Main Group Met. Chem., 2011;34(1-2):7–25 © 2011 by Walter de Gruyter • Berlin • Boston. DOI 10.1515/MGMC.2011.002

Use of C,N-chelated triorganotin(IV) fluoride for fluorination of organic compounds, coordination compounds, phosphines, silanes and stannanes

Petr Švec and Aleš Růžička*

Department of General and Inorganic Chemistry, Faculty
of Chemical Technology, University of Pardubice,
Studentská 573, CZ-532 10, Pardubice, Czech Republic

*Corresponding author
e-mail: ales.ruzicka@upce.cz

Abstract

C,N-chelated triorganotin(IV) compounds containing the L^{CN} ligand, where L^{CN} is $\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}^-$, reveal the monomeric structure in solution as well as in the solid state with pentacoordinated tin atom in trigonal bipyramidal coordination polyhedra. These compounds were used as mild and very efficient metathetical fluorinating agents in fluorinations of various organic, inorganic substrates and organometallic species containing E-Cl (E=C, Si, P, S and metal) bond(s) (metal halides, phosphines, silanes, etc.) as well as the F ion selective carriers with low detection limits.

Keywords: C,N-ligand; fluoride; fluorination; organotin(IV) compounds; structure.

Introduction

Main group organometallic fluorides have been the focus of considerable attention for several decades, whereas the most intensively studied group of the Periodic system seems to be group 14 with the majority of germanium and tin chemistry. These compounds could be prepared by metathetical fluorination of tin(IV) halides by alkaline metal fluorides.

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 by X-ray diffraction techniques in the solid state (Wardell and Spenser, 1994). 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., $Sn[C(SiMe_2Ph)_3]Me_2F$ (Al-Juaid et al., 1987), $Sn[C(SiMe_3)_3]Ph_2F$ (Al-Juaid et al., 1987), $Sn[C_6H_2(Me_3\text{-}2,4,6)_3]Me_2F$ (Reuter and Puff, 1989), and $Sn(CH_2SiMe_3)_3F$ (Beckmann et al., 2003), with a four-coordinated tin central atom, are monomeric with a Sn-F terminal single bond distance approximately 1.96Å (Kolb et al., 1991). Latest reports in this field deal with triorganotin(IV) fluorides of Men_3SnF (Beckmann et al., 2005) and $(R_2FSn)_2CH_2$ type, where the second type of compound was studied as stable fluoride-selective carriers (Chaniotakis et al., 2004). The X-ray based studies of complex difluorotriorganostannates $[Ph_3SnF_2]^-$ (Beckmann et al., 2002) and $[(Ph_2FSn)_2CH_2F]^-$ (Dakternieks et al., 1995) also appeared.

In the case of diorganotin(IV) difluorides, only a limited number of monomeric species are known, because a whole class of these compounds tends to form insoluble polymeric chains or nets via intermolecular associations (Tudela et al., 1996), or hypervalent complexes with excess of fluoride ion, which were studied at -100°C by ^{19}F and ^{119}Sn NMR spectroscopy (Dakternieks and Zhu, 1992). Only one purely monomeric diorganotin compound has been described in the solid state by crystallographic techniques (Leung et al., 2003). It is a quinoline substituted dialkyltin difluoride (Figure 1A) which was prepared by reaction of alkyltin(II) compound with tin(II) fluoride in boiling THF. There are two more published compounds with $[(CH_3)_2N(CH_2)_3]^-$ (Pieper et al., 1997) and $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}^-$ (Mehring et al., 2001) ligands (Figure 1B and C) where one of the fluorine atoms from the first part of the molecule is connected to the adjacent molecule by one or two oxygen atom bridges.

In addition, X-ray based investigations of some difluorotriorganostannates also appeared (Dakternieks et al., 1995; Beckmann et al., 2002). Concerning the group of monomeric monoorganotin(IV) fluorides there was only one monomeric compound prepared by a reaction of tris(2,6-dimethoxyphenyl)methanol with SnF_2 in diluted H_2SO_4 providing tris(2,6-dimethoxyphenyl)methylstannyltrifluride (Figure 1D) (Dostal et al., 1993). The tin atom in this compound is seven-coordinated and is described by the authors as the distorted monocapped-trigonal-antiprism with Sn-F bond lengths from 1.948(7) to 1.975(6) Å.

In the past two decades, organotin(IV) fluorides became a very promising group of compounds not only from the point of view of interesting structural motifs (Murphy et al., 1997; Dorn et al., 1997; Jagirdar et al., 1999) but also for their possible application particularly the metathetical halide for fluoride exchange reactions. The fluorination ability of Me_3SnF for metathetical fluorination of mainly group 4 cyclopentadienyl substituted compounds was recently investigated (Dorn et al., 1997; Murphy et al., 1997; Jagirdar et al., 1999; Erben et al., 2007). The application of triorganotin(IV) fluorides, namely Ph_3SnF, deals with liquid-solid phase-transfer catalyzed fluorinations of alkyl halides and sulfonates, where Ph_3SnF acts as phase-transfer catalyst via continuous formation of lipophilic

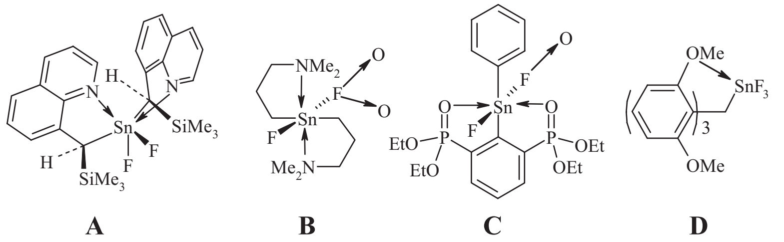


Figure 1 Structure of monomeric diorganotin difluorides.

$Ph_3SnF_2^-$ (Gingras' salt) anions entering organic phase in the form of the potassium salt (Druce et al., 1969; Nesmeyanov et al., 1972, 1975; Samuel et al., 1973; Gingras, 1991; Herzog et al., 1994; Beckmann et al., 2002; Cauzzi et al., 2002; Makosza and Bujok, 2004, 2005).

Chlorosilanes can be transformed to appropriate fluorosilanes, which are highly demanded by industry, by several methods and reagents (Damrauer and Simon, 1988; Kunai et al., 1996): $BF_3{\cdot}OEt_2$, 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). Kifer and van Dyke (1969, 1972) made partially fluorinated polysilanes by PF_5 or Ph_3CBF_4 methods. Generally, there are many disadvantages of the above-mentioned methods, for example, higher prize, instability, lower selectivity, toxicity and the need to use more than an equimolar amount of reagent. Also, the reaction time and high temperature is also needed to obtain satisfactory yield of fluorinated products. Lickiss and Lucas (1996) made fluorosilanes using ultrasound activation or started the reactions by a small amount of water. As reagents they used Na_2SiF_6 or $(NH_4)_2SiF_6$ in 1,2-dimethoxyethane (DME, <0.005% H_2O) but when the starting chlorosilanes contained a sterically demanding group (e.g., *t*-Bu_2SiCl_2) the reaction time at reflux conditions was approximately 2 weeks.

Fluorophospines can be prepared by the following methods: (i) by reaction of RLi with $ClPF_2$ (Heuer and Schmutzler, 1988); and (ii) reaction of $RPCl_2$ with SbF_3 or HF (Drozd et al., 1967). The yield of appropriate fluorophospine is approximately 20% in the case where R is alkyl and is increasing up to 35% if R is aryl. Fluorophosphines or organophosphonic acid fluorides are also prepared from corresponding chlorophosphines or organophosphonic acid chlorides by treating the substrate with various fluorinating agents, e.g., CsF (Krolevets et al., 1988), SbF_3 (Adamov et al., 1988), SF_5Cl (Fraser et al., 1972) or HF (Riesel and Haenel, 1991).

Acyl fluorides, fluoroformates and fluorinated phosgene are more stable than their chloro or bromo analogs and useful, for example, in peptide or natural products synthesis (Wakselman and Savrda, 1992; Carpino et al., 1996; Cotarca and Eckert, 2004). Several methods have been developed for acyl fluoride synthesis. Acyl chlorides or bromides were converted to the corresponding fluorides using $(CF_3)_2Cd$ (Morrison and Krause, 1981), Ishikawa's reagent $[CF_3CF_2CHFN(C_2H_5)_2]$ (Wong and Rando, 1982), aerosol fluorination (Adcock and Cherry, 1987), SF_4 or DAST (O'Sullivan et al., 1999) and various forms of HF and other fluorides serving as fluorine source (Olah et al., 1956; Olah et al., 1979; Liu et al., 1989). Cyclic ketones (Hara et al., 1995), alcohols, aldehydes (Zupan et al., 1989), carboxylic acids, acyl chlorides or *t*-Bu esters (in BrF_3) (Cohen et al., 2006) can also be converted into the respective acyl fluorides. Unfortunately most of the reagents used for these purposes must be stored in Teflon® or copper containers or, under pressure, react very exothermically with water, and also the selection of solvents which can be used with them is rather limited.

Sulfuryl fluoride is produced by direct reaction of elemetar fluorine with sulfur dioxide. Thionyl fluoride can be produced by the reaction of thionyl chloride with fluoride sources such as SbF_3 (Smith and Muetterties, 1960). Methanesulfonyl fluoride, benzenesulfonyl fluoride and substituted benzenesulfonyl fluorides are usually prepared by the reaction of the respective substrate with hydrogen fluoride at elevated temperatures in the presence of a chromium-magnesium catalyst with yields varying from 81% up to quantitative yields (Varfolomeev et al., 2001). Procedures using KF/CaF_2 (Ichihara et al., 1986) or KF/18-crown-6 (Lee et al., 1988) systems for preparation of various organosulfonyl fluorides were also described.

Binary metal fluorides such as CoF_3 are highly valuable reactants and materials for industry and are mainly prepared by reactions of metal halide or elemental metal with fluorine (Olah et al., 1992; Howe-Grant, 1995; Banks, 2000; Nakajima et al., 2000).

The most interesting current trend in organometallic or in coordination chemistry is the study of compounds containing tuned bi- and polydentate ligands. The main intention is the direct control of metal center properties by an effectively designed ligand. One of the preferred methods is the use of chelating ligand, where the metal atom is bonded to the ligand by two or more covalent or coordination bonds. This method is very efficient if five- or six-membered metallacycles are formed, which stabilize metal-carbon bonds and yield to these complexes interesting physicochemical properties. The most often studied organometallic compounds (Holmes, 1990; Jastrzebski, 1991a; Jastrzebski et al., 1991b; Jastrzebski and van Koten, 1993; Chuit et al., 1996; Buntine et al., 1999; Mitzel et al., 1999; Albrecht and van Koten, 2001; Akiba, 2002; Morales-Morales and Jensen, 2007) of this type are depicted in Figure 2.

This review summarizes the work of our group in the field of the use of C,N-chelated (containing $L^{CN}=\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}^-$ ligand – Figure 2A) organotin(IV) fluorides for metathetical fluorination during the past 8 years (Bareš et al., 2004;

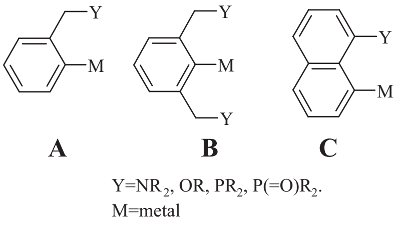


Figure 2 Organometallic compounds containing C, Y- or Y, C,Y-chelating ligands.

Novák et al., 2005, 2006, 2007; Chandra et al., 2006; Švec et al., 2007).

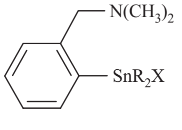
Results and discussion

Triorganotin(IV) fluorides: preparation and structure

Compounds **5–8** were prepared by the reaction of the appropriate triorganotin(IV) chlorides **1–4** and KF in a water/diethyl ether mixture (see Scheme 1). The purity of the compounds was established by ESI/MS spectrometry, elemental analysis, and multinuclear NMR spectroscopy (Bareš et al., 2004; Švec et al., 2007).

The structure of crystalline compounds **5–8** were determined by X-ray diffraction. Selected interatomic distances and angles are presented in Figure 3. All compounds reveal the monomeric structure without any intermolecular Sn···F contacts. The intermolecular Sn···F distances being in the range of 4.610–6.257 Å for **5** and **8**. The sum of van der Waals radii (Bondi, 1964) of Sn and F is 3.63 Å. In both compounds, the geometry of the central tin atom is that of distorted trigonal bipyramid with the electronegative atoms (N, F) in axial, and all carbon atoms in equatorial positions, which is in accordance to previously published results (Altmann et al., 1998; Rippstein et al., 1999a,b; Varga et al., 2001; Růžička et al., 2003b). The sum of interatomic angles in the equatorial plane is approaching the ideal value of 360° (e.g., 358.34° and 357.62° for **5** and **8**).

The extensions of N-Sn-F angles [e.g., 167.37(5)° for **5**, and 166.83(6)° for **8**] are similar to angles observed in the literature for the ligand (L^{CN}) used (Rippstein et al., 1999a,b). The extra large torsion angles (C1, C2, C7, N1: 32.10° for **5** and C11, C12, C17, N1: 34.57° for **8**) indicate the deviation of the CH$_2$ ligand group from the plane defined by C1 (C11 in **8**), Sn1, and N1 atoms, are probably caused by different electronic properties of fluorine in comparison with Cl and Br analogs (Roesky and Haiduc, 1999).



R/X	Cl	F
Me	**1**	**5**
n-Bu	**2**	**6**
t-Bu	**3**	**7**
Ph	**4**	**8**

Scheme 1 Preparation of compounds **5–8** by the reaction of the appropriate triorganotin(IV) chlorides **1–4** and KF in a water/diethyl ether mixture.

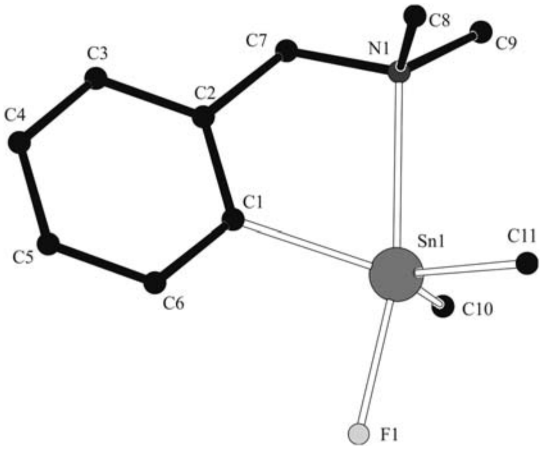


Figure 3 Molecular structure of compound **5**, hydrogens are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-F1 2.0384(10), Sn1-N1 2.4899(14), F1-Sn1-N1 167.37(5); for **6**: Sn-F 2.0804(16), Sn-N 2.526(3), F-Sn-N 168.80(8); for **8**: Sn1-F1 2.0242(12), Sn1-N1 2.5294(18), F1-Sn1-N1 166.82(6).

The Sn-F bond distances are somewhat longer [2.0384(10) Å (**5**), 2.0804(16) Å (**6**), 2.0242(12) Å (**8**)] than those found in monomeric tetracoordinated species (1.96 Å) (Kolb et al., 1991). Such elongation of these bonds is caused by intramolecular interaction of the amino donor group in the *trans* position to the fluorine atom. The average Sn-F and Sn-F′ distance in polymeric fluorides is 2.15Å (Wardell and Spenser, 1994). The Sn-N distances [Sn1-N1 2.4899(14), Sn-N 2.526(3), and Sn1-N1 2.5294(18)], which lie within the range found in the Cambridge Crystallographic Data Base (2.424–2.548 Å) for triorganotin compounds with L^{CN} [e.g., L^{CN}Me$_2$SnCl (Rippstein et al., 1999a) 2.531Å, L^{CN}Ph$_2$SnCl (Varga et al., 2001) 2.519Å, L^{CN}Ph$_2$SnBr (van Koten et al., 1976) 2.511 Å]. The only rarity from the set of triorganotin compounds containing L^{CN} as a ligand is compound **3**. It contains tetracoordinated tin atom and the distance between Sn and N atoms is significantly increased to 2.908 Å (Novák et al., 2004).

