluorine atom is located 4.898 Å from the tin centre (4.610 and 6.257 Å for Me or Ph analogs) [7].

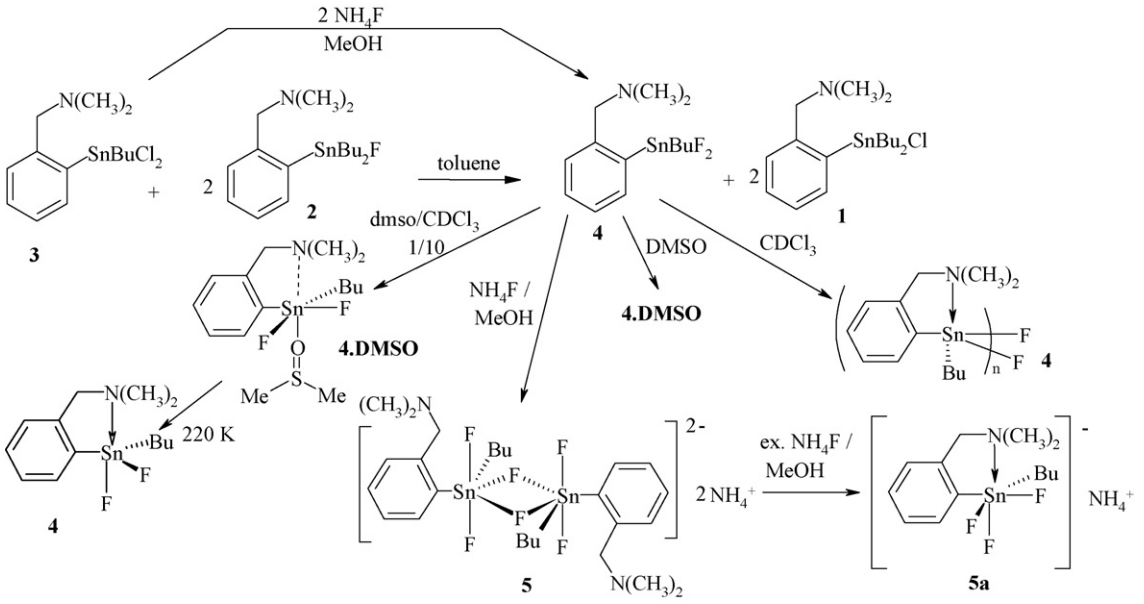
Two different methods were used for replacing chlorine by fluorine atom(s) in **3**. The first method is based on the known fluorination ability of {2-[$(CH_3)_2NCH_2$]C_6H_4}$n$$Bu_2$SnF (**2**) [7,8,9,10] and the second one is reaction with dried NH_4F (excess) in dichloromethane under an argon atmosphere.

The first method yields the white crystals which are insoluble in non-polar solvents, but slightly soluble in chloroform and soluble in coordinating solvents such as DMSO, acetonitrile or nitrobenzene. The best solubility was determined for chloroform/DMSO 10/1 mixture. The composition and structure in solution depends dramaticaly on the solvent used and temperature (Scheme 1). In chloroform, is proposed a polymeric structure suggestion supported by the ^{19}F NMR spectra, where two very broad signals were found at room temperature and no signal was observed at 220 K. In weakly coordinating solvents such as nitrobenzene or acetonitrile, the tetrameric structure was deduced from ESI-MS measurements. The structure in DMSO is monomeric with dynamically exchanging fluorine atoms (from axial to equatorial position of trigonal bipyramid).

When compound **3** was treated with two equivalents of NH_4F the product of similar properties was found as for the first method. Addition of one equivalent of NH_4F to **4** in methanol led to the formation of dimeric ionic species **5** which upon addition of further equivalents of NH_4F gave probably monomeric species **5a**. Structures were deduced from MS spectra patterns and low temperature ^{19}F NMR spectra where three terminal fluorine atoms are bonded to tin ($^1J(^{119}Sn,^{19}F)$ ≈3100 Hz). Also broad quartet in ^{119}Sn NMR spectra located in region typical for a six-coordinated tin atom (−438.4 ppm) supporting the same structure and behavior prediction which was recently found for a Ph analog of 4 [8].

2.2. Fluorination activity of **2**

Based on the previous successful fluorination [7,8] of titanocene dichloride and several organotin(IV) chlorides by **2**, we tried to fluorinate some chlorosilanes, chlorophosphine and metal halides. In the case of chlorosilanes (Table 1) this



Scheme 1.

Table 1
Fluorination experiments

Run	Substrate	Conditions	Product	Conversion [%][a]
1	(4-CH_3O-Ph)Ph_2SiCl	Benzene, R.T., 1 eq. of **2**, 1 d	(4-CH_3OPh)Ph_2SiF	100
2	(4-CH_3O-Ph)Ph_2SiCl	Benzene, R.T., 5 eq. of KF, 1 mol% of **2**, 1% mol of 18-crown-6, 7 d	(4-CH_3OPh)Ph_2SiF	90
3	*c*-HexPh_2SiCl	THF, R.T., 1 eq. of **2**, 5 h	*c*-HexPh_2SiF	100
4	BzPh_2SiCl	$CDCl_3$, R.T., 1 eq. of **2**, 2 h	BzPh_2SiF	100
5	BzPh_2SiCl	THF, reflux, 5 eq. of KF, 1% mol of **2**, 1% mol of 18-crown-6, 15 h	BzPh_2SiF	95
6	*n*-OctPh_2SiCl	$CDCl_3$, R.T., 1 eq. of **2**, 2 h	*n*-OctPh_2SiF	100
7	*n*-OctPh_2SiCl	THF, reflux, 5 eq. of KF, 1% mol of **2**, 1% mol of 18-crown-6, 15 h	*n*-OctPh_2SiF	95
8	*t*-Bu_2SiCl_2	Benzene, R.T., 2 eq. of **2**, 1 d	*t*-Bu_2SiF_2	100
9	*t*-Bu_2SiCl_2	Toluene, R.T., 5 eq. of KF, 1% mol of **2**, 1% mol 18-crown-6, 8 d	*t*-Bu_2SiF_2 + *t*-Bu_2SiFCl + *t*-Bu_2SiCl_2	–
10	Me_2SiHCl	Benzene, R.T., 1 eq. of **2**, 1 d	Me_2SiHF	100
11	$PhSiH_2Cl$	Toluene, R.T., 1 eq. of **2**, 1 d	$PhSiH_2F$	100
12	(η^1-C_5H_5)-1-$SiMe_3$-1-$SiMe_2Cl$	C_6D_6, R.T., 1 eq. of **2**, 1 min	(η^1-C_5H_5)-1-$SiMe_3$-1-$SiMe_2F$	100
13	$PhPCl_2$	C_6D_6, R.T., 2 eq. of **2**, 1 h	$PhPF_2$	100
14	$FeBr_2$	THF, R.T., 2 eq. of **2**, 2 d	FeF_2	100
15	$AlCl_3$	Benzene, R.T., 3 eq. of **2**, 2 d	AlF_3	100
16	$NiCl_2$	THF, reflux, 2 eq. of **2**, 1 h	NiF_2	100
17	$CoCl_2$	THF, R.T., 2 eq. of **2**, 1 d	CoF_2	100
18	$CaCl_2$	THF, R.T., 2 eq. of **2**, 2 d	CaF_2	100
19	$CoCl_3$	THF, R.T., 3 eq. of **2**, 2 d	CoF_3	100
20	$PbCl_2$	THF, reflux, 2 eq. of **2**, 1 d	PbF_2	45
21	$ZrCl_4$	Toluene, R.T., 4 eq. of **2**, 2 d	ZrF_4	90
22	$PdCl_2$	THF, R.T., 2 eq. of **2**, 1 d	PdF_2	n.o.