The structure of the studied compounds in chloroform solution at 300 K has been established by various multinuclear NMR techniques. The ^{119}Sn NMR chemical shift values of compounds **5–8** are collected in Table 1. Only one signal split to a doublet [due to $^{1}J(^{119}\mathrm{Sn}, ^{19}\mathrm{F})$, Table 1] has been observed in all of the ^{119}Sn spectra. The values are shifted somewhat upfield but still in the range for compounds with a five-coordinated tin atom (Holeček et al., 1983, 1990a,b). The values of $\delta(^{119}\mathrm{Sn})$ for insoluble compounds of the R$_3$SnF type, with oligo- or polymeric structure and five-coordinated tin atoms, obtained in solid state NMR studies, and the compounds of this study are comparable. [For example, $\delta(^{119}\mathrm{Sn})$ for **8** and $\delta(^{119}\mathrm{Sn})_{iso}$ for Ph$_3$SnF (Bai et al., 1991), which is a linear polymer with a rod-like structure with five-coordinated tin atoms (Tudela et al., 1992) differ by 13.3 ppm]. Similar linear chains were observed in the solid state structure of PhMe$_2$SnF; this

Table 1 The δ(^{119}Sn) NMR and (^1J(^{119}Sn,^{19}F) [Hz]) values for L^{CN}R$_2$SnX in comparison with literature values for R$_3$SnF.

R\X	LR$_2$SnX			R$_3$SnF^a ref. (Bai et al., 1991)
	F	Cl	Br	
Me	-53.8 (**5**) (2034)	-47.1 ref. (Z. Padělková and A. Růžička, unpublished results)	-55.7^b ref. (Jastrzebski et al., 1991c)	24.3 (1300)
n-Bu	-77.1 (**6**) (2114)	-51.7 ref. (Růžička et al., 1998)	-44.4 ref. (Růžička et al., 1998)	-9.3 (1291)
t-Bu	-92.1 (**7**) (2197)	17.5 ref. (Novák et al., 2004)	–	-13.1 (1260)
Ph	-198.6 (**8**) (2148)	-177.1 ref. (Růžička et al., 2001)	-180.8 ref. (Růžička et al., 2001)	-211.9 (1530)

^{a}Obtained from the solid state ^{119}Sn NMR spectra.

^{b}Analogous compound, where one benzylic hydrogen is substituted by the methyl group.

compound depolymerize when dissolved in toluene to yield oligomers with 10–50 basic structural units (depending on concentration and temperature) (Beckmann et al., 2003). The values of δ(^{119}Sn) for PhMe$_2$SnF (-49.3 ppm CP/MAS, -53.0 ppm toluene-d$_8$) differ only slightly from the value observed for compound **5** (-53.8 ppm L^{CN}Me$_2$SnF). Molecules of compounds L^{CN}(*n*-Bu)$_2$SnF (**6**) and L^{CN}(*t*-Bu)$_2$SnF (**7**) obviously have a five-coordinated tin atom, as demonstrated by the upfield shift tendency of δ(^{119}Sn) in L^{CN}R$_2$SnF and R$_3$SnF, respectively. Similar conclusions can be made from juxtaposition of δ(^{119}Sn) values of L^{CN}R$_2$SnF and L^{CN}R$_2$SnX (X=Br, Cl). The five-coordinated geometry of the tin atom in these compounds has been confirmed by X-ray diffraction (Rippstein et al., 1999a; Varga et al., 2001), ^{119}Sn CP MAS NMR (Růžička et al., 2001), and ^{1}H, ^{13}C, ^{15}N, and ^{119}Sn NMR studies in different solvents (Růžička et al., 1998) recently. Differences between extreme δ(^{119}Sn) values (L^{CN}R$_2$SnF vs. L^{CN}R$_2$SnX; approximately 20–30 ppm) are caused by the electronic properties of polar groups, rather than by different coordination numbers of tin atoms, in contrast to L^{CN}(*n*-Bu)$_2$SnCl (-51.7 ppm, c. n. 5) (Růžička et al., 1998) and PhMe$_2$SnCl (+98.0 ppm, c. n. 4) (Apodaca et al., 2001). By contrast, the value of δ(^{119}Sn) in compound **3** does not correlate with the previously found shifts, and values obtained from the literature (e.g., -53.9 ppm for [(*t*-Bu)$_2$PhSn]$_2$O) (Lockhart et al., 1989) and is caused by another type of coordination (Novák et al., 2004).

The coupling constants ^1J(^{119}Sn,^{19}F) of the compounds studied are typical for terminal Sn-F bonds, for example, approximately 2100 Hz (Beckmann et al., 2002), whereas the oligo- or polymeric compounds R$_3$SnF with bridging connections (Mercier et al., 1988) Sn-F···Sn have practically half-values. Only one sharp signal with resolved ^1J(^{19}F,$^{119/117}$Sn) coupling, and integral ratio of signals typical for only one Sn-F interaction, has been observed in each ^{19}F NMR spectrum. The ^{19}F NMR chemical shifts of the studied compounds (from -178.8 to -207.9 ppm, see Table 1) are in agreement with a few reported values for the terminal Sn-F bonds in five-coordinated triorganotin(IV) compounds; (Me$_3$SiCH$_2$)$_3$SnF (-207.2 ppm) (Beckmann et al., 2003), PhMe$_2$SnF·pyridine (-168.6 ppm) (Sau et al., 1980; Beckmann et al., 2003) and N(CH$_2$CH$_2$CH$_2$)$_3$SnF (-166.3 ppm) (Kolb et al., 1991). The measured coupling constants ^1J(^{119}Sn,^{13}C) and calculated interatomic angles C(1)-Sn-C(1) (Holeček et al., 1983, 1990a,b) are collected in Table 2.

These values are characteristic for five-coordinated triorganotin(IV) species. The ^{1}H and ^{119}Sn NMR spectra in different solvents and at variable temperature (VT) were measured in order to detect previously described (e.g., ionization of compounds or weakening of Sn-N bond) intramolecular processes (Růžička et al., 1998, 2003).

Because the compounds **5**–**8** reveal similar behavior in all measured spectra, only compound **5** was selected for this investigation. The VT spectra were measured in the range 185–300 K. Chloroform (as a non-coordinating solvent), acetone (as a coordinating solvent) and methanol (as a coordinating solvent with an acidic hydrogen atom) were selected for these purposes.

The values of δ(^{1}H) for all signals in all spectra differ in a few hundredths of ppm. The values of δ(^{119}Sn) are similar with the decrease in temperature. The coupling constant ^1J(^{119}Sn,^{19}F) decreases by 50–70 Hz with decreasing temperature; this indicates only slight weakening of the Sn-F bond. The values of δ(^{119}Sn) for **5** vary slightly (-64.9 to -46.0 ppm) in all solvents used, and are in the previously mentioned range for five-coordinated triorganotin(IV) species with terminal and covalent Sn-X bonds.

Compounds **5**, **6** and **8** were tested by the structural-correlation method originally given by Bürgi (1975) and elaborated for tin compounds by Britton and Dunitz (1981) that maps the pathway for the S$_N$2 reaction of triorganotin halides SnC$_3$XY with nucleophiles. In the case of **5**, **6** and **8**, the relevant geometrical data, i.e., the Sn-N and Sn-F bond lengths, the average C-Sn-N bond angle vs. Sn-N bond length, and the average C-Sn-F bond angle vs. Sn-F bond length match perfectly well with the theoretical curves deduced from crystallographic evidence (Padělková et al., 2005).

From the findings described above, one can conclude that compounds **5**–**8** are easy accessible monomeric triorganotin(IV) fluorides which exhibit the same structure in

Table 2 Selected NMR parameters of **5**–**8**.

R	LR$_2$SnF (5–8)			
	δ(^{19}F) (ppm)	^1J(^{19}F,^{119}Sn) (Hz)	^1J(^{119}Sn,^{13}C) (Hz)	Angle C-Sn-C^a
Me	-178.8	2023	531.5	127
n-Bu	-196.3	2103	515.9	126
t-Bu	-207.9	2188	470.1	122
Ph	-182.3	2141	792.0	123

^{a}Calculated from refs. (Holeček et al., 1983, 1990a,b).

the solid state and in solutions in different solvents at VT. The tin atom is five-coordinated with three carbons in axial and, fluorine and nitrogen [-$CH_2N(CH_3)_2$], respectively, in equatorial positions of a slightly distorted trigonal bipyramid which indicate the fact that the strength of the Sn-F bond could be influenced by the *trans* effect of amino nitrogen and thus used for metathetical exchange reactions for different types of inorganic as well as organic halides. The compound **6** – the di-n-butyl substituted one, has been selected for testing this reactivity.

Fluorination of C,N-chelated diorganotin(IV) halides

A more complicated situation during a preparation of fluoride derivatives of diorganotin(IV) than triorganotin(IV) fluorides containing L^{CN} ligand was observed, and although compound $(L^{CN})_2PhSnCl$ is the triorganotin(IV) one, it belongs to this group because of its reactivity.

Four different methods (**A–D**) were used for replacing of halide by fluorine atom(s) in $(L^{CN})_2PhSnCl$ and $(L^{CN})_2SnX_2$ (X=Cl, Br, I). Method **A** is based on reaction of the appropriate halide with an excess of KF in water/benzene or dichlormethane mixture. Method **B** is the reaction with dried NH_4F (excess) in dichloromethane under an argon atmosphere. Method **C** uses the KF/18-crown-6/benzene fluorination system, and method **D** is based on the fluorination ability of $L^{CN}(n\text{-}Bu)_2SnF$ (**6**).

Using fluorination methods **A** and **D** the only product for $(L^{CN})_2SnX_2$ is the monomeric diorganotin(IV) difluoride $(L^{CN})_2SnF_2$ in essentially quantitative yields. Surprisingly, no water was coordinated to $(L^{CN})_2SnF_2$ after the reactions in system **A**. Another surprise is the ability of triorganotin(IV) compound **6** (system **D**) to fluorinate, presumably, more reactive diorganotin(IV) compounds $(L^{CN})_2SnX_2$. The reaction time was dependent on the system used, from a few hours (**D**) to the days in the case of reaction of $(L^{CN})_2PhSnCl$ with KF (**A**). After 2 days of reaction of $(L^{CN})_2PhSnCl$ with KF three signals in the ^{119}Sn NMR spectrum appeared: -252.8 ppm [minor signal of unreacted $(L^{CN})_2PhSnCl$], -370.4 ppm [doublet, $^1J(Sn, F)=2565$ Hz] which was assigned to partially reacted $(L^{CN})_2SnClF$ with ~20% of integral of major signal of $(L^{CN})_2SnF_2$ [-383.5 ppm, triplet, $^1J(Sn, F)=2677$ Hz]. In the ^{19}F NMR spectrum two signals were observed [-172.5 ppm – with satellites $^1J(Sn, F)=2565$ Hz for $L^{CN}{}_2SnClF$ and -178.39 ppm – with satellites $^1J(Sn, F)=2677$ Hz for $(L^{CN})_2SnF_2$]. Increasing the reaction time to 5 days gave pure $(L^{CN})_2SnF_2$. The tin atom coordination geometry in $(L^{CN})_2SnF_2$ (Figure 4) is distorted octahedral with *C,C-transoid* and nitrogen and fluorine atoms mutually *cis* similar to $(L^{CN})_2SnX_2$ (Novák et al., 2005a,b, 2006; Padělková et al., 2005). The lengths of Sn-F bonds [1.981(1) and 1.991(2) Å] are in the middle of the range delineated by the two extremes found for monomeric triorganotin(IV) fluorides (1.96–2.08 Å) (Bareš et al., 2004; Novák et al., 2005, 2006, 2007; Chandra et al., 2006; Švec et al., 2007). The molecular geometry of $(L^{CN})_2SnF_2$ is also very similar to the recently reported quinoline substituted diorganotin(IV) difluoride (Figure 1A) (Leung et al., 2003).

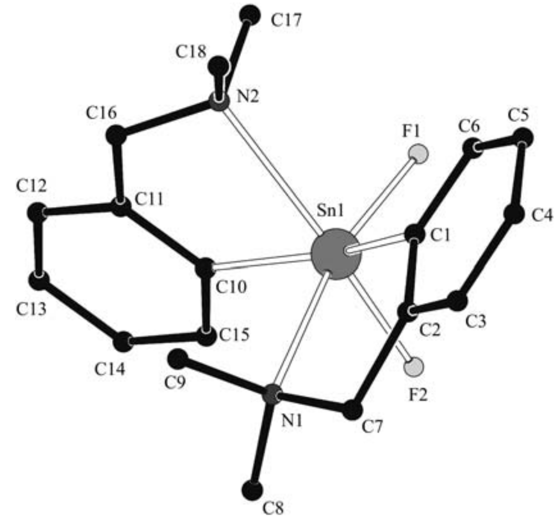


Figure 4 Molecular structure of compound **5**, hydrogens are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-F1 1.991(1), Sn1-F2 1.981(1), Sn1-N1 2.597(1), Sn1-N2 2.496(2), Sn1-C1 2.123(2), Sn1-C10 2.129(2), F1-Sn1-F2 89.64(4), N1-Sn1-N2 104.05(4), N1-Sn1-C10 90.03(5), C1-Sn1-N2 90.29(5), C1-Sn1-C10 155.12(6), F1-Sn1-N1 167.13(4), F1-Sn1-N2 82.79(4), F2-Sn1-N2 166.60(4), F2-Sn1-N1 85.57(4), F1-Sn1-C1 95.61(5), F1-Sn1-C10 102.35(5), C1-Sn1-N1 73.73(5), N1-Sn1-C10 90.03(5), C1-Sn1-F2 101.48(5), C1-Sn1-N2 75.23(5).

When $(L^{CN})_2PhSnCl$ was fluorinated by KF in water (**A**) compound $(L^{CN})_2SnF_2$ was obtained as the only soluble product. Phenyl group migration (Dakternieks and Zhu, 1992), described in the class of organotin compounds by Dakternieks and Zhu, occurred during the course of reaction. To exclude the presence of water, which has been supposed to be the reason for phenyl group migration, a vacuum dried NH_4F in dried dichloromethane (**B**) as the fluorinating medium was used, but the result was the same as in the previous case. The desired product, monomeric $(L^{CN})_2SnPhF$, was prepared by methods **C** and **D**. The composition of this compound has been proven by NMR. The ^{19}F NMR spectrum in $CDCl_3$ at 300 K reveals a single resonance at -193.5 ppm with resolved tin satellites [$^1J(^{19}F, ^{119}Sn)=2240$ Hz] and there is a doublet in the ^{119}Sn NMR spectrum at -216.1 ppm with similar coupling constant [$^1J(^{119}Sn, ^{19}F)=2232$ Hz]. All parameters are comparable with $L^{CN}Ph_2SnF$ (**8**) [$\delta(^{119}Sn)=-198.6$ ppm; $\delta(^{19}F)=-182.3$ ppm; $^1J(^{119}Sn, ^{19}F)=2141$ Hz]. Based on similarities of these parameters and patterns of ^1H NMR spectra to $(L^{CN})_2PhSnCl$, we also proposed similar structures for both compounds (monomeric with TBP geometry with N and F atoms in axial positions).

When $L^{CN}PhSnCl_2$ was reacted with two equivalents of NH_4F in dichloromethane, complex $[L^{CN}PhSnF_3]^-$ was observed as the major species (more than 95%, the rest was $[(L^{CN}SnF_3)_2\text{-}\mu\text{-}(F)_2]^{2-}$ – based on the same ^{19}F NMR spectra parameters at 250 K in methanol). In insoluble part, $(L^{CN}PhSnF_2)_n$ was identified as a byproduct with the aid of solid state ^{19}F NMR and ESI/MS measurements.

Reaction of $L^{CN}PhSnCl_2$ with an excess of KF in water/benzene mixture (method **A**) gave the totally insoluble product. This product has been investigated by means of ^{19}F solid state NMR. The spectrum obtained is very similar (by signal locations) to ^{19}F spectrum of product of reaction of $L^{CN}Ph_2SnCl$ with an excess of NH_4F in methanol. This fact led us to the speculation that the products of both reactions are similar, and that the potassium counterion bearing species are insoluble. Method **C** reveals two products, the soluble one which was investigated by NMR in benzene and the insoluble one studied with the aid of solid state NMR.