[a] Based on ^1H, ^{29}Si, ^{31}P and ^{119}Sn NMR spectra.

fluorination method seems to be very effective, hence a catalytic version was also attempted. Chlorosilanes can be transformed to appropriate fluorosilanes by several methods and reagents [14,15]: $BF_3{\cdot}OEt_2$, SbF_3, ZnF_2, NH_4F, CuF_2, Na_2SiF_6, $NaPF_6$, $NaSbF_6$, $NaBF_4$, Me_3SnF, AgF, PF_5, Ph_3CBF_4, SbF_3, $NOBF_4$, NO_2BF_4 and CuF_2/CCl_4, but it is not very easy to obtain selectively fluorosilanes containing Si–H bond(s). Van Dyke et al. made partially fluorinated polysilanes by PF_5 or Ph_3CBF_4 methods. There are disadvantages of these reagents as for example price, instability, lower selectivity, toxicity and the need to use more than an equimolar amount of reagent. Reaction times may be long and high temperature is also needed to obtain satisfactory yields of fluorinated products. Lickiss and Lucas [16] made fluorosilanes using ultrasound activation or started the reactions by small amount of water. As reagents they used Na_2SiF_6 or $(NH_4)_2SiF_6$ in 1,2-dimethoxyethane (DME, less than 0.005% H_2O) but when the starting chlorosilanes contained sterically demanding groups (as for example *t*-Bu_2SiCl_2) the reaction time at reflux conditions was about 2 weeks. Fluorophosphines can be prepared by several methods including (i) reaction of RLi with $ClPF_2$ [17] (ii) reaction of $RPCl_2$ with SbF_3 or HF [18]. The yield of the appropriate fluorophospine is about 20% in case of R = alkyl and increases up to 35% if R = aryl.

Chlorosilanes and $PhPCl_2$ (runs 1, 3, 4, 6, 8, 10, 11, 12 and 13 Table 1) were fluorinated by an equimolar amount of 2, essentially quantitatively and selectively in a few minutes (run 12) or hours. The catalytic versions of the reactions (18-crown-6 was used for KF transfer) were successful and it seems that the only limitation is the reaction time which is much longer for sterically hindered silanes (run 9). The fluorination of metal halides is also successful even for such strong fluorination agents as CoF_3. Problems occurred only in the case of PbF_2, where the low solubility of starting material is probably the reason of slower reaction and $PdCl_2$ cannot be fluorinated by this method.

3. Experimental

Both {2-[$(CH_3)_2NCH_2$]C_6H_4}*n*Bu_2SnCl (**1**) and {2-[$(CH_3)_2NCH_2$]C_6H_4}*n*Bu_2SnF (**2**) have been prepared by procedures reported in refs. [7,11], NaF was used as fluorinating agent instead of KF. Single crystals of both compounds were obtained by *vacuo* sublimation (30 °C/1 Pa) of crude material and reveal the same patterns of NMR spectra and elemental analysis as published previously. {2-[$(CH_3)_2NCH_2$]C_6H_4}*n*$BuSnCl_2$ (**3**) was prepared as published elsewhere [11]. Chlorosilanes, phosphines and metal halides were prepared according to literature [19] or obtained from commercial sources. The purity and composition of metal fluorides (except of GeF_4 and WF_6, where the identity was deduced only from boiling points) were checked by powder diffraction methods on a Bruker D8 ADVANCE or Nonius Kappa CCD device in powder diffraction mode and compared to the library (DIFFRAC*plus* Evaluation Package Diffrac*plus* SEARCH) and crystallographic databases displaying good agreement with stored data.

3.1. NMR spectroscopy

The NMR spectra were recorded as solutions in methanol D_4, C_6D_6, $CDCl_3$ on a Bruker Avance 500 spectrometer

(equipped with *Z*-gradient 5 mm probe) at 300, 250 or 220 K ^{1}H (500.13 MHz), ^{119}Sn{^{1}H} (186.50 MHz) and ^{19}F{^{1}H} (470.53 MHz). The assignments of signals in ^{1}H spectra were made from standard 2D measurements. The solutions were obtained by dissolving of 5–40 mg of each compound in 0.5 ml of deuterated solvents. The ^{1}H chemical shifts were calibrated relative to the signal of residual $CHCl_3$ ($\delta = 7.27$) and benzene (7.16), methanol ($\delta = 3.31$), respectively, and the ^{19}F chemical shifts are referred to external CCl_3F ($\delta = 0.0$). The ^{119}Sn chemical shifts are referred to external neat tetramethylstannane ($\delta = 0.0$). Positive chemical shifts values denote shifts to the higher frequencies relative to the standards. ^{119}Sn NMR spectra were measured using the inverse gated-decoupling mode.

3.2. Mass spectrometry

Electrospray ionization (ESI) mass spectra (MS) were measured on the ion trap analyser Esquire3000 or qTOF analyser micrOTOF-Q (both Bruker Daltonics, Bremen, Germany) in the range *m*/*z* 50–2000. The sample was dissolved in acetonitrile or methanol and analysed by direct infusion at the flow rate 5 μl/min both in the negative- and positive-ion modes. The ion source temperature was 300 °C (180 °C, qTOF), the flow rate and the pressure of nitrogen were 4 l/min and 10 psi (0.4 bar, qTOF), respectively. The isolation width for MS/MS experiments was $\Delta m/z = 8$, and the collision amplitude was 0.9 V (qTOF, colision energy 20 eV).

3.3. X-ray crystallography

The single crystals of **2** were obtained by *vacuo* sublimation.

Data for colorless crystals were collected at 150(1) K on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å), and graphite monochromator. The structures were solved by direct methods (SIR92 [20]). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97 [21]). Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or of 1.5 U_{eq} for the methyl moiety. Absorption corrections were carried on, using either multi-scans procedure (PLATON [22] or SORTAV [23]) or Gaussian integration from crystal shape (Coppens [24]).

A full list of crystallographic data and parameters including fractional coordinates is deposited at the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

Crystallographic data for **2**: $C_{17}H_{30}NFSn$, $M = 386.11$, orthorhombic, *Pbca*, $a = 16.2540(2)$, $b = 11.8460(3)$, $c = 19.0280(4)$ Å, $\beta = 90.00°$, $Z = 8$, $V = 3663.74(13)$ Å^3, $D_c =$ g cm^{-3}, $\mu = 1.396$ mm^{-1}, $T_{min} = 0.737$, $T_{max} = 0.812$; 48031 reflections measured ($\theta_{max} = 27.5°$), 4207 independent ($R_{int} = 0.0415$), 3442 with $I > 2\sigma(I)$, 185 parameters, $S = 1.055$, *R1*(obs. data) = 0.0356, *wR2*(all data) = 0.0930; max., min. residual electron density = 1.863, −1.895 eÅ^{-3}. CCDC deposition number: 607136.

3.4. {2-[(CH$_3$)$_2$NCH$_2$]C$_6$H$_4$}nBuSnF$_2$ (**4**)