Compound $(L^{CN}PhSnF_2)_n$ was prepared from $L^{CN}PhSnCl_2$ in essentially quantitative yield by method **D**. Its solubility is very limited in almost all solvents. Only ^1H and ^{19}F NMR spectra were measured from low concentration samples in methanol. These spectra reveal one set of signals in ^1H NMR and two broad signals with 1:1 in ^{19}F NMR (-142.8 and -154.5 ppm, broad signals 1:1). In solid state ^{19}F NMR spectrum two broad signals (-136.8 and -148.5 ppm, 1:1) of similar pattern and location were observed as in methanolic solution. The ESI/MS spectra gave additional information about the composition of $(L^{CN}PhSnF_2)_n$, the signal *m/z* 1064 was assigned to the $[M\text{-}CH_3N{=}CH_2]^+$ ion which is probably the part of trimeric structure $(L^{CN}PhSnF_2)_3$. This presumably trimeric structure dissolves quantitatively and immediately upon addition of exactly three equivalents of NH_4F in methanol to yield pure $[L^{CN}SnPhF_3]^-$. When further portions of NH_4F were added the small amount of phenyl group migration products as $[(L^{CN}SnF_3)_2\text{-}\mu\text{-}(F)_2]^{2-}$ appeared.

Two different methods were used for replacing of chlorine by fluorine atom(s) in *n*-butyl analog of $L^{CN}PhSnCl_2$. The first method is based on known fluorination ability of **6** and the second one is the reaction with dried NH_4F (excess) in dichloromethane under an argon atmosphere (Figure 5).

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 dramatically on the solvent used and temperature. In chloroform, there is 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 slightly 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 TBP).

When the compound $L^{CN}(n\text{-Bu})SnCl_2$ was treated only with two equivalents of NH_4F, the product of similar properties as found for the first method was revealed. An addition of one equivalent of NH_4F to $(L^{CN}(n\text{-Bu})SnF_2)_n$ in methanol caused the formation of dimeric species which upon addition of further equivalents of NH_4F probably gave monomeric species. Similar behavior of such compounds was recently found for a Ph analog of $[NH_4]^+[L^{CN}(n\text{-Bu})SnF_3]^-$ and was suggested from MS spectra pattern. From low temperature ^{19}F NMR spectra it was deduced that three terminal fluorine atoms are bonded to tin $[^1J(^{119}Sn, ^{19}F)\approx 3100$ Hz], and the same structure is supported by broad quartet in ^{119}Sn NMR spectra located in the region typical for a six-coordinated tin atom (-438.4 ppm).

The reaction of three equivalents of $[NH_4]^+[L^{CN}(n\text{-Bu})SnF_3]^-$ and $Pr(OTf)_3$ led to dimeric arrangement $[L^{CN}(n\text{-Bu})SnF(\mu\text{-F})_2SnL^{CN}(n\text{-Bu})F]\cdot 2HOTf$. Two different polymorphs of polymeric $[L^{CN}(n\text{-Bu})SnF_2]_n$ have been obtained by crystallization. These compounds were used in design of ion selective carriers (Chandra et al., 2006).

When the product of fluorination of $L^{CN}(n\text{-Bu})SnCl_2$ had been crystallized from methanol solution crystals of $[L^{CN}(n\text{-Bu})SnF_2]_n$ were obtained. The almost linear polymeric structure

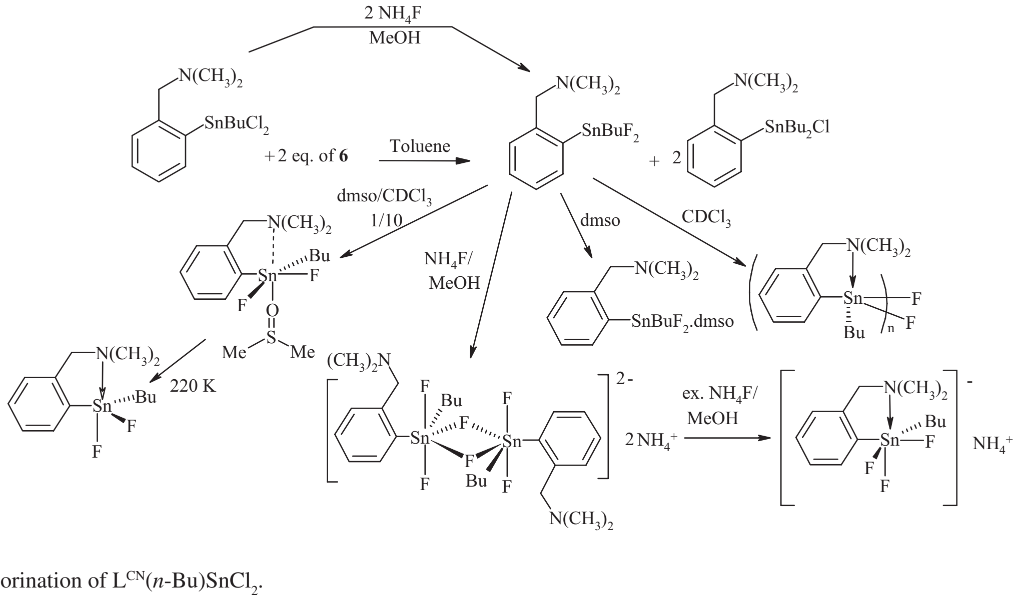


Figure 5 Fluorination of $L^{CN}(n\text{-Bu})SnCl_2$.

where the six-coordinated tin atoms are connected by one fluorine bridge is very different from previously found structure of $L^{CN}(n\text{-Bu})SnCl_2$, where a zig-zag chain appears, dimeric $[L^{CN}(n\text{-Bu})SnF(\mu\text{-}F)_2SnL^{CN}(n\text{-Bu})F]\cdot 2HOTf$ or monomeric $(L^{CN})_2SnF_2$. This fact is demonstrated mainly in differences in Sn-F bond lengths and Sn-F-Sn angles (Figure 6). Both distances of the terminal and bridging fluorine to tin atoms are comparable to the values found in the literature and, for example, for $(L^{CN})_2SnF_2$ (Novák et al., 2005b). The non-equal distances for bridging Sn-F bonds were found. Very strong intramolecular connection Sn-N comparable to monomeric triorganotin fluorides (Bareš et al., 2004) or monoorganotin halides (Novák et al., 2006) was found for all compounds.

The different polymorph $[L^{CN}(n\text{-Bu})SnF_2]_n$ of the same compound has been obtained from methanolic solution of fluorination product of $L^{CN}(n\text{-Bu})SnCl_2$ and ammonium fluoride in the first crystallization crop. The second crop gave the mixture of both polymorphs – needles and blocks in approximately 4:1 ratio. The structure of both polymorphs is similar from the point of view of found main interatomic distances and angles but in a closer investigation of polymeric chain there is a major difference in mutual orientation of butyl and ligand moieties through this chain. Whereas the same orientation of butyl moieties are in the first one, the second one is opposite (approximately 180° rotated perpendicularly to the polymer axis) (Figure 6). This phenomenon can be interpreted either by the polymer chemistry or inorganic chemistry nomenclature as isotactic and syndiotactic polymers or infinite chain of optical (in octahedral coordination vicinity of tin atoms) A,C (alternating) or A,A isomers.

Surprisingly, the single crystals of $(L^{CN}PhSnF_2)_n$ were obtained after more than 2 years. The structure of $(L^{CN}PhSnF_2)_n$ (Švec et al., 2009) is linear polymeric. It crystallizes as a linear polymer with 'rod-like' F-Sn-F chains. The tin atom in the solid state is six-coordinated and tin atoms are interconnected by one bridging fluorine. This compound is almost insoluble in all common organic solvents, which is a limitation for the structural study in solution by multinuclear NMR spectroscopy. In contrast to $[L^{CN}(n\text{-Bu})SnF_2]_n$ which crystallizes as two polymorphs (isotactic and syndiotactic polymer), $(L^{CN}PhSnF_2)_n$ was isolated only as the syndiotactic polymer. The distances Sn1-F1 (2.141 Å, bridging fluorine) and Sn1-F2 (2.081 Å, terminal fluorine) are somewhat longer than in syndiotactic $[L^{CN}(n\text{-Bu})SnF_2]_n$ (2.058 Å and 1.986 Å, respectively). By contrast, the distance Sn1-N1 is shorter in the case of $(L^{CN}PhSnF_2)_n$ (2.438 Å vs. 2.554 Å). The interatomic angles of the F-Sn-F chains are almost straight for both syndiotactic $[L^{CN}(n\text{-Bu})SnF_2]_n$ (173.77°) and $(L^{CN}PhSnF_2)_n$ (176.96°).

Prepared compounds were studied by DSC and theoretical calculations at the B3LYP/LANL2DZ level too.

Fluorination of C,N-chelated monoorganotin(IV) halides

Compounds $L^{CN}SnX_3$ (X=Cl, Br, I) were prepared by conversion of $L^{CN}Li$ with one molar equivalent of tin(IV) halide in relatively low yield. Such a low yield is typical for monoorganotin compounds (Thoonen et al., 2004) and in this specific case is probably caused by high Lewis acidity of tin atom, and thus the formation of a stannate species as an unidentified byproduct. Compounds $L^{CN}SnX_3$ are relatively stable to air and moisture and no decomposition or hydrolysis was observed after a long exposure of compounds on a watch glass under laboratory conditions.

$L^{CN}SnBr_3$ as the most stable and easily prepared compound from the studied set was treated with two different fluorinating agents to obtain a defined organotin fluoride (Figure 7). Firstly, we mixed $L^{CN}SnBr_3$ with three molar equivalents of dried NH_4F in dichloromethane and the mixture was stirred for several days. In this mixture, four different species were observed. Based on our previous study and ^{119}Sn and ^{19}F NMR spectra of the mixture, we can identify two of the compounds as $[L^{CN}Sn(F)_2\text{-}\mu\text{-}(F)_2\text{-}(F)_2SnL^{CN}]^{2-}$, i.e., a dinuclear species consistent of two six-coordinated tin atoms bridged by two fluorine atoms, the coordination sphere of tin is completed by three terminal fluoride atoms and one carbon atom originated from the ligand [$\delta(^{119}Sn)$=-605.5 ppm (d of d of t); $^1J(^{119}Sn, ^{19}F)$=2628 and 1470 Hz], and $[L^{CN}SnF_5]^{2-}$ [$\delta(^{119}Sn)$= -685.0 ppm (d of q); $^1J(^{119}Sn, ^{19}F)$=2530 and 1165 Hz]. The structure of this compound is suggested to be identical to

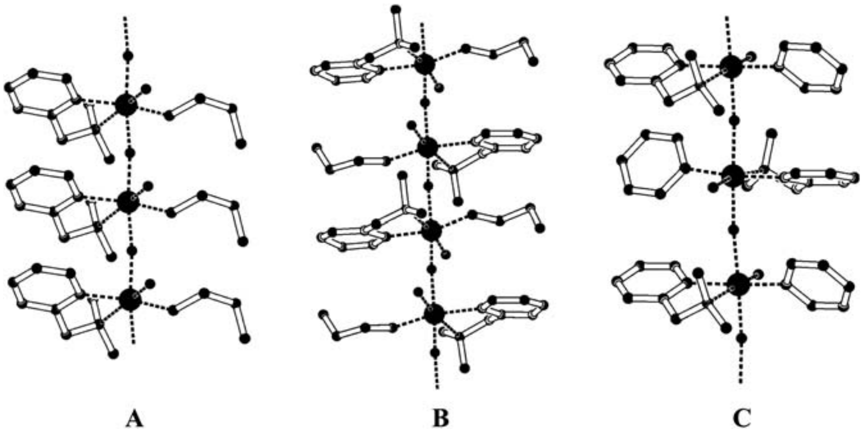


Figure 6 Comparative view of isotactic $[L^{CN}(n\text{-Bu})SnF_2]_n$ (A), syndiotactic $[L^{CN}(n\text{-Bu})SnF_2]_n$ (B), and syndiotactic $(L^{CN}PhSnF_2)_n$ (C).

$$\mathrm{L^{CN}SnX_3} \xrightarrow{\text{3 eq. of } \mathbf{6}} \mathrm{[L^{CN}SnF_2(\mu^2\text{-}F)_2]_n}$$

Figure 7 Fluorination of monoorganotin(IV) compounds; X=Cl, Br, I.

complex $[\mathrm{L^{CN}SnF_5}]^{2-}$ reported recently by us and similar to complex $[\mathrm{PhSnF_5}]^{2-}$ reported earlier by Dakternieks and Zhu (1992). On each tin *pseudo*-octahedral center, there are one carbon and five terminal fluorine atoms, four in equatorial and one in axial positions. The logical step going from dinuclear $[\mathrm{L^{CN}Sn(F)_2\text{-}\mu\text{-}(F)_2\text{-}(F)_2SnL^{CN}}]^{2-}$ to monomeric $[\mathrm{L^{CN}SnF_5}]^{2-}$, complex $[\mathrm{L^{CN}SnF_4}]^{-}$, with a presumably strong intramolecular N→Sn interaction and hence a six-coordinated tin central atom, was unfortunately not observed in the reaction mixture. The very minor species observed in the mixture can be identified as $\mathrm{L^{CN}SnF_3{\cdot}HOCH_3}$ [$\delta(^{119}\mathrm{Sn})$=-561.4 (d of t); $^1J(^{119}\mathrm{Sn}, {}^{19}\mathrm{F})$=2670 and 2676 Hz] and its isomer [$\delta(^{119}\mathrm{Sn})$=-556.0 (d of t); $^1J(^{119}\mathrm{Sn}, {}^{19}\mathrm{F})$=2673 and 2650 Hz] similar to the suggestion of Silvestru (Varga et al., 2005) with coordinated methanol as a solvate. When an excess of $\mathrm{NH_4F}$ (~20 eq.) is mixed together with $\mathrm{L^{CN}SnBr_3}$ overnight, complex $[\mathrm{L^{CN}SnF_5}]^{2-}$ is observed by the NMR techniques as the major product, the minor impurities were assigned to $[\mathrm{L^{CN}Sn(F)_2\text{-}\mu\text{-}(F)_2\text{-}(F)_2SnL^{CN}}]^{2-}$.

Secondly, $\mathrm{L^{CN}SnBr_3}$ was treated with one to three equivalents of $\mathrm{L^{CN}}(n\text{-}\mathrm{Bu})_2\mathrm{SnF}$ (**6**). After all reactions, nearly theoretical amount of $\mathrm{L^{CN}}(n\text{-}\mathrm{Bu})_2\mathrm{SnBr}$, as the product of fluorine for bromine atom metathetical exchange, was identified as the toluene only soluble product, which indicates a high conversion of $\mathrm{L^{CN}SnBr_3}$ to a fluoride-containing species. In the case of a toluene washed product ($[\mathrm{L^{CN}Sn(F)_2\text{-}\mu\text{-}(F)_2}]_n$) of reaction of $\mathrm{L^{CN}SnBr_3}$ with three equivalents of **6** the CP/MAS NMR and ESI/MS spectra were measured. An oligomeric structure can be deduced of all the indications: (i) positive-ion ESI/MS spectra where the highest observable tin containing isotopic cluster was *m/z* 1216, which is close to the molecular weight of a tetramer (M_W=1244) in negative-ion ESI/MS spectra the main signal *m/z* 330 corresponds to $[\mathrm{L^{CN}SnF_4}]^{-}$; (ii) species are insoluble in common organic solvents and water; and (iii) relatively high melting point in comparison to $\mathrm{L^{CN}SnBr_3}$. To explore the possibility of further complexation of fluoride ion, an excess of $\mathrm{NH_4F}$ in methanol was added to $[\mathrm{L^{CN}Sn(F)_2\text{-}\mu\text{-}(F)_2}]_n$ in the NMR tube. Based on ^{1}H, ^{19}F and ^{119}Sn NMR spectra parameters, the major species in solution was identified as $[\mathrm{L^{CN}Sn(F)_2\text{-}\mu\text{-}(F)_2\text{-}(F)_2SnL^{CN}}]^{2-}$. The remaining very minor signals in NMR spectra belong to the same complexes as $\mathrm{L^{CN}SnF_3{\cdot}HOCH_3}$.

Fluorination of N,C,N-chelated organotin(IV) halides

To make the closest comparison of C,N- and N,C,N-chelating ligand analogical compounds [where LNCN is 2,6-bis(dimethylaminomethyl)phenyl-] were studied (Me, *n*-Bu, Ph). Fluorination of $\mathrm{L^{NCN}Me_2SnCl}$ by KF and 18-crown-6 in benzene yielded $\mathrm{L^{NCN}Me_2SnF}$ which revealed similar structural behavior [e.g., five-coordinated tin atom $\delta(^{119}\mathrm{Sn})$=-83.5 (d); $^1J(^{119}\mathrm{Sn},{}^{19}\mathrm{F})$=2160 Hz] in solution as the above-described analog $\mathrm{L^{NCN}Me_2SnF}$ with a five-coordinated tin center and the dynamic exchange of nitrogen donors.

Compound $\mathrm{L^{NCN}}(n\text{-}\mathrm{Bu})_2\mathrm{SnF}$, prepared in biphasic system ether/water similarly as **6**, revealed the same structural behavior in non-coordinating solvents as was found for $\mathrm{L^{NCN}Me_2SnF}$ with retained covalent Sn-F bond [in $\mathrm{CDCl_3}$ at 300 K $\delta(^{119}\mathrm{Sn})$=-96.0 ppm (d); $^1J(^{119}\mathrm{Sn}, {}^{19}\mathrm{F})$=2195 Hz; $\delta(^{119}\mathrm{Sn})$=-107.1 ppm (d); $^1J(^{119}\mathrm{Sn}, {}^{19}\mathrm{F})$=2286 Hz; $\mathrm{CDCl_3}$ (235K); $\delta(^{119}\mathrm{Sn})$=-107.7 ppm (d); $^1J(^{119}\mathrm{Sn}, {}^{19}\mathrm{F})$=2320 Hz; toluene-*d8*, (190 K)]. In the proton NMR spectrum measured at 290 K, only one set of broad signals for $\mathrm{-CH_2N}$ and $\mathrm{NMe_2}$ moieties was observed, which decoalesce with the decrease in temperature [$\mathrm{-CH_2N}$ at 280K and $\mathrm{N(CH_3)_2}$ at 260 K]. Only negligible shift of these signals to the higher field is caused by strengthening on Sn-N interaction. One sharp signal at -186.0 ppm with satellites [$^1J(^{19}\mathrm{F}, {}^{119}\mathrm{Sn})$=2150 Hz] in the ^{19}F NMR spectrum gave further evidence of the monomeric structure with covalent and terminal Sn-F bond. This structural arrangement retained in whole temperature range (300–210 K) and only a few hertz decrease in the value of $^1J(^{19}\mathrm{F}, {}^{119}\mathrm{Sn})$ is caused by shortening of interaction between Sn and donor atoms and consequent elongation of tin-fluorine bond. By contrast, in methanol solution similar dynamic equilibrium as found for $\mathrm{L^{NCN}}(n\text{-}\mathrm{Bu})_2\mathrm{SnCl}$ or Br with the Sn-X bond ionization was observed (Jambor et al., 2001a; Růžička et al., 2003a) The dynamic process (Figure 8) was determined on the basis of VT ^{119}Sn and ^{19}F NMR spectra in methanol. One singlet resonance was observed: -165.9 ppm corresponding to the structural type depicted in Figure 8B and the broad doublet -198.8 ppm with $^1J(^{119}\mathrm{Sn},{}^{19}\mathrm{F})$=2294 Hz related to the type **A** as a result of dissociation of Sn-F bond at room temperature. At 260 K new singlet at +53.4 ppm appeared in the spectrum. Such a downfield shift is characteristic for process of ionization leading to the limit ionic structure **C** ($[\mathrm{L^{NCN}}(n\text{-}\mathrm{Bu})_2\mathrm{Sn}]^{+}$) as a consequence of strengthening of Sn-N interaction and five- or better [3+2] coordinated tin center. With the further decrease of temperature to 200 K the only detectable signal was $\delta(^{119}\mathrm{Sn})$=48.8 ppm which is owing to a further

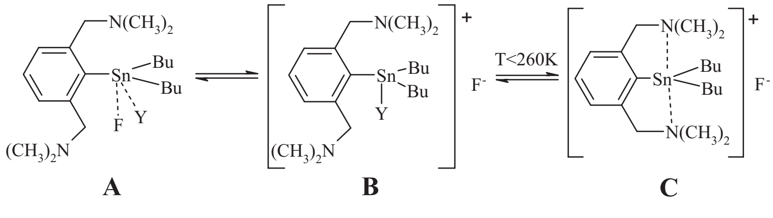


Figure 8 Structural behavior of $\mathrm{L^{NCN}}(n\text{-}\mathrm{Bu})_2\mathrm{SnF}$ in the methanol solution; Y: molecule of solvent.

increase of Sn-N bonds strength and an extrusion of methanol molecule from tin coordination sphere as shown in the limit structure C. In the ^{19}F NMR spectrum at 260 K two broad signals at -149.0 ppm with $^{1}J(^{19}\text{F},^{119}\text{Sn})$=2398 Hz, corresponding to structure **A**, and -130.0 ppm, which corresponds to values of free F ion, were observed. Decreasing the temperature to the limit 170 K adjacent broad signals were detected (-131.1; -137.8; -146.2; -147.9; -150.4 at 170 K). The signal with the tin satellites observed at higher temperature (-149.0 ppm; 260 K) was getting broader and at 200 K was not detected which can be explained by Sn-F bond dissociation and ionic structure formation. The next signals at lower temperature can be explained by an interaction of 'naked' fluoride ion with the solvent molecules.

N,C,N-chelated diorganotin(IV) fluorides

The previously discussed products of fluorination of $L^{CN}PhSnCl_2$ were only slightly soluble in methanol. The structural investigation was based on ^{1}H, ^{119}Sn and low temperature ^{19}F NMR spectral data. Very complicated multiplets in the ^{119}Sn spectra and very broad signals in the ^{19}F NMR spectra at room temperature were found. The similar structural behavior was assigned to the derivative $[L^{NCN}PhSnF_3]^-$ by means of multinuclear NMR spectroscopy in the chloroform solution. In contrast to analogs of $L^{NCN}PhSnCl_2$ containing the L^{CN} ligand, all fluoroderivatives of $L^{NCN}PhSnCl_2$ revealed very good solubility in methanol and even in $CDCl_3$ and CD_2Cl_2.

Firstly, two equivalents of NH_4F in CH_2Cl_2 were added to $L^{NCN}PhSnCl_2$ which lead, according to ^{19}F and ^{119}Sn NMR spectra, to the dominant formation of $[L^{NCN}PhSnF_3]^-$. This compound reveals characteristic broadened doublet of triplets (dt) in ^{119}Sn NMR spectrum measured in methanol [$\delta(^{119}\text{Sn})$= -486.6 ppm with $^{1}J(^{119}\text{Sn},^{19}\text{F})$=2770 and 2635 Hz]. A similar spectral pattern and chemical shift has been observed in ^{119}Sn NMR spectrum of $[Bu_4N]^+$ $[Ph_2SnF_3]^-$ [-402 ppm; $^{1}J(^{119}\text{Sn}, ^{19}\text{F})$=2310 (d) and 2250 (t) Hz] (Dakternieks and Zhu, 1992) and for $[L^{CN}PhSnF_3]^-$ moiety [-484.8 ppm with $^{1}J(^{119}\text{Sn}, ^{19}\text{F})$=2626 and 2706 Hz]. A triplet [-143.0 ppm; $^{1}J(^{19}\text{F}, ^{119}\text{Sn})$=2581 Hz and $^{2}J(^{19}\text{F}, ^{19}\text{F})$=32 Hz] and a doublet [-159.9 ppm; $^{1}J(^{19}\text{F}, ^{119}\text{Sn})$=2745 Hz and $^{2}J(^{19}\text{F}, ^{19}\text{F})$=32 Hz] with integral ratio 1:2 were found in ^{19}F NMR spectrum at 250 K. Further addition of NH_4F into the sample of $[L^{NCN}PhSnF_3]^-$ did not lead to change of NMR spectral patterns.

Some reactions of $L^{NCN}PhSnCl_2$ led to the formation of identical monoorganotin(IV) derivatives, which were found in the case of reactivity of $L^{NCN}SnBr_3$ (*vide infra*) as a result of a previously described phenyl group migration process (Dakternieks and Zhu, 1992). The reaction of $L^{NCN}PhSnCl_2$ with 20 molar equivalents of ammonium fluoride gave the described $[L^{NCN}PhSnF_3]^-$ in an equilibrium with $[NH_4]^+[L^{NCN}SnF_4]^-$ which are sparingly soluble in $CDCl_3$. The ^{119}Sn NMR spectrum in this solvent shows the major doublet of triplet for $[L^{NCN}PhSnF_3]^-$ -488.3 ppm with two comparable Sn-F couplings 2792 Hz and 2577 Hz and the second rather complex multiplet [-601.3 ppm (ddt) $^{1}J(^{119}\text{Sn}, ^{19}\text{F})\approx$2430 Hz] which corresponds to $[NH_4]^+[L^{NCN}SnF_4]^-$. The ^{19}F NMR spectrum at 295 K contained a couple of very broad signals and one broadened triplet at -138.6 ppm with $^{1}J(^{19}\text{F}, ^{119}\text{Sn})$=2745 Hz and $^{2}J(^{19}\text{F}, ^{19}\text{F})$=32 Hz. In the same spectrum at 220 K some signals are sharper [-136.9 ppm with $^{1}J(^{19}\text{F}, ^{119}\text{Sn})$=2752 Hz and -165.6 ppm with $^{1}J(^{19}\text{F}, ^{119}\text{Sn})$=2606 Hz ($[L^{NCN}PhSnF_3]^-$)] but remaining signals which belong to $[NH_4]^+[L^{NCN}SnF_4]^-$ retained unchanged (*vide infra*).

After the reaction of $L^{NCN}PhSnCl_2$ with two equivalents of $L^{CN}(n\text{-Bu})_2SnF$ the toluene insoluble residue was analyzed by ESI/MS. The highest intensity isotopic peak with the highest *m/z* value was 1161 $[M+H]^+$ in positive ion mode which can be assigned to compound $[(L^{NCN})SnF_2(\mu\text{-F})_2]_3$. In the negative ion mode, there is the main peak *m/z*=387 which belongs to anion $[(L^{NCN})SnF_4]^-$. The trimeric organization of $[(L^{NCN})SnF_2(\mu\text{-F})_2]_3$ comes apart owing to solvent leading to the zwitterionic compound $[H^+{\cdot}L^{NCN}SnF_4^-]$ that will be discussed later and also ^{1}H, ^{19}F and ^{119}Sn NMR spectra of $[(L^{NCN})SnF_2(\mu\text{-F})_2]_3$ measured in chloroform are identical with spectra of $[H^+{\cdot}L^{NCN}SnF_4^-]$ (*vide infra*). Insoluble products formed by this reaction were identified to be identical with Ph_2SnF_2 and Ph_3SnF detected in reactivity of $L^{CN}PhSnCl_2$ by ^{19}F CP/MAS NMR spectroscopy.

N,C,N-chelated monoorganotin(IV) fluorides

Compound $L^{NCN}SnBr_3$ is very reactive towards the moisture and its molecular structure can be described as a distorted octahedron with nearly equivalent Sn-Br and Sn-N bonds. In the case of reactivity of $L^{NCN}SnBr_3$ two synthetic pathways were used.

When only three equivalents of NH_4F were used for fluorination of $L^{NCN}SnBr_3$, poorly soluble products in non-coordinating solvents were obtained. Although these species revealed relatively higher solubility in methanol we were not able to identify their structures even from low temperature proton and ^{19}F NMR spectra. We can suggest the presence of partially fluorinated products making various types of oligomers through halide bridges with the increase of temperature. This suggestion can be supported mainly by study of ^{19}F NMR spectra. At 290 K a sharp singlet -131.86 ppm with satellites $^{1}J(^{19}\text{F}, ^{119}\text{Sn})$=2561 Hz was observed, which belongs to a terminal fluorine bonded to tin atom, but without any further coupling to fluorine atoms, and very broad signal in the range -142 to -154 ppm. In this area of spectrum at 220 K eight new rather broad signals without any couplings were visible. Earlier sharp signals are becoming very broad with the loss of satellites at the same conditions. At the same time two new signals appeared at -163.6 and -167.4 ppm with $^{1}J(^{19}\text{F}, ^{119}\text{Sn})\approx$1785 Hz which is typical for bridging fluorine atoms and which is in good agreement with an oligomeric structure.

In the next reaction, an excess of NH_4F was applied which led to formation of $[NH_4]^+[L^{NCN}SnF_4]^-$ characterized by ^{119}Sn and ^{19}F NMR spectra in methanol. The ^{19}F NMR spectrum at 290 K reveals two broad signals at -143.6 and -153.2 ppm. With a decrease of temperature to 250 K the original signal at -143.6 ppm was sharper, the tin couplings were observed [$^{1}J(^{19}\text{F}, ^{119}\text{Sn})$=2529 Hz] and the second signal disappeared. A further decrease of temperature did not change the spectral pattern [220 K: -142.9 ppm; $^{1}J(^{19}\mathrm{F}, ^{119}\mathrm{Sn})$=2531 Hz]. The long time measurement of ^{119}Sn NMR spectrum gave additional structural information; an unsymmetrical quintet [$\delta(^{119}\mathrm{Sn})$= -603.5 ppm; $^{1}J(^{119}\mathrm{Sn}, ^{19}\mathrm{F})\approx$2300 Hz] was observed thus supporting the description of $[\mathrm{NH_4}]^+[\mathrm{L^{NCN}SnF_4}]^-$ as hypercoordinated (six-coordinated tin) ionic species where there are four nearly equivalent terminal fluorine atoms and one ligand with dynamically exchanging donor atoms. To exclude ammonium fluoride from the reaction systems, previously successful $\mathrm{L^{CN}}(n\text{-Bu})_2\mathrm{SnF}$ was used as a fluorinating agent. In toluene insoluble fraction [toluene filtrate contained only $\mathrm{L^{CN}}(n\text{-Bu})_2\mathrm{SnBr}$] was analyzed by ESI/MS measurements. The same spectral patterns as in the case of formation of $[\mathrm{L^{NCN}SnF_2}(\mu\text{-F})_2]_3$ were observed. This product is insoluble in inert solvents such as toluene but dramatically reactive with, for example, $\mathrm{CDCl_3}$ and methanol giving $[\mathrm{H^+} \cdot \mathrm{L^{NCN}SnF_4^-}]$ as a zwitterionic product of acidic proton abstraction and the further amine quarternization. The monomeric zwitterionic stannate structure (Figure 9), where one $\mathrm{L^{NCN}}$ ligand is bonded in a bidentate manner to the tin atom and the second arm is protonated. The tin coordination octahedron is next formed by four non-equivalent Sn-F [for F1 1.983(4) Å, for F2 (*trans* to N1) 1.961(2) Å, for F3 2.030(2) Å, for F4 1.952(4) Å] bonds.

The distance Sn-F1 is somewhat shorter in comparison with Sn-F2 and F4, respectively, as a result of *trans*-effect of the donor amino group. A much bigger elongation can be seen in the case of the Sn-F3 bond owing to the existence of hydrogen bonding [N2-H2···F3 (2.757(3) Å]. Similar bond lengths were found in the sole published mono-organotin fluoride with terminal fluorine atoms (Sn-F: 1.956; 1.948 and 1.975 Å) (Dostal et al., 1993). The main deviation from the octahedral shape are the values of N1-Sn-F1 angle [174.36(1)°, ideally 180°] and C1-Sn-F2 [103.83(3)°, ideally 90°].

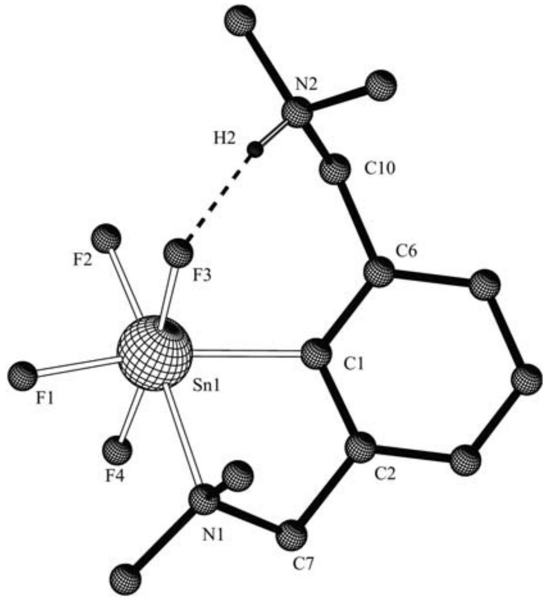


Figure 9 Molecular structure of $[\mathrm{H^+{\cdot}L^{NCN}SnF_4^-}]$. Hydrogen atoms are omitted for clarity. The selected distances [Å] and angles [°]: Sn(1)-N(1) 2.325(2), Sn(1)-F(1) 1.9522(14), Sn(1)-F(2) 1.9613(14), Sn(1)-F(3) 2.0302(13), Sn(1)-F(4) 1.9835(14), Sn(1)-C(1) 2.150(2), F(2)-Sn(1)-N(1) 174.35(7), F(4)-Sn(1)-N(1) 83.20(7), F(3)-Sn(1)-N(1) 97.84(6).