The compound **3** (2.20 g, 5.8 mmol) was dissolved in 50 ml of toluene and **2** (4.47 g, 11.6 mmol) was added. White crystals of **4** appeared immediately upon addition. The soluble part was filtered off and the solid was washed twice with the same solvent and dried in *vacuo*. The volatiles from the filtrate were *vacuo* removed and the {2-[(CH$_3$)$_2$NCH$_2$]C$_6$H$_4$}*n*Bu$_2$SnCl was identified by NMR and m.p. as the sole product [11]. For **4**: yield 71%. m.p. 251–255 °C. ^{1}H NMR ($CDCl_3$, 300 K, ppm): 7.98 (br, 1H-6); 7.38 (br, 2H-4,5), 7.18 (d, 1H-3); 3.72 (s, 2H-NCH$_2$); 2.45 (s, 6H-NCH$_3$); 1.65 (br anisochronous, 2H-H1′); 1.41 (br, 2H-H2′); 1.24 (br, 2H-H3′); 0.94 (*t*, 3H-H4′). ^{19}F{^{1}H} NMR ($CDCl_3$, 295 K, ppm): −177.6 (bs), −181.9 (bs). ^{1}H NMR (DMSO-d_6, 295 K, ppm): 7.80 (br s, 1H-6); 7.30 (br, 2H-4,5), 7.15 (br, 1H-3); 2.28 (s, 6H-NCH$_3$); 1.67 (br, 2H-H1′); 1.37 (br, 2H-H2′); 1.27 (br, 2H-H3′); 0.89 (*t*, 3H-H4′). ^{19}F{^{1}H} NMR (DMSO-d_6, 295 K, ppm): −159.8 (br, w1/2 = 300 Hz). ^{1}H NMR ($CDCl_3$/DMSO-d_6 (v/v) 10/1, 300 K, ppm): 7.80 (br s, 1H-6); 7.24 (bs, 2H-4,5), 7.07 (br, 1H-3); 3.59 (s, 2H-NCH$_2$); 2.33 (s, 6H-NCH$_3$); 1.66 (m, 2H-H1′); 1.37 (br m, 4H-H2′, H3′); 0.87 (*t*, 3H-H4′). ^{19}F{^{1}H} NMR ($CDCl_3$/DMSO-d_6 (v/v) 10/1, 295 K, ppm): −157.2 (br - w1/2 = 224 Hz, $^{1}J(^{19}F, ^{119}Sn) = 2884$ Hz). ^{119}Sn{^{1}H} NMR ($CDCl_3$/DMSO-d_6 (v/v) 10/1, 295 K, ppm): −364.9 (*t* $^{1}J(^{119}Sn, ^{19}F) = 2886$ Hz). ^{1}H NMR ($CDCl_3$/DMSO-d_6 (v/v) 10/1, 250 K, ppm): 7.88 (br s, 1H-6); 7.38 (bs, 2H-4,5), 7.21 (br, 1H-3); 3.70 (s, 2H-NCH$_2$); 2.46 (s, 6H-NCH$_3$); 1.75 (br s, 2H-H1′); 1.45 (br m, 4H-H2′, H3′); 0.99 (*t*, 3H-H4′). ^{19}F{^{1}H} NMR ($CDCl_3$/DMSO-d_6 (v/v) 10/1, 250 K, ppm): −153.6 (br), −156.6 (br). ^{1}H NMR ($CDCl_3$/DMSO-d_6 (v/v) 10/1, 220 K, ppm): 7.88 (br s, 1H-6); 7.40 (bs, 2H-4,5), 7.24 (br, 1H-3); 3.71 (d, 2H-NCH$_2$, $^{2}J(^{1}HA, ^{1}HB) = 120$ Hz)); 2.23 (AX pattern, 6H-NCH$_3$, $^{2}J(^{1}HA, ^{1}HX) = 115$ Hz); 1.74 (br s, 2H-H1′); 1.45 (br m, 4H-H2′, H3′); 1.00 (br, 3H-H4′). ^{19}F{^{1}H} NMR ($CDCl_3$/DMSO-d_6 (v/v) 10/1, 220 K, ppm): −153.6 (br), −156.6 (br). ESI-MS: MW = 349. Positive-ion ESI/MS: *m*/*z* 679, $[2M-F]^+$, 3%; *m*/*z* 330, $[M-F]^+$, 18%; *m*/*z* 136, $[H(L^{CN})+H]^+$, 100%. Negative-ion ESI/MS: *m*/*z* 945, $[3M-Bu-(CH_3)_2NH]^-$, 100%. Elemental analysis (%): C, 44.8; H, 6.0; N, 4.1; calcd. for $C_{13}H_{21}F_2NSn$: C, 44.9; H, 6.1; N, 4.0.

3.5. ([{2-[(CH$_3$)$_2$NCH$_2$]C$_6$H$_4$}nBuSnF$_3$]$^-$)$_2$ 2([NH$_4$]$^+$) (**5**)

The compound **4** (291 mg, 0.84 mmol) was dissolved in 25 ml of dichloromethane and 1 eq. of NH_4F (31 mg, 0.84 mmol) was added. The reaction mixture was stirred for 1 h. Afterwards dichloromethane was *vacuo* removed and white crystals of **5** were obtained. Yield 93%. m.p. 276–279 °C. ^{1}H NMR (CD_3OD, 295 K, ppm): 7.84 (d, 1H-6), 7.33 (m, 2H-4,5), 7.17 (d, 1H-3), 3.69 (s, 2H-NCH$_2$), 2.44 (s, 6H-NCH$_3$), 1.81 (m, 2H-H1′), 1.48 (m, 4H-H2′, H3′), 0.98 (*t*, 3H-H4′). ^{1}H NMR (CD_3OD, 250 K, ppm): 7.86 (d, 1H-6), 7.35 (m, 2H-4,5), 7.20 (d, 1H-3), 3.73 (s, 2H-NCH$_2$), 2.46 (s, 6H-NCH$_3$), 1.79 (m, 2H-H1′), 1.36 (m, 4H-H2′, H3′), 1.00