Very close to this arrangement are also the hydrolytic products of chlorine and bromine analogs (Jambor et al., 2001a; Thoonen et al., 2006). The distance Sn-N1 [2.325(2) Å] is the strongest reported contact Sn-N in this type of compounds [2.386(4) Å and 2.400(1) Å for $\mathrm{L^{NCN}SnBr_3}$ and 2.3700(3) Å for its hydrolysis product (Jambor et al., 2001a)]. This structure is retained in $\mathrm{CDCl_3}$, which is supported by ^{1}H, ^{119}Sn and ^{19}F NMR spectra. In the proton spectrum of $[\mathrm{H^+{\cdot}L^{NCN}SnF_4^-}]$ at 295 K, there is signal at 9.78 ppm assigned to the $\mathrm{R_3NH^+}$ group. In aliphatic part of spectrum two broad signals (4.58 and 3.83 ppm) belonging to two different $\mathrm{\text{-}CH_2N}$ groups were found, as well as another two (2.89 and 2.64 ppm) for methyl of $\mathrm{NMe_2}$ groups; these signals are unchanged with lowering the temperature. Complex multiplet (doublet of doublets of triplets) with the center of gravity at -601.2 ppm and coupling $^{1}J(^{119}\mathrm{Sn}, ^{19}\mathrm{F})\approx$2520 Hz was visible in the ^{119}Sn NMR spectrum, this supports the non-equivalency of terminal fluorine atoms. Measured ^{19}F NMR spectrum at 290 K gave no additional information about the structure because only one major signal at -141 ppm and two minor very broad signals at -148.5 and -161.7 ppm were found. With lowering the temperature to 250 K, the major signal (-141 ppm) becomes broader and the remaining two signals are sharpened [-148.2 ppm with $^{1}J(^{19}\mathrm{F}, ^{119}\mathrm{Sn})$=2267 Hz and -161.8 ppm with $^{1}J(^{19}\mathrm{F}, ^{119}\mathrm{Sn})$=1593 Hz]. A further decrease in temperature led to broadening of these signals again.

A different NMR spectral pattern was found directly after dissolution of $[\mathrm{L^{NCN}SnF_2}(\mu\text{-F})_2]_3$ in methanol-*d4*. We proposed the equilibrium of a couple of species which led after some minutes to the formation of $[\mathrm{H^+{\cdot}L^{NCN}SnF_4^-}]$. In the ^{119}Sn NMR spectrum (295 K) two doublets of triplets at -576.8 ppm with $^{1}J(^{119}\mathrm{Sn}, ^{19}\mathrm{F})$=2485 Hz and -579.3 ppm with $^{1}J(^{119}\mathrm{Sn}, ^{19}\mathrm{F})$=2670 Hz which could be assigned to two different isomers of $[\mathrm{L^{NCN}SnF_3{\cdot}O(H)Me}]$ type were found. The third signal is split into a pseudo-quartet of triplets (or better doublet of triplets of triplets) at -604.9 ppm with $^{1}J(^{119}\mathrm{Sn}, ^{19}\mathrm{F})$=2560 and 1595 Hz, which could be assigned to a dinuclear $[\mathrm{L^{NCN}SnF_2}(\mu\text{-F})_2]_2$, with two terminal and two bridging fluorine atoms.

The ^{19}F NMR spectrum at 295 K gave no useful information because very broad and unresolved signals were obtained. These signals are much sharper at 250 K, but they are not consistent with the proposed monomeric structure of two isomers of $[\mathrm{L^{NCN}SnF_3{\cdot}O(H)Me}]$ type were found. With regard to the existence of two new signals at -150.7 ppm (d) with $^{1}J(^{119}\mathrm{Sn}, ^{19}\mathrm{F})$=2770 Hz, $^{2}J(^{19}\mathrm{F}, ^{19}\mathrm{F})$=19.8 Hz and -168.5 ppm (t) with $^{1}J(^{119}\mathrm{Sn}, ^{19}\mathrm{F})$=1536 Hz and $^{2}J(^{19}\mathrm{F}, ^{19}\mathrm{F})$=19.8 Hz with integral ratio 4:1 we presume a formation of new oligomeric species of $[(\mathrm{L^{NCN}SnF_2})_2(\mu\text{-F})]_n$ type.

Fluorination of complexes of Ti, Sb, and Bi

The potential use of compounds **5**–**8**, and $(\mathrm{L^{CN}})_2\mathrm{SnF_2}$ as fluorinating agents similarly as in the case of $\mathrm{Me_3SnF}$ (Herzog et al., 1994), was tested in reaction with titanocene dichloride. Two equivalents of compound $\mathrm{L^{CN}}(n\text{-Bu})_2\mathrm{SnF}$ or $\mathrm{L^{CN}Ph_2SnF}$, or one equivalent of $(\mathrm{L^{CN}})_2\mathrm{SnF_2}$, respectively, were mixed with one equivalent of titanocene dichloride, and stirred in dichloromethane at 35°C, in the air. Within 3 h the color changed from orange to yellow and the desired compound (Cp_2TiF_2) (Druce et al., 1969; Nesmeyanov et al., 1972, 1975; Samuel et al., 1973; Cauzzi et al., 2002) was isolated essentially quantitatively by easy washing the product with cold pentane, no trace of starting material was observed.

Two competitive experiments for juxtaposition of the fluorinating power of the commonly used Me_3SnF (Herzog et al., 1994) and **6** were also made. Two equivalents of both Me_3SnF (freshly sublimed and finely powderized) and **6** were mixed together with one equivalent of Cp_2TiCl_2 in both methylene dichloride (40°C, 3 h) and toluene (80°C, 10 min). In both experiments the conversion of Cp_2TiCl_2 to Cp_2TiF_2 was quantitative and no trace of Me_3SnCl was detected; only the signal -47.1 ppm due to $L^{CN}(n\text{-Bu})_2SnCl$ was detected in the ^{119}Sn NMR spectra of reaction residue. The reaction in toluene was finished in less than 10 min and seems to be much faster than the published one (Me_3SnF, 4 h) (Herzog et al., 1994).

The first monomeric organoantimony(III) difluorides, containing Y,C,Y chelating ligands ($[2,6\text{-}(YCH_2)_2C_6H_3]SbF_2$; Y=MeO, *t*-BuO or Me_2N), were prepared in reasonable yield by the reaction of corresponding dichlorides ($[2,6\text{-}(YCH_2)_2C_6H_3]SbCl_2$ Y=MeO, *t*-BuO or Me_2N) with two equivalents of organotin(IV) agents Me_3SnF or $L^{CN}(n\text{-Bu})_2SnF$, respectively. Analogous bismuth compounds were also prepared by using **6** only (Dostál et al., 2008).

Fluorination of various substrates

The fluorination experiments of some chlorosilanes (Švec et al., 2007), chlorophosphines (Švec et al., 2007), sulfochlorides (P. Švec, Z. Padělková, A. Růžička, J. Holeček, unpublished results), carboxylic acid chlorides (Švec et al., 2008), metal halides (Švec et al., 2007), etc., to demonstrate the versatility of the method of use of **6** in equimolar or a catalytic version were investigated.

Used chlorosilanes and $PhPCl_2$ (entries 1, 3, 4, 6, 8, 10, 11, 12 and 13; Table 3) were fluorinated by an equimolar amount of **6** essentially quantitatively and selectively in a few minutes (entry 12) or hours, also the catalytic versions of 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 (entry 9). The fluorination of metal halides is also successful even for such strong fluorination agents as CoF_3 and WF_6. Problems

Table 3 Fluorination experiments of some chlorosilanes and metal halides.

Entry	Substrate	Conditions	Product	Conversion (%)[a]
1	$(4\text{-}CH_3O\text{-}Ph)Ph_2SiCl$	Benzene, R.T., 1 eq. of **6**, 1 day	$(4\text{-}CH_3OPh)Ph_2SiF$	100
2	$(4\text{-}CH_3O\text{-}Ph)Ph_2SiCl$	Benzene, R.T., 5 eq. of KF, 1 mol% of **6**, 1% mol of 18-crown-6, 7 days	$(4\text{-}CH_3OPh)Ph_2SiF$	90
3	$c\text{-}HexPh_2SiCl$	THF, R.T., 1 eq. of **6**, 5 h	$c\text{-}HexPh_2SiF$	100
4	$BzPh_2SiCl$	$CDCl_3$, R.T., 1 eq. of **6**, 2 h	$BzPh_2SiF$	100
5	$BzPh_2SiCl$	THF, reflux, 5 eq. of KF, 1% mol of **6**, 1% mol of 18-crown-6, 15 h	$BzPh_2SiF$	95
6	$n\text{-}OctPh_2SiCl$	$CDCl_3$, R.T., 1 eq. of **6**, 2 h	$n\text{-}OctPh_2SiF$	100
7	$n\text{-}OctPh_2SiCl$	THF, reflux, 5 eq. of KF, 1% mol of **6**, 1% mol of 18-crown-6, 15 h	$n\text{-}OctPh_2SiF$	95
8	$t\text{-}Bu_2SiCl_2$	Benzene, R.T., 2 eq. of **6**, 1 day	$t\text{-}Bu_2SiF_2$	100
9	$t\text{-}Bu_2SiCl_2$	Toluene, R.T., 5 eq. of KF, 1% mol of **6**, 1% mol 18-crown-6, 8 days	$t\text{-}Bu_2SiF_2$+ $t\text{-}Bu_2SiFCl$+ $t\text{-}Bu_2SiCl_2$	–
10	Me_2SiHCl	Benzene, R.T., 1 eq. of **6**, 1 day	Me_2SiHF	100
11	$PhSiH_2Cl$	Toluene, R.T., 1 eq. of **6**, 1 day	$PhSiH_2F$	100
12	$(\eta^1\text{-}C_5H_5)\text{-}1\text{-}SiMe_3\text{-}1\text{-}SiMe_2Cl$	C_6D_6, R.T., 1 eq. of **6**, 1 min	$(\eta^1\text{-}C_5H_5)\text{-}1\text{-}SiMe_3\text{-}1\text{-}SiMe_2F$	100
13	$PhPCl_2$	C_6D_6, R.T., 2 eq. of **6**, 1 h	$PhPF_2$	100
14	$FeBr_2$	THF, R.T., 2 eq. of **6**, 2 days	FeF_2	100
15	$AlCl_3$	Benzene, R.T., 3 eq. of **6**, 2 days	AlF_3	100
16	$NiCl_2$	THF, reflux, 2 eq. of **6**, 1 h	NiF_2	100
17	$CoCl_2$	THF, R.T., 2 eq. of **6**, 1 day	CoF_2	100
18	WCl_6	THF, R.T.[b], 6 eq. of **6**, 2 days	WF_6	100
19	$CaCl_2$	THF, R.T., 2 eq. of **6**, 2 days	CaF_2	100
20	$CoCl_3$	THF, R.T., 3 eq. of **6**, 2 days	CoF_3	100
21	$PbCl_2$	THF, reflux, 2 eq. of **6**, 1 day	PbF_2	45
22	$ZrCl_4$	Toluene, R.T., 4 eq. of **6**, 2 days	ZrF_4	90
23	$GeCl_4$	Toluene, R.T.[b], 4 eq. of **6**, 1 day	GeF_4	83
24	$PdCl_2$	THF, R.T., 2 eq. of **6**, 1 day	PdF_2	n.o.
25	$MoCl_5$	THF, R.T., 5 eq. of **6**, 2 days	Mixture of various[c] $MoCl_xF_{5\text{-}x}$	–

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

[b] During addition of **6** to the reaction mixture the temperature was maintained at -40°C.

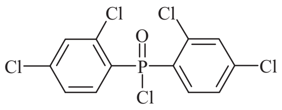
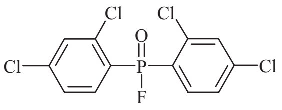
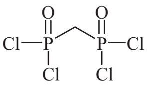
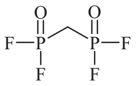
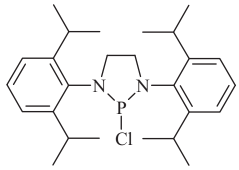
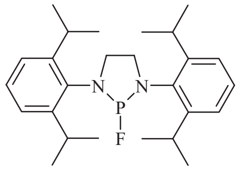
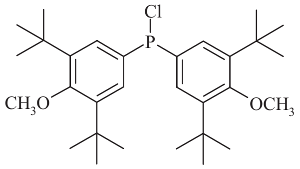
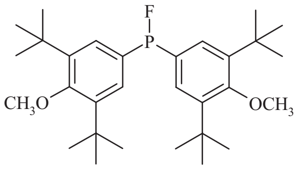
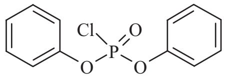
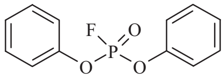
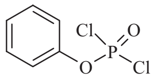
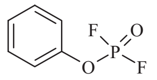
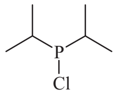
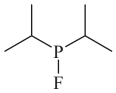
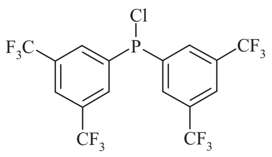
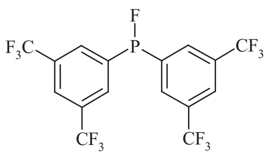
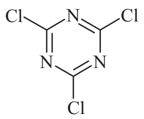
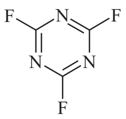
[c] Conversion of **6** to **2** was ~60%.

occurred only in the case of PbF_2, where the low solubility of starting material is probably the reason of slower reaction, fluorination of $MoCl_5$ ended with the mixture of $MoCl_xF_{5-x}$ and $PdCl_2$ cannot be fluorinated by this method.

The typical procedure is as follows: amount of 40–200 mg of appropriate substrate was added to **6** at conditions summarized in Table 3, and the mixture was stirred for 1 min (entry 12) up to 8 days (catalytic entry 9), the sample was filtered, in the case of heterogeneous reactions or paramagnetic species, and the solvent removed *in vacuo* (in the case of entries 9, 18 and 23 the products were trapped at liquid nitrogen temperature), then the deuterated benzene or chloroform was added and the composition and purity of material was checked by GC-MS and multinuclear NMR spectroscopy (Damrauer and Simon, 1988; Kunai, et al., 1996; Lickiss and Lucas, 1996). The products can be separated by washing of **2** by pentane or by (*vacuo*) distillation, characterization of metal fluorides was performed by powder X-ray diffraction methods.

Fluorination of various chlorophosphines, organochlorophosphates and cyanuric chloride proceeds relatively quickly even at room temperature (Table 4).

Table 4 Fluorination experiments of some organochlorophosphines, organochlorophosphates and cyanuric chloride.

Entry	Substrate	Conditions	Product	Conversion (%)[a]
1	PCl_5	5 eq. **6**, $CDCl_3$, R.T., 5 min	PF_5	100
2		1 eq. **6**, C_6D_6, R.T., 5 min		100
3		4 eq. **6**, C_6D_6, R.T., 5 min		100
4		1 eq. **6**, C_6D_6, R.T., 5 min		100
5		1 eq. **6**, C_6D_6, R.T., 1 day		~50
6		1 eq. **6**, C_6D_6, R.T., 30 min		100
7		2 eq. **6**, C_6D_6, R.T., 30 min		100
8		1 eq. **6**, $CDCl_3$, R.T., 30 min		100
9		1 eq. **6**, C_6D_6, R.T., 1 h		100
10		3 eq. **6**, $CDCl_3$, R.T., 5 min[b]		100

[a] Based on ^{1}H, ^{19}F, ^{31}P and ^{119}Sn NMR spectroscopy.
[b] For further details see text.

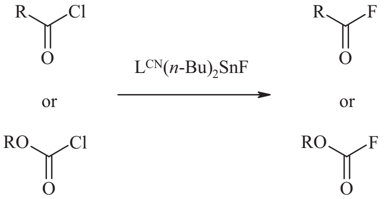


Figure 10 Use of $L^{CN}(n\text{-Bu})_2SnF$ for preparation of acyl fluorides and fluoroformates.

The next series of compounds where the high potential of $L^{CN}(n\text{-Bu})_2SnF$ (**6**) for preparing acyl fluorides, fluoroformates and other fluorides was shown (Figure 10).

Compound **6** reacts (Table 5, Figure 10) with various chloroformates to exclusively form fluoroformates (entries 1–5), with acyl chlorides to acyl fluorides (entries 6–13), with methanesulfonyl chloride to its fluoride (entry 14) and various phosgene precursors or derivatives to form fluorinated phosgene or thiophosgene. Di- and triphosgene gave, in the presence of moisture, fluorinated phosgene; when the reaction of triphosgene was carried out in a sealed tube, a complex composed of two $\{2\text{-}[(CH_3)_2N(H)^+CH_2]C_6H_4\}(n\text{-Bu})_2SnCl$ units and SiF_6^{2-} was observed (Švec et al., 2010). The reaction of 4,4′-dimethoxytrityl chloride yielded a fluorinated product almost quantitatively. All these reactions proceed rapidly, under very mild conditions and the equimolar amount of **6** was used. The process developed is selective and chlorine atoms bonded to alkyl groups remain unchanged as demonstrated in runs 11 and 12. *N*-Cyclohexyl-*N*-ethyl carbamoyl chloride is rather unreactive under the conditions used (entry 5) .

To test for a possible catalytic procedure, fluorination of tri(ethylene glycol) bis(chloroformate) was selected because of the relatively high thermal stability and boiling points of both reactant and suggested product. Ten molar equivalents of KF (530 mg), one molar equivalent of tri(ethyleneglycol) bis(chloroformate) (250 mg) and one molar percent of **6** were suspended in a reaction tube equipped with a Teflon® Young valve, in toluene. The closed tube was heated under ultrasound activation at 85°C for 1 h. The KF was filtered off and the solvent was evaporated. The multinuclear NMR spectra of the yellowish oily product proved approximately 42% conversion to tri(ethyleneglycol) bis(fluoroformate). Under the same conditions but without **6**, no conversion to fluorinated product was observed.

When we tried to expand the series of compounds to different types of organic halides we found that *tert*-butyl chloride, 1-bromooctane, benzyl bromide, 4-nitrobenzyl chloride, 2,6-dichlorobenzonitrile, 2-chlorobenzonitrile, α,α,α-trichlorotoluene, cyclohexyl, and *tert*-butyl acetates did not react with **6**. Only phenyl acetate gave acetyl fluoride in ca. 25% yield when refluxed in toluene for 20 h.

The advantages of reagent **6** over other systems, compounds and methods, are very short reaction times, compound **6** is not volatile, is less toxic, and normal glassware can be used. Additionally, compound **6** is extremely soluble in all organic solvents, is stable in the air for years, and can be recycled directly after distilling the product off by reaction with excess of KF (in water/diethyl ether mixture) in very high yields (usually more than 90%).

The general description of the fluorinating method is as follows: the starting substrates were dissolved in various solvents (see Table 5) and compound **6** (equimolar amount) was added in one portion. The products were separated from the reaction mixture by distillation or by trap-to-trap distillation and identified by multinuclear NMR spectroscopy and by GC/MS and ESI/MS techniques. Chromatography can also be used as a separating method but in these cases distillation, trap-to-trap distillation and crystallization are the easiest ways for obtaining pure products. During the reaction the composition of each reaction mixture was determined by ESI/MS techniques and the reaction was stopped when no peak for $\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}(n\text{-Bu})_2SnF{+}H$ at *m/z* 388 in positive ion mode was observed. The reaction progress was also monitored by ^1H and ^{119}Sn NMR spectroscopy.

The last experiments include fluorinations of compounds containing the S-Cl bond(s) (Table 6). Surprisingly, only in the case of thionyl chloride and sulfuryl chloride, the quantitative conversion to respective products was observed. Other substrates seem to be somewhat unreactive even if elevated temperature is used.

Unusual reaction of cyanuric chloride with $L^{CN}(n\text{-Bu})_2SnF$, $L^{CN}(n\text{-Bu})_2SnCl$ and $L^{CN}Ph_2SnCl$

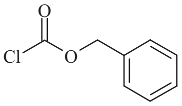
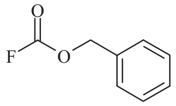
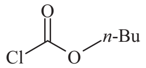
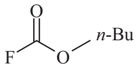
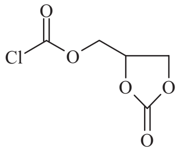
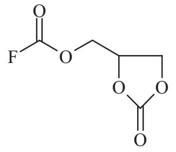
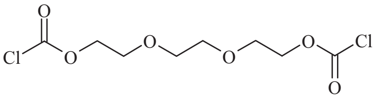
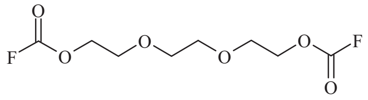
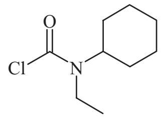
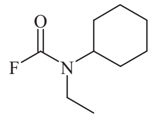
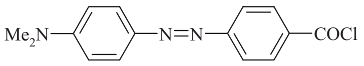
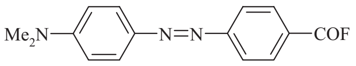
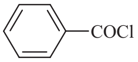
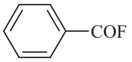
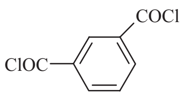
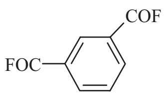
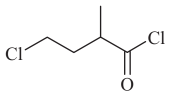
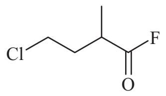
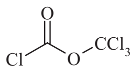
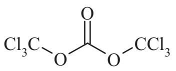
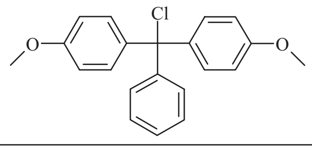
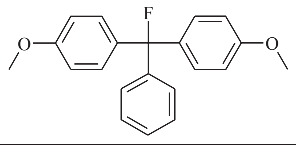
The reaction of cyanuric chloride with three equivalents of $L^{CN}(n\text{-Bu})_2SnF$ resulted in total fluorination of the substrate with $L^{CN}(n\text{-Bu})_2SnCl$ being the byproduct. The products were identified using ^1H, ^{13}C, ^{19}F and ^{119}Sn NMR spectroscopy. The reaction was completed in 5 min at room temperature.

When only one equivalent of $L^{CN}(n\text{-Bu})_2SnF$ was used, the formation of [2-(fluoromethyl)phenyl]di-*n*-butyltin(IV) chloride and 4,6-dichloro-*N,N*-dimethyl-1,3,5-triazine-2-amine was observed (Scheme 2). The reaction proceeds at room temperature and is finished in 5 h. Products were identified using ^1H, ^{13}C, ^{19}F and ^{119}Sn NMR spectroscopy. The formation of the 4,6-dichloro-*N,N*-dimethyl-1,3,5-triazine-2-amine was confirmed by XRD techniques (Figure 11). Unfortunately no single crystals of the [2-(fluoromethyl)phenyl]di-*n*-butyltin(IV) chloride were obtained to date.

By contrast, if two equivalents of $L^{CN}(n\text{-Bu})_2SnF$ were used at the same reaction conditions, a mixture of $L^{CN}(n\text{-Bu})_2SnCl$, [2-(fluoromethyl)phenyl]di-*n*-butyltin(IV) chloride, partially fluorinated cyanuric chloride and 4,6-dichloro-*N,N*-dimethyl-1,3,5-triazine-2-amine was observed with the help of multinuclear NMR spectroscopy. This indicates there must be a competition between fluorination and migration of the *N,N*-dimethylamino group.

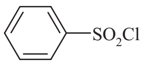
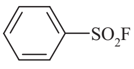
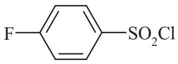
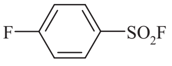
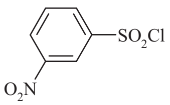
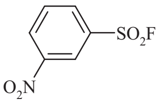
The latter results led us to the idea of using $L^{CN}(n\text{-Bu})_2SnCl$ instead of $L^{CN}(n\text{-Bu})_2SnF$ in the reaction. If equimolar amounts (1:1 ratio) of starting cyanuric chloride and $L^{CN}(n\text{-Bu})_2SnCl$ were used, the formation of only 4,6-dichloro-*N,N*-dimethyl-

Table 5 Preparation of fluoroformates, acyl fluorides and fluorophosgene.

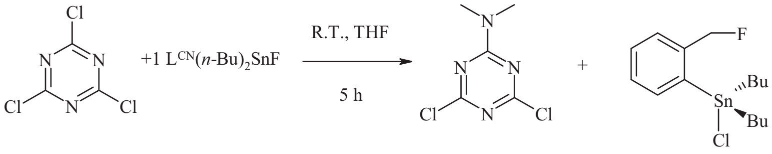
Entry	Substrate	Conditions	Product	JC (%)[a]
1		Et$_2$O, R.T., 1 eq. of **6**, 10 min		100
2		Et$_2$O, R.T., 1 eq. of **6**, 10 min		100
3		Et$_2$O, R.T., 1 eq. of **6**, 10 min		100
4		Et$_2$O, R.T., 2 eq. of **6**, 3 h		100
5		Toluene, reflux, 1 eq. of **6**, 12 h		30
6		Benzene, R.T., 1 eq. of **6**, 1 h		100
7		Et$_2$O, R.T., 1 eq. of **6**, 1 h		100
8		Et$_2$O, R.T., 2 eq. of **6**, 10 min		100
9	CH_3COCl	Et$_2$O, 0°C, 1 eq. of **6**, 3 h	CH_3COF	100
10	CH_3CH_2COCl	Et$_2$O, 0°C, 1 eq. of **6**, 3 h	CH_3CH_2COF	100
11	$ClCH_2CH_2CH_2COCl$	Et$_2$O, R.T., 1 eq. of **6**, 1 h	$ClCH_2CH_2CH_2COF$	100
12		Et$_2$O, R.T., 1 eq. of **6**, 1 h		100
13	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COCl$	Et$_2$O, R.T., 1 eq. of **6**, 10 min	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COF$	100
14	CH_3SO_2Cl	Et$_2$O, R.T., 1 eq. of **6**, 10 min	CH_3SO_2F	100
15	$CSCl_2$	tol.-d$_8$, R.T., 2 eq. of **6**, 10 min	A mixture of fluorinated compounds	100
16	$COCl_2$	tol.-d$_8$, R.T., 2 eq. of **6**, 10 min	COF_2	100
17		tol.-d$_8$, R.T., 4 eq. of **6**, 10 min, H$_2$O	COF_2	100
18		tol.-d$_8$, R.T., 6 eq. of **6**, 10 min, H$_2$O	COF_2	100
19		Et$_2$O, R.T., 1 eq. of **6**, 30 min		100

1,3,5-triazine-2-amine and [2-(chloromethyl)phenyl]-di-*n*-butyltin(IV) chloride was observed by multinuclear NMR spectroscopy. Raising the amount of L^{CN}(*n*-Bu)$_2$SnCl to 3:1 ratio did not provide a full substitution of all three chlorine atoms with *N,N*-dimethylamino groups, because signals of starting L^{CN}(*n*-Bu)$_2$SnCl and *in situ* formed [2-(chloromethyl)

Table 6 Fluorination experiments of thionyl chloride, sulfuryl chloride and some organosulfonyl chlorides.

Entry	Substrate	Conditions	Product	Conversion (%)[a]
1	$SOCl_2$	2 eq. **6**, C_6D_6, R.T., 1 min	SOF_2	100
2	SO_2Cl_2	2 eq. **6**, C_6D_6, R.T., 1 min	SO_2F_2	100
3	CH_3SO_2Cl	1 eq. **6**, Et_2O, R.T, 1 day	CH_3SO_2F	~95
4		1 eq. **6**, toluene, reflux, 5 h		~60
5		1 eq. **6**, toluene, reflux, 5 h		~60
6		1 eq. **6**, toluene, reflux, 3 h		~90

[a]Based on ^{1}H, ^{19}F and ^{119}Sn NMR spectroscopy.



Scheme 2 Unexpected substitution reaction of cyanuric chloride and $L^{CN}(n\text{-Bu})_2SnF$.

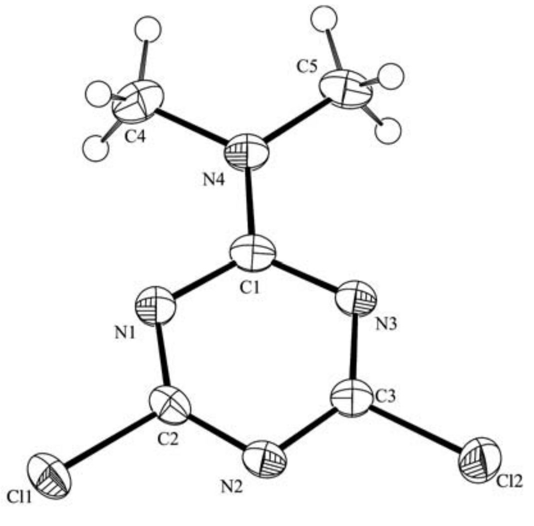


Figure 11 The molecular structure (ORTEP 50% probability level) of 4,6-dichloro-*N,N*-dimethyl-1,3,5-triazine-2-amine. Selected interatomic distances [Å] and angles [°]: Cl1-C2 1.731(3), Cl2-C3 1.733(3), N3-C3 1.306(4), N3-C1 1.366(4), N2-C3 1.329(4), N2-C2 1.332(4), N1-C2 1.310(4), N1-C1 1.363(4), N4-C1 1.323(4), N4-C4 1.459(4), N4-C5 1.458(4), C3-N3-C1 113.2(2), C3-N2-C2 110.3(2), C2-N1-C1 113.6(2), C1-N4-C4 119.9(3), C1-N4-C5 122.1(3), C4-N4-C5 118.0(2), N1-C2-N2 129.4(3), N1-C2-Cl1 115.5(2), N2-C2-Cl1 115.1(2), N4-C1-N1 118.0(3), N4-C1-N3 118.5(3), N1-C1-N3 123.4(3), N3-C3-N2 130.0(3), N3-C3-Cl2 115.6(2), N2-C3-Cl2 114.4(2).

phenyl]di-*n*-butyltin(IV) chloride in approximately 1:1 ratio were observed by ^{119}Sn NMR spectroscopy. If the reaction mixture was refluxed in toluene, the equilibrium of the reaction moved slowly back by the reverse substitution of the *N,N*-dimethylamino group and the chlorine atom, raising the assay of starting $L^{CN}(n\text{-Bu})_2SnCl$ in the reaction mixture. Similar results were obtained when $L^{CN}Ph_2SnCl$ was used instead of $L^{CN}(n\text{-Bu})_2SnCl$, changing only the value of ^{119}Sn NMR shift from +69 ppm (for the butyl derivative) to -57 ppm in the case of [2-(chloromethyl)phenyl]diphenyltin(IV) chloride.

X-Ray crystallography

The single crystals of 4,6-dichloro-*N,N*-dimethyl-1,3,5-triazine-2-amine were obtained by *vacuo* sublimation. Data for colorless crystals were collected at 150(1) K on a Nonius KappaCCD diffractometer (Bruker-Nonius B. V., Delft, Netherlands) using MoKα radiation (λ=0.71073 Å), and graphite monochromator. The structures were solved by direct methods [SIR92 (Altomare et al., 1994)]. All reflections were used in the structure refinement based on *F2* by full-matrix least-squares technique [SHELXL97 (Sheldrick, 1997)]. Hydrogen atoms were mostly localized on a difference Fourier map; however, to ensure uniformity of treatment of crystal, all hydrogens 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 Gaussian integration from crystal shape Coppens (1970). 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: international code +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

Crystallographic data for 4,6-dichloro-*N,N*-dimethyl-1,3,5-triazine-2-amine: $C_5H_6Cl_2N_4$, M=193.04, monoclinic, $P2_1/m$, *a*=7.6851(4), *b*=6.5992(5), *c*=8.4528(4) Å, β=111.573(3)°, Z=2, V=398.65(4) Å^3, D_c=1.608 g cm^{-3}, μ=0.750 mm^{-1}, T_{min}=0.832, T_{max}=0.955; 3594 reflections measured (θ_{max}=27.5°), 978 independent (R_{int}=0.0307), 819 with *I>2σ(I)*, 67 parameters, *S*=1.137, *R1*(obs. data)=0.0394, *wR2* (all data)=0.0921; max., min. residual electron density=0.416, -0.406 e Å^{-3}. CCDC deposition number: 775754.