(*t*, 3H-H4′). $^{19}F\{^1H\}$ NMR (CD_3OD, 250 K, ppm): −164.6 (br). ^1H NMR (CD_3OD, 220 K, ppm): 7.81 (d, 1H-6), 7.25 (s, 2H-4,5), 7.14 (br, 1H-3), 3.62 (br s, 2H-NCH_2), 2.42 (s, 6H-NCH_3), 1.74 (m, 2H-H1′), 1.43 (m, 4H-H2′, H3′), 0.97 (*t*, 3H-4′). $^{19}F\{^1H\}$ NMR (CD_3OD, 220 K, ppm): −131.8 (br), −161.8 (br), −165.1 (br). ESI-MS: MW = 772 Positive-ion ESI/MS: *m/z* 679, $[M-2*NH_4F\text{-}F]^+$, 18%; *m/z* 368, $[1/2M-F+H]^+$, 38%, *m/z* 350, $[1/2M-NH_4F+H]^+$, 17%; *m/z* 330, $[1/2M-NH_4F\text{-}F]^+$, 100%. Negative-ion ESI/MS: *m/z* 717, $[M-NH_4F\text{-}NH_4]^-$, 1%; *m/z* 368, $[1/2M-NH_4]^-$, 100%, *m/z* 348, $[1/2M-NH_4\text{-}HF]^-$, 12%; *m/z* 328, $[1/2M-NH_4\text{-}2*HF]^+$, 14%; *m/z* 308, $[1/2M-NH_4\text{-}3*HF]^-$, 1%. Elemental analysis (%): C, 40.7; H, 6.5; N, 7.5; calcd. for $C_{26}H_{32}F_6N_4Sn_2$: C, 40.45; H, 6.75; N, 7.3.

3.6. $[\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}nBuSnF_3]^-[NH_4]^+$ (**5a**)

Compound **3** (250 mg, 0.66 mmol) was dissolved in 10 ml of dichloromethane and NH_4F (20 eq., excess) was added. The reaction mixture was stirred for 8 h. Afterwards the soluble part was filtered off and the volatiles were *vacuo* removed. The product was dissolved in CD_3OD. ^1H NMR (CD_3OD, 300 K, ppm): 7.80 (s, 1H-6), $^3J(^{119}Sn, ^1H)$ = 94.6 Hz, 7.36 (s, 1H-4, 5), 7.11 (s, 1H-3), 3.69 (s, 2H, NCH_2), 2.45 (s, 6H, NCH_3), 1.78 (m, 2H-1′), 1,45 (m, 4H −2′,3′), 0.96 (*t*, 3H −4′). $^{19}F\{^1H\}$ NMR (CD_3OD, 300 K, ppm): −133.3 (bs, NH_4F), −135.4 (s), −153.8 (s), −157.5 (bs). $^{119}Sn\{^1H\}$ NMR (CD_3OD, 300 K, ppm): −438.4 (bq), $^1J(^{119}Sn, ^{19}F) \approx 3100$ Hz. $^{19}F\{^1H\}$ NMR (CD_3OD, 250 K, ppm): −131 (bs), −137.43 (s); $^1J(^{19}F, ^{119}Sn)$ = 2945 Hz, −137.96 (bs, NH_4F), −159.4 (s); $^1J(^{19}F, ^{119}Sn)$ = 2902 Hz. $^{19}F\{^1H\}$ NMR (CD_3OD, 220 K, ppm): −131 (s); $^1J(^{19}F, ^{119}Sn)$ = 2531 Hz, −137.96 (bs, NH_4F), −159 (s); $^1J(^{19}F, ^{119}Sn)$ = 2880 Hz.

4. Typical procedure of chlorosilanes, chlorophosphine and metal halides fluorination

The amount of 40–200 mg of appropriate substrate was added to **2** at conditions summarized in Table 1, and the mixture was stirred for 1 min (run 12) up to 8 days (catalytic run 9), the sample was filtered, in the case of heterogenous reactions or paramagnetic species, and the solvent removed in *vacuo* (in the case of run 9 the product was trapped at liquid nitrogen temperature), then deuterated benzene or chloroform was added and the composition and composition of material was checked by GC–MS and multinuclear NMR spectroscopy [7,11,14,15,16]. The products were separated by washing of **1** by pentane in the case of insoluble metal fluorides or by (*vacuo*) distillation in the case of fluorosilanes and fluorophosphine.