Conclusions

In the previous sections it was shown that the C,N-chelated triorganotin(IV) fluorides are easy accessible monomeric species with trigonal bipyramidal tin central atom geometry. These compounds are very active in fluorination of various organometallic halides (groups 4 and 14), metal halides, chlorosilanes, chlorophosphines, organochlorophosphates and organosulfonyl chlorides, the challenge here seems to be a fluorination of organic species as well as the biomaterial, including the use of isotope ^{18}F labeled species.

The tin coordination geometry in the set of the N,C,N-chelated triorganotin(IV) fluorides is also trigonal bipyramidal, but the ionization of the Sn-F bond and thus the formation of 'naked' fluoride ion occurred but the high potential fluorination activity of these compounds still needs to be discovered.

A much more complicated situation occurred in the study of both C,N- and N,C,N-chelated diorganotin(IV) fluorides because of reactivity known as the phenyl group migration process, and although the first stable and free diorganotin(IV) difluoride was prepared and structurally characterized, the main result of fluorination in this class of compounds was the formation of insoluble oligo- or polymeric species which can be easy to overtake to soluble ionic hypercoordinated fluorostannates. This phenomenon was used in the design of ion selective carriers.

The situation in the case of C,N- and N,C,N-chelated monoorganotin(IV) fluorides is similar to the diorganotin(IV) group, i.e., the formation of insoluble oligo- or polymeric species which can adopt a ionic halide into the coordination sphere to form soluble ionic hypercoordinated fluorostannates. In the case of N,C,N-chelated compounds a zwitterionic tetrafluorostannate was prepared and structurally characterized.

Fluorination of various substrates containing E-Cl (E=C, Si, P, S and metal) bond(s) were described. These reactions usually proceed relatively quickly even at room temperature and the conversion of the substrate to the corresponding product is essentially quantitative.

Acknowledgments

The authors wish to thank Dr. Josef Bareš, Dr. Petr Novák and Ms. Hana Vaňkátová for synthetic work, Dr. Ivana Císařová (Charles University in Prague, Czech Republic) and Dr. Zdeňka Padělková for X-ray measurements, and Prof. Jaroslav Holeček for fruitful discussions. The financial support of the Science Foundation of the Czech Republic (Grant No. 207/10/0215) and the Ministry of Education of the Czech Republic (Project VZ0021627501) is greatly acknowledged.

References

Adamov, A. V.; Krolevets, A. A.; Popov, A. G.; Petrovskii, P. V. Isopropyldifluoridephosphine. *Zh. Obshch. Khim.* **1988**, *58*, 1157.

Adcock, J. L.; Cherry, M. L. Aerosol direct fluorination – A developing synthesis technology and an entry level mechanistic tool – A short review. Ind. Eng. Chem. Res. 1987, 26, 208–215.

Akiba, K. *Chemistry of Hypervalent Compounds*; New York: Wiley-VCH, **2002**.

Albrecht, M.; van Koten, G. Platinum group organometallics based on "Pincer" complexes: Sensors, switches, and catalysts. *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781.

Al-Juaid, S. S.; Dhaher, S. M.; Eaborn, C.; Hitchcock, P. B. Preparation and crystal structures of the crowded organotin fluorides $(PhMe_2Si)_3CSnMe_2F$, $(Me_3Si)_3CSnMe_2F$, and $(Me_3Si)_3CSnPh_2F$. *J. Organomet. Chem.* **1987**, *325*, 117–127.

Altmann, R.; Jurkschat, K.; Schuermann, M. o-bis(haloorganostannyl) benzenes as powerful bidentate Lewis acids toward halide ions. *Organometallics* **1998**, *17*, 5858–5866.

Altomare, A.; Cascarone, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. Early finding of preferred orientation – A new method. *J. Appl. Crystallogr.* **1994**, *27*, 1045–1050.

Apodaca, P.; Cervantes-Lee, F.; Pannell, K. H. Mixed aryl-alkyl organotin compounds. *Main Group Met. Chem.* **2001**, *24*, 597–601.

Bai, H. P.; Harris, R. K.; Reuter, H. Solid-state ^{119}Sn NMR studies of coordination in triorganyltin fluorides. *J. Organomet. Chem.* **1991**, *408*, 167–172.

Banks, R. E. Ed. *Fluorine Chemistry at the Millennium: Fascinated by Fluorine*; Elsevier Science, **2000**.

Bareš, J.; Novák, P.; Nádvorník, M.; Lébl, T.; Jambor, R.; Císařová, I.; Růžička, A.; Holeček, J. Monomeric triorganotin(IV) fluorides containing a C,N-chelating ligand. *Organometallics* **2004**, *23*, 2967–2971.

Beckmann, J.; Dakternieks, D.; Duthie, A.; Tiekink, E. R. T. Observation of inter- and intramolecular C—H…F hydrogen bonding in Gingras' salt: $[n\text{-}Bu_4N]^+[Ph_3SnF_2]^-$. *J. Organomet. Chem.* **2002**, *648*, 204–208.

Beckmann, J.; Horn, D.; Jurkschat, K.; Rosche, F.; Schürmann, M.; Zachwieja, U.; Dakternieks, D.; Duthie, A.; Lim, E. K. L. Triorganotin fluoride structures: A ligand close-packing model with predominantly ionic Sn-F bonds. *Eur. J. Inorg. Chem.* **2003**, 164–174.

Beckmann, J.; Dakternieks, D.; Duthie, A. The first dimeric triorganotin fluoride: Stabilization by unsymmetrically oriented menthyl substituents. *Organometallics* **2005**, *24*, 773–776.

Bondi, A. Van der Waals volumes+radii. *J. Phys. Chem.* **1964**, *68*, 441–451.

Britton, D.; Dunitz, J. D. Chemical-reaction paths. 7. Pathways for S_N2 and S_N3 substitution at Sn(IV). *J. Am. Chem. Soc.* **1981**, *103*, 2971–2979.

Buntine, M. A.; Kosovel, F. J.; Tiekink, E. R. T. A comparison between crystallographic and theoretical structures for three hypervalent $RSnCl_3$ compounds. *Phosphorous Sulfur Silicon Relat. Elem.* **1999**, *15*, 261–270 and references cited therein.

Bürgi, H. B. Stereochemistry of reaction paths as determined from crystal-structure data – Relationship between structure and energy. *Angew. Chem. Int. Ed. Engl*. **1975**, *14*, 460–473.

Carpino, L. A.; Bayermann, M.; Wenschuh, H.; Bienert, M. Peptide synthesis via amino acid halides. *Acc. Chem. Res*. **1996**, *29*, 268–274.

Cauzzi, D.; Graiff, C.; Marazzi, M.; Predieri, G.; Tiripicchio, A. Preparation of Ti(IV), Zr(IV) and Sn(IV) metal alkyls containing the $(Pr^iO)_3SiCH_2$ fragment. *J. Organomet. Chem*. **2002**, *663*, 256–262.

Chandra, S.; Švec, P.; Růžička, A.; Lang, H. Organotin compounds: an ionophore system for fluoride ion recognition. *Anal. Chim. Acta* **2006**, *577*, 91–97.

Chaniotakis, N.; Jurkschat, K.; Müller, D.; Perdikaki, K.; Reeske, G. Reeske, Bis[di-*n*-alkyl(fluoro)stannyl]methanes, $(R_2FSn)_2CH_2$ (R=*n*-octyl, *n*-dodecyl): Stable fluoride-selective carriers. *Eur. J. Inorg. Chem*. **2004**, 2283–2288.

Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reye, C. Unexpected basicity of a hexacoordinate silicon compound, {2,6-bis[(dimethylamino) methyl]phenyl}bis(1,2-benzenediolato)silicate. *Chem. Eur. J*. **1996**, *2*, 342–347.

Cohen, O.; Sasson, R.; Rozen, S. A new method for making acyl fluorides using BrF_3. *J. Fluorine Chem*. **2006**, *127*, 433–436.

Coppens, P. In *Crystallographic Computing*. Ahmed, F. R.; Hall, S. R.; Huber, C. P., Eds. Copenhagen: Munksgaard **1970**, pp. 255.

Cotarca, L.; Eckert, H. *Phosgenations – A Handbook*; Wiley: Weinheim, **2004**.

Dakternieks, D.; Zhu, H. Hypervalent monoorgano- and diorganotin(IV) fluoride complexes: a fluorine-19 and tin-119 study of inter- and intramolecular dynamics in solution. *Organometallics* **1992**, *11*, 3820–3825.

Dakternieks, D.; Jurkschat, K.; Zhu, H.; Tiekink, E. R. T. Bis(halodiphenylstannyl)alkanes as bidentate Lewis acids toward halide ions. *Organometallics* **1995**, *14*, 2512–2521.

Damrauer, R.; Simon, R. A.; Kanner, B. Synthesis of fluorosilanes from chlorosilanes: the use of hexafluorosilicates. *Organometallics* **1988**, *7*, 1161–1164.

Dorn, H.; Murphy, E. F.; Roesky, H. W. Organometallic fluorides of the lanthanide and actinide elements. *J. Fluorine Chem*. **1997**, *86*, 121–125.

Dostal, S.; Stoudt, J.; Fanwick, P.; Sereatan, W. F.; Kahr, B.; Jackson, J. E. Correlation of structure and internal dynamics for (tris(2,6-dimethoxyphenyl)methyl)tin trihalides: a homologous series of seven-coordinate tin compounds. *Organometallics* **1993**, *12*, 2284–2291.

Dostál, L.; Jambor, R.; Růžička, A.; Jirásko, R.; Císařová, I.; Holeček, J. The synthesis of organoantimony(III) difluorides containing Y,C,Y pincer type ligands using organotin(IV) fluorinating agents. *J. Fluorine Chem*. **2008**, *129*, 167–172.

Drozd, G. I.; Ivin, S. Z.; Sheluchenko, V. V.; Tetel'baum, B. I. Synthesis of aryl- and alkyl-phosphonous difluorides. *J. Gen. Chem. USSR* **1967**, *37*, 906–912.

Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Srivastava, R. C.; Frazer, M. J.; Newton, W. E. Metallocene halides. 2. Low frequency infrared and Raman spectra of dicyclopentadienyldihalogeno-titanium(IV), -zirconium(IV) and -hafnium(IV). *J. Chem. Soc. A* **1969**, *18*, 2814.

Erben, M.; Merna, J.; Hermanová, S.; Císařová, I.; Padělková, Z.; Dušek, M. Fluorosilyl-substituted cyclopentadienyltitanium(IV) complexes: synthesis, structure, and styrene polymerization behavior. *Organometallics* **2007**, *26*, 2735–2741.

Fraser, C. J. W.; McCartney, M. E.; Sharp, D. W. A.; Winfield, J. M. Oxidative fluorination of substituted phosphines with sulfur chloride pentafluoride. *J. Inorg. Nucl. Chem*. **1972**, *34*, 1455.

Gingras, M. Tetrabutylammonium difluorotriphenylstannate as a new anhydrous synthetic equivalent to TBAF. *Tetrahedron Lett*. **1991**, *32*, 7381–7384.

Hara, S.; Chen, S. Q.; Hatakeyama, T.; Fukuhara, T.; Sekiguchi, M.; Yoneda, N. Electrochemical fluorinative α-cleavage of cyclic ketones. Synthesis of fluorocarboxylic acid esters. *Tetrahedron Lett*. **1995**, *36*, 6511–6514.

Herzog, A.; Liu, F. Q.; Roesky, H. W.; Demsar, A.; Keller, K.; Noltemeyer, M.; Pauer, F. Trimethyltin fluoride: A new fluorinating reagent for the preparation of organometallic fluorides. *Organometallics* **1994**, *13*, 1251–1256.

Heuer, L.; Schmutzler, R. A new approach to the synthesis of aryldifluorophosphines. Formation of cis-dichloro-bis(aryldifluorophosphine)platinum(II) complexes. *J. Fluorine Chem*. **1988**, *39*, 197–216.

Holeček, J.; Nádvorník, M.; Handlíř, K.; Lyčka, A. ^{13}C and ^{119}Sn NMR study of some four- and five-coordinate triphenyltin(IV) compounds. *J. Organomet. Chem*. **1983**, *241*, 177–184.

Holeček, J.; Nádvorník, M.; Handlíř, K.; Lyčka, A. Dependence of [^1J(Sn-119,C-13)] on the mean C-Sn-C angle in phenyltin(IV) compounds. *Z. Chem*. **1990a**, *30*, 265–266.

Holeček, J.; Nádvorník, M.; Handlíř, K.; Lyčka, A. C-13 and Sn-119 NMR-spectra of diphenyltin(IV) and dibenzyltin(IV) compounds and their complexes. *Collect. Czech. Chem. Commun*. **1990b**, *55*, 1193–1207.

Holmes, R. R. The stereochemistry of nucleophilic substitution of tetracoordinate silicon. *Chem. Rev*. **1990**, *90*, 17–31.

Howe-Grant, M., Ed. *Fluorine Chemistry: A Comprehensive Treatment* (Encyclopedia Reprint Series); Wiley-InterScience, **1995**.

Ichihara, J.; Matsuo, T.; Hanafusa, T.; Ando, T. The combination of potassium fluoride and calcium fluoride – A useful heterogeneous fluorinating reagent. *J. Chem. Soc. Chem. Comm*. **1986**, *10*, 793–794.

Jagirdar, B.; Murphy, E. F.; Roesky, H. W. Organometallic fluorides of the main group metals containing the C-M-F fragment. *Prog. Inorg. Chem*. **1999**, *48*, 351–455.

Jambor, R.; Císařová, I.; Růžička, A.; Holeček, J. {2,6-Bis[(dimethylamino)methyl]phenyl-*N*2,*C*1,*N*6}diphenyltin(II) bromide monohydrate. *Acta Crystallogr*. **2001a**, *C57*, 373–374.

Jambor, R.; Růžička, A.; Brus, J.; Císařová , I.; Holeček, J. Structure of [2,6-bis(dimethylamino)methyl]phenyltin tribromide hydrate. *Inorg. Chem. Commun*. **2001b**, *4*, 257–260.

Jastrzebski, J. T. B. H. *Intramolecular Coordination in Organotin Chemistry*. Rijksuniversiteit te Utrecht: Utrecht, The Netherlands, **1991a** and references cited therein.

Jastrzebski, J. T. B. H.; Boersma, J.; Esch, P. M.; van Koten, G. Intramolecular penta- and hexacoordinate tetraorganotin compounds containing the 8-(dimethylamino)-1-naphthyl ligand. *Organometallics* **1991b**, *10*, 930–935.

Jastrzebski, J. T. B. H.; Boersma, J.; van Koten, G. Organotin(IV) compounds 2-$(Me_2NCHR)C_6H_4(SnR'R''Br)$ with a fixed *s-cis* arrangement of the chiral carbon and tin centers. Crystal structure of 2-$(Me_2NCHBu^t)C_6H_4SnMePhBr$. *J. Organomet. Chem*. **1991c**, *413*, 43–53.

Jastrzebski, J. T. B. H.; van Koten, G. Intramolecular coordination in organotin chemistry. *Adv. Organomet. Chem*. **1993**, *35*, 241–294.

Kifer, E. W.; Van Dyke, C. H. Partially fluorinated derivatives of disiloxane. *J. Chem. Soc. – Chem. Commun*. **1969**, 1330.

Kifer, E. W.; Van Dyke, C. H. Use of phosphorus pentafluoride as a fluorinating agent in organosilicon chemistry 3. Synthesis and characterization of some new fluorosiloxanes. *Inorg. Chem*. **1972**, *11*, 404–409.

Kolb, U.; Dräger, M.; Jousseaume, B. Triorganotin compounds, [2-(methoxycarbonyl)-1,4-cyclohexadien-1-yl]dimethyltin halides: intra- and intermolecular unfolding of an inner tetrahedron to distorted trigonal bipyramids (X = Cl, Br, I) and a distorted octahedron (X = F). *Organometallics* **1991**, *10*, 2737–2742.