4.1. $(4\text{-}CH_3OPh)Ph_2SiF$

^1H NMR ($CDCl_3$, 300 K, ppm): 7.67 (m, phenyl H); 7.45 (m, phenyl H), 3.61 (s, methoxy H). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −167.9 (s, $^1J(^{29}Si, ^{19}F)$ = 282 Hz). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −11.1 (d, $^1J(^{19}F, ^{29}Si)$ = 282 Hz).

4.2. $c\text{-}HexPh_2SiF$

^1H NMR ($CDCl_3$, 300 K, ppm): 7.63 (d, phenyl H); 7.40 (m, phenyl H), 1.83 (m, cyclohexyl H), 1.74 (m, cyclohexyle H), 1.36 (m, cyclohexyle H). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −177.9 (s, $^1J(^{29}Si, ^{19}F)$ = 315 Hz). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −3.2 (d, $^1J(^{19}F, ^{29}Si)$ = 315 Hz).

4.3. $BzPh_2SiF$

^1H NMR ($CDCl_3$, 300 K, ppm): 7.78 (d, phenyl and benzyl H); 7.63 (m, phenyl and benzyl H), 2.72 (d, phenyl-CH_2- H). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −169.8 (s, $^1J(^{29}Si, ^{19}F)$ = 285 Hz).

4.4. $n\text{-}OctPh_2SiF$

^1H NMR ($CDCl_3$, 300 K, ppm): 7.55 (d, phenyl H); 7.37 (m, phenyl H), 1.33 (m, octyl H), 1.17 (m, octyl H), 0.85 (*t*, octyl H). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −171.3 (s, $^1J(^{29}Si, ^{19}F)$ = 287 Hz).

4.5. $t\text{-}Bu_2SiF_2$

b.p. 129–130 °C. ^1H NMR ($CDCl_3$, 300 K, ppm): 1.06 (s, *t*-butyle H). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −156.5 (s, $^1J(^{29}Si, ^{19}F)$ = 327 Hz). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −8.2 (*t*, $^1J(^{19}F, ^{29}Si)$ = 327 Hz).

4.6. $PhSiH_2F$

b.p. 112–113 °C. ^1H NMR ($CDCl_3$, 300 K, ppm): 7.66 (d, phenyl H), 7.33 (m, phenyl H), 5.17 (d, $^1J(^{19}F, ^1H)$ = 51 Hz). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −156.5 (s, $^1J(^{29}Si, ^{19}F)$ = 286 Hz). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −7.16 (d, $^1J(^{19}F, ^{29}Si)$ = 286 Hz).

4.7. Me_2SiHF

b.p. −9 °C. NMR spectra were not recorded due to low boiling point.

4.8. $(\eta^1\text{-}C_5H_5)\text{-}1\text{-}SiMe_3\text{-}1\text{-}SiMe_2F$

b.p. 50 °C/400 Pa. ^1H NMR ($CDCl_3$, 295 K, ppm): 6.76 (br s, η^1-C_5H_5), 6.38 (br s, η^1-C_5H_5), 0.00 (d, $SiMe_2F$ $^1J(^1H, ^{19}F)$ = 6.85 Hz), −0.02 (s, $SiMe_3$). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 295 K, ppm): −151.43 (s, $^1J(^{29}Si, ^{19}F)$ = 279 Hz).

4.9. $PhPF_2$

b.p. 122–123 °C. ^1H NMR ($CDCl_3$, 300 K, ppm): 7.40 (m, phenyl H), 7.20 (m, phenyl H). $^{19}F\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): −90.75 (d, $^1J(^{15}P, ^{19}F)$ = 1163 Hz). $^{15}P\{^1H\}$ NMR ($CDCl_3$, 300 K, ppm): 206.54 (*t*, $^1J(^{19}F, ^{15}P)$ = 1163 Hz).

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