Krolevets, A. A.; Adamov, A. V.; Popov, A. G.; Martynov, I. V. Reaction of *N*-acetyl-N-ethylamidochloranhydrides of alkylphosphonic acids with cesium fluoride. *Zh. Obshch. Khim.* **1988**, *58*, 2628–2629.

Kunai, A.; Sakurai, T.; Toyoda, E.; Ishikawa, M. Selective synthesis of fluoro-, fluorohydro-, and chlorofluorosilanes from hydrosilanes with the use of a $CuCl_2$(CuI)/KF reagent. *Organometallics* **1996**, *15*, 2478–2482 and references cited therein.

Lee, I.; Shim, Ch. S.; Chung, S. Y.; Kim, H. Y.; Lee, H. W. Cross-interaction constants as a measure of the transition-state structure. 1. The degree of bond formation in nucleophilic-substitution reactions. *J. Chem. Soc. Perk. T. 2: Phys. Organic Chem.* **1988**, *11*, 1919–1923.

Leung, W. -P.; Kwok, W. -H.; Zhou, Z. -Y.; Mak, T. C. W. Structural and mechanistic studies of halogenation of a tin(II) *N*-functionalized alkyl. *Organometallics* **2003**, *22*, 1751–1755.

Lickiss, P. D.; Lucas, R. Rate increases in the fluorination of bulky chlorosilanes caused by ultrasound or by water. *J. Organomet. Chem.* **1996**, *510*, 167–172.

Liu, H.; Wang, P.; Sun, P. Polymer-supported potassium fluoride – a versatile fluorination reagent. *J. Fluorine Chem.* **1989**, *43*, 429–433.

Lockhart, T. P.; Puff, H.; Shuh, W.; Reuter, W.; Mitchell, T. N. Metal–metal spin coupling through chalcogenides. Correlation of $^{2}J(^{119}Sn, ^{119}Sn)$ with molecular structure. Crystal structure of $[(2\text{-}MeC_6H_4CH_2)_3Sn]_2O$ and $[(2\text{-}MeC_6H_4)_3Sn]_2O$. *J. Organomet. Chem.* **1989**, *366*, 61–72.

Makosza, M.; Bujok, R. A new type of phase-transfer catalysis via continuous transfer of fluoride anions to the organic phase in the form of potassium difluorotriphenylstannate. *Tetrahedron Lett.* **2004**, *45*, 1385–1386.

Makosza, M.; Bujok, R. Cocatalysis in phase-transfer catalyzed fluorination of alkyl halides and sulfonates. *J. Fluorine Chem.* **2005**, *126*, 209–216.

Mehring, M.; Vrasidas, I.; Horn, D.; Schürmann, M.; Jurkschat, K. The *O,C,O*-coordinating pincer-type ligand $\{2,6\text{-}[P(O)(OEt)_2]_2\text{-}4\text{-}t\text{-}Bu\text{-}C_6H_2\}$- in organotin chemistry. Halide exchange, cyclization, and novel coordination mode. *Organometallics* **2001**, *20*, 4647–4653.

Mercier, F. A. G.; Maddour, A.; Gielen, M.; Biesemans, M.; Willem, R. Crystal structures of mu(2)-fluoro- and mu(2)-salicylaldoximato-bridged mu(3)-oxo-tris(dimethyltin(IV)) bis(salicylaldoximate). *Organometallics* **1998**, *17*, 5933–5936.

Mitzel, N. W.; Losehand, U.; Richardson, A. Two successive steps of hypercoordination at tin: The gas-phase and solid-state structures of (*N,N*-dimethylaminoxy)trimethylstannane. *Organometallics* **1999**, *18*, 2610–2614.

Morales-Morales, D.; Jensen, C., Eds. *The Chemistry of Pincer Compounds*; Elsevier Science, **2007**.

Morrison, J. A.; Krause, L. J. Trifluoromethyl group 2B compounds: bis(trifluoromethyl)cadmium.base. New, more powerful ligand-exchange reagents and low-temperature difluorocarbene sources. *J. Am. Chem. Soc.* **1981**, *103*, 2995–3001.

Murphy, E. F.; Murugavel, R.; Roesky, H. W. Organometallic fluorides: compounds containing carbon-metal-fluorine fragments of *d*-block elements. *Chem. Rev.* **1997**, *97*, 3425–3468.

Nakajima, T.; Zemva, B.; Tressaud, A. *Advanced Inorganic Fluorides: Synthesis, Characterization and Applications*; Elsevier Science, **2000**.

Nesmeyanov, A. N.; Nogina, O. V.; Fedin, E. I.; Dubovitskii, V. A.; Kvasov, B. A.; Petrovskii, P. V. Transfer of electron influences in some cyclopentadienyl derivatives of titanium as investigated by H-1, F-19 and C-13 NMR methods. *Dokl. Akad. Nauk. SSR Ser. Khim.* **1972**, *205*, 857.

Nesmeyanov, A. N.; Fedin, E. I.; Petrovskii, P. V.; Dubovitskii, V. A.; Nogina, O. V.; Kochetkova, N. S. C-13 NMR spectra and electronic effects in cyclopentadienyl derivatives of metals. 2. Reference point for chemical-shifts of key carbon-atoms in series of C substituents. *J. Struct. Chem. USSR* **1975**, *16*, 705–710.

Novák, P.; Císařová, I.; Jambor, R.; Růžička, A.; Holeček, J. Coordination behaviour of the 2-(*N,N*-dimethylaminomethyl) phenyl ligand towards the di-*t*-butylchlorotin(IV) moiety. *Appl. Organomet. Chem.* **2004**, *18*, 241–243.

Novák, P.; Brus, J.; Císařová, I.; Růžička, A.; Holeček, J. Double-*C,N*-chelated tri- and diorganotin(IV) fluorides. *J. Fluorine Chem.* **2005a**, *126*, 1531–1538.

Novák, P.; Padělková, Z.; Kolářová, L.; Císařová, I.; Růžička, A.; Holeček, J. Structure and properties of double-*C,N*-chelated tri- and diorganotin(IV) halides. *Appl. Organomet. Chem.* **2005b**, *19*, 1101–1108.

Novák, P.; Padělková, Z.; Císařová, I.; Kolářová, L.; Růžička, A.; Holeček, J. Structural study of *C,N*-chelated monoorganotin(IV) halides. *Appl. Organomet. Chem.* **2006**, *20*, 226–232.

Novák, P.; Císařová, I.; Kolářová, L.; Růžička, A.; Holeček, J. Structure of *N,C,N*-chelated organotin(IV) fluorides. *J. Organomet. Chem.* **2007**, *692*, 4287–4296.

Olah, G. A.; Kuhn, S.; Beke, S. Darstellung und untersuchung organischer fluorverbindungen. 20. Darstellung von sauerefluoriden. *Chem Ber.* **1956**, *89*, 862–864.

Olah, G. A.; Welch, J. T.; Vankar, Y. D.; Nojima, M.; Kerekes, I.; Olah, J. A. Synthetic methods and reactions. 63. Pyridinium poly(hydrogen fluoride) (30% pyridine-70% hydrogen fluoride): a convenient reagent for organic fluorination reactions. *J. Org. Chem.* **1979**, *44*, 3872–3881.

Olah, G. A.; Chambers, R. D.; Prakash, G. K. S., Eds. *Synthetic Fluorine Chemistry*; Wiley-InterScience, **1992**.

O' Sullivan, A. C.; Struber, F.; Ley, S. V. Use of the potassium ion as a template for the selective derivatization of the antibiotic X-206. *J. Org. Chem.* **1999**, *64*, 6252–6256.

Padělková, Z.; Císařová, I.; Růžička, A. Dibromobis[2-(*N,N*-dimethylaminomethyl)phenyl]tin(IV). *Acta Crystallogr.* **2005**, *E61*, M2691–M2693.

Pieper, N.; Klaus-Mrestani, C.; Schürmann, M.; Jurkschat, K.; Biesemans, M.; Verbruggen, I.; Martins, J. C.; Willem, R. Synthesis, molecular structure, and stereochemical nonrigidity of bis(3-(dimethylamino)propyl)difluorostal dihydrate, $\{[Me_2N(CH_2)_3]_2SnF_2{*}2H_2O\}$, and enhanced reactivity of its fluoride adduct $\{[Me_2N(CH_2)_3]_2SnF_3\}\text{-}Bu_4N^+$ toward dichloromethane. *Organometallics* **1997**, *16*, 1043–1052.

Růžička, A.; Pejchal, V.; Holeček, J.; Lyčka, A.; Jacob, K. ^{119}Sn, ^{15}N, ^{13}C, and ^{1}H NMR study of the intramolecular Sn–N donor–acceptor interaction in [2-(dimethylaminomethyl)phenyl]stannanes. *Collect. Czech. Chem. Commun.* **1998**, *63*, 977–989.

Růžička, A.; Jambor, R.; Brus, J.; Císařová, I.; Holeček, J. Solution and cross-polarization/magic angle spinning NMR investigation of intramolecular coordination Sn-N in some organotin(IV) *C,N*-chelates. *Inorg. Chim. Acta* **2001**, *323*, 163–170.

Růžička, A.; Dostál, L.; Jambor, R.; Buchta, V.; Brus, J.; Císařová, I.; Holčapek, M.; Holeček, J. Structure and in vitro antifungal activity of [2,6-bis(dimethylaminomethyl)phenyl]diphenyltin(IV) compounds. *Appl. Organomet. Chem.* **2002**, *16*, 315–322.

Růžička, A.; Jambor, R.; Císařová, I.; Holeček, J. Structural study of 2,6-bis[(dimethylaminomethyl)phenyl]butyl stannanes: Non-conventional behaviour of triorganotin(IV) halides. *Chem. Eur. J*. **2003a**, *9*, 2411–2418.

Růžička, A.; Lyčka, A.; Jambor, R.; Novák, P.; Císařová, I.; Holčapek, M.; Erben, M.; Holeček, J. Structure of azo dye organotin(IV) compounds containing a *C,N*-chelating ligand. *Appl. Organomet. Chem*. **2003b**, *17*, 168–174.

Reuter, H.; Puff, H. Trimesityltin hydroxide and trimethyltin fluoride as models for determining so-called normal tin-oxygen and tin-fluoride bond-lenghts. *J. Organomet. Chem*. **1989**, *379*, 223–234.

Riesel, L.; Haenel, J. A simple synthesis of fluoro(organyl)phosphanes. *Z. Anorg. Allg. Chem*. **1991**, *603*, 145–150.

Rippstein, R.; Kickelbick, G.; Schubert, U. Influence of the Lewis acidity of the tin atom on the magnitude of the intramolecular Sn-N interaction in 2-$(Me_2NCH_2)C_6H_4Sn(X)RR'$. *Monatsh. Chem*. **1999a**, *130*, 385–399.

Rippstein, R.; Kickelbick, G.; Schubert, U. Synthesis and structures of 2-$[Me_2NCH_2CH_2N(Me)CH_2]C_6H_4$ substituted tin compounds. *Inorg. Chim. Acta* **1999b**, *290*, 100–104.

Roesky, H. W.; Haiduc, I. Fluorine as a structure-directing element in organometallic fluorides: discrete molecules, supramolecular self-assembly and host-guest complexation. *J. Chem. Soc. Dalton Trans*. **1999**, 2249–2264.

Samuel, E.; Ferner, R.; Bigorgne, M. Low-frequency infrared and Raman-spectra of cyclopentadienyl compounds of titanium, zirkonium, and hafnium. *Inorg. Chem*. **1973**, *12*, 881–887.

Sau, A. C.; Carpino, A. L.; Holmes, R. R. Synthesis and ^{1}H NMR studies of some pentacoordinate tin(IV) complexes derived from triphenyltin halides. *J. Organomet. Chem*. **1980**, *197*, 181–197.

Sheldrick, G. M. *SHELXL-97*, *A Program for Crystal Structure Refinement*; Göttingen, Germany; University of Göttingen, **1997**.

Smith, W. C.; Muetterties, E. L. Thionyl fluoride. *Inorg. Syn*. **1960**, *6*, 162–163.

Švec, P.; Novák, P.; Nádvorník, M.; Padělková, Z.; Císařová, I.; Kolářová, L.; Růžička, A.; Holeček, J. Structure of *C,N*-chelated nButyltin(IV) fluorides and their use as fluorinating agents of some chlorosilanes, chlorophosphine and metal halides. *J. Fluor. Chem*. **2007**, *128*, 1390–1395.

Švec, P.; Eisner, A.; Kolářová, L.; Weidlich, T.; Pejchal, V.; Růžička, A. Use of *C,N*-chelated di-*n*-butyltin(IV) fluoride for the synthesis of acyl fluorides, fluoroformates and fluorophosgene. *Tetrahedron Lett*. **2008**, *49*, 6320–6323.

Švec, P.; Padělková, Z.; Růžička, A.; Holeček, J. Crystal structure of polymeric [2-dimethylaminomethyl)phenyl]phenyltin(IV) difluoride. *Main Group Met. Chem*. **2009**, *32*, 217–218.

Švec, P.; Černošková, E.; Padělková, Z.; Růžička, A.; Holeček, J.Tri- and diorganostannates containing 2-(N,N-dimethylaminomethyl) phenyl ligand. *J. Organomet. Chem*. **2010**, *695*, 2475–2485.

Thoonen, S. H. L.; Deelman, B. J.; van Koten, G. Synthetic aspects of tetraorganotins and organotin(IV) halides. *J. Organomet. Chem*. **2004**, *689*, 2145–2157.

Thoonen, S. H. L.; van Hock, H.; de Wolf, E.; Lutz, M.; Spek, A. L.; Deelman, B. J.; van Koten, G. Synthesis of novel terdentate N,C,N′-coordinated butyltin(IV) complexes and their redistribution reactions with $SnCl_4$. *J. Organomet. Chem*. **2006**, *691*, 1544–1553.

Tudela, D.; Gutierrez-Puebla, E.; Monge, A. Crystal-structure of triphenyltin fluoride. *J. Chem. Soc. Dalton Trans*. **1992**, 1069–1071.

Tudela, D.; Fernandez, R.; Belsky, V. K.; Zavodnik, V. E. Structural chemistry of triorganotin fluorides. The crystal structure of tricyclohexyltin fluoride revisited. *J. Chem. Soc. Dalton Trans*. **1996**, 2123–2126.

van Koten, G.; Noltes, J. G.; Spek, A. L. Crystal and molecular structure of C,N-{2-[(dimethylamino)methyl]phenyl}diphenyltin bromide. *J. Organomet. Chem*. **1976**, *118*, 183–189.

Varfolomeev, L. I.; Grodetskii, S. A.; Dudkin, V. V.; Kalk, V. R.; Katyanova, V. R.; Kozlov, N. A.; Kurakov, V. A.; Matveev, A. A.; Kaurova, G. I.; Moldavskii, D. D.; Matalin, V. A.; Timofeev, S. N.; Fedorova, T. E.; Shkultetskaya, L. V.; Furin, G. G.; Ki, V. Ch. Russian patent RU2183621 C1, Patent application RU 2001-105579.

Varga, R. A.; Schürmann, M.; Silvestru, C. Hypervalent organotin (IV) derivatives containing $[2-(Me_2NCH_2)C_6H_4]Sn$ moieties. Competition between nitrogen and chalcogen atoms for coordination to the metal centre. *J. Organomet. Chem*. **2001**, *623*, 161–167.

Varga, R. A.; Silvestru, C.; Deleanu, C. Synthesis, solution behaviour and X-ray structures of $[2-(Me_2NCH_2)C_6H_4]SnCl_3$ and $[2-(Me_2NCH_2)C_6H_4]SnCl_3$-DMSO.*Appl. Organomet. Chem*. **2005**, *19*, 153–160.

Wakselman, M.; Savrda, J. *N*-alkoxycarbonyl amino-acid *N*-carboxyanhydrides and *N,N*-dialkoxycarbonyl amino-acid fluorides from *N,N*-diprotected amino-acids. *J. Chem. Soc. Chem. Commun*. **1992**, 812–813.

Wardell, J. L.; Spenser, G. M. *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed. Wiley: New York, Vol. 8, **1994**; pp. 4172.

Wong, C. G.; Rando, R. R. Inactivation of bovine opsin by all-trans-retinoyl fluoride. *J. Am. Chem. Soc*. *104*, **1982**, 7374–7375.

Zupan, M.; Stavber, S.; Planinsek, Z. Mild conversion of primary alcohols and aldehydes to acid fluorides with caesium fluoroxysulphate. *Tetrahedron Lett*. **1989**, *30*, 6095–6096.