New Observations Concerning the Reactivity of Triorganotin Fluorides

Thomas Lambertsen, Reinhard Schmutzler*

Introduction

The recent publications of H. W. Roesky et al. [1,2] concerning the use of Me₃SnF as a fluorinating reagent, prompt us to report some results of our own investigations on triorganotin fluorides [3]. Several efforts have been made to elucidate the molecular structure of Me₃SnF by single crystal X-ray diffraction [4,5] but, due to disordering effects, no reliable atomic coordinates could be determined. However, both studies give evidence for a polymeric zigzag-chain structure with bridging fluorine atoms. These structural features indicate weakly bonded fluorine, which might, therefore, be reactive in metathetical halogen-fluorine substitution reactions.

The first structural report on a polymeric organofluoroorganostannane(IV) [6], the 2:1 addition product of Me₂SnF₂ and NEt₄F, illustrated the ability of organotin(IV) fluorides to form fluorostannates with novel structural features. Since the only reported structure of a monomeric 1:1 fluoride adduct of Me₃SnF [7], the [Me₃SnF₃⁻]⁻ ion, was in error [8], further synthetic efforts seemed warranted.

An attempt by H. C. Clark et al. [9] to synthesize Me₃SnPF₆ from Me₃SnBr and AgPF₅ in liquid SO₂ failed. A promising alternative preparation may be the direct action of PF₅ on Me₃SnF in MeCN.

Results and Discussion

The assumption of a considerable fluorinating ability of Me₃SnF proved to be correct. In fact, any compound examined containing “hydrolyzable” chlorine was found to undergo quick fluorination when Me₃SnF was simply dispersed in the neat educt. Exemplary of this type of reaction, the fluorination of PhPCl₂, Cl₂PCH₂PCl₂ and (CH₂Cl)MeSiCl₃ is described. Substoichiometric amounts of Me₃SnF are quickly dissolved in PhPCl₂ at room temperature. ³¹P NMR spectra of such reaction mixtures show, beside the PhPCl₂ singlet at 162 ppm, a triplet at 208 ppm (¹(PF) = 1114 Hz) due to the well known PhPF₂ [10]. The only evidence for a side-product is a doublet at 205 ppm (¹(PF) = 1114 Hz), and the corresponding ¹⁹F NMR signal (−125 ppm, d, ¹(PF) = 1140 Hz), which we assign to PhPCIF, the monofluorinated intermediate. Since the volatilities of PhPF₂ and Me₃SnCl are practically identical (31−32 °C/11 mm Hg [10], −140 °C), the separation of these compounds by distillation was impossible. The facile solubility of Me₃SnCl in almost any solvent hindered the extractive separation of the products.

The lower boiling points of (CH₂Cl)MeSiF₂ and F₂PCH₂PF₂ allowed an easier separation by distillation of these rapidly formed products, but the higher heat of reaction could also cause the escape of vapours from the reaction vessel. To ensure a complete conversion of the chlorines in the absence of vapours, these reactions were carried out in sealed glass tubes. Although the boiling point of the highly pyrophoric F₂PCH₂PF₂ (44 °C) [11] is much lower than that of PhPF₂, the crude distil-
late still contained approximately 33 wt.-% of Me₃SnCl.

A few seconds after the solids were mixed, even PCl₅ reacted with Me₃SnF in an exothermic reaction, accompanied by evolution of a strongly fuming gas. The reaction was probably induced by moisture and promoted by the formation of liquid Me₃SnCl, which served as a solvent. In a modified reaction of Me₃SnF with a saturated solution of PCl₅ in xylene, the gaseous product was identified by IR spectroscopy as PF₅. PCl₅ was found to undergo a similar fluorination reaction with SbF₅.

Triorganofluorostannanes can also “fluorinate” calcium halides with formation of CaF₂ and the corresponding triorganoalostannane. As an example, the reaction of Ph₃SnF and n-Bu₃SnF with CaBr₂ in a 1:1 water – methanol – mixture was studied. After 20 minutes the reaction mixture was simply filtered, the solvents were evaporated in vacuo, and the residue was extracted with CH₂Cl₂, filtered and dried in vacuo. No precautions to exclude air or moisture had to be taken. The bromostannanes were isolated in yields of at least 73%. This “recovery-reaction” of soluble triorganoalostannanes seems to be advantageous over the reaction of triorganofluorostannanes with NaCl or NaBr in THF [13], but also to the heating with concentrated aqueous hydrogen halide solutions, e.g. of HCl [14], or with acid halides. Antifouling coatings, often containing triorganofluorostannanes, are used to prevent incrustations by marine organisms. A “solubilization-effect” by salts of alkaline earth metals in the sea water should be of importance for the “activation” of the fluorostannanes in such coatings. On treatment of Me₃SnF with Grignard reagents [14], a comparable halogen exchange has been observed.

The Me₃Sn polymer may also be attacked by fluoride ions. The degree of fluoride addition and of the associated solubilization of Me₃SnF strongly depends on the kind of solvent and on the nature of the fluoride added. By far the highest concentration of dissolved Me₃SnF was achieved by the use of alkali fluorides in methanol. The concentration of Me₃SnF that could be achieved increased with increasing molecular mass (and solubility) of the fluorides (NaF: ~20 g/l; KF: ~150 g/l; CsF: >500 g/l). The viscosity of the solutions of “Cs[Me₃SnF₂]” increased considerably with increasing concentra-

tion. While NaF did not noticeably influence the solubility of Me₃SnF in methanol (2.45 g/100 g at 31.3 °C[14]), CsF increased it more than 25-fold. A 1:1 ratio of fluoride and Me₃SnF was established in these solutions at equilibrium but, contrary to comparable reaction mixtures containing organic fluorides and Ph₃SnF [15,16], no crystal-line addition products were isolated.

The ¹⁹F NMR spectrum of “KF·Me₃SnF” in CD₂OD was examined at low temperatures. The spectrum at −70 °C indicated the precipitation of a phase rich in KF and the formation of metastable, linear fluorostannates of the estimated average composition K[(Me₃SnF)ₓ]₂F (δ¹⁹F bridging = −133, ¹J(¹⁹Sn-F)=1292.4 Hz, ¹J(¹⁷Sn-F)=1230.8 Hz, δ¹⁹F nonbridging = −145). Me₃SnF was not noticeably dissolved in aqueous solutions of alkali fluorides, but when it was dispersed in a boiling, concentrated solution of KF at approximately 160 °C, a white smoke condensing as a white cotton-like solid, was formed. Although Me₃SnF was found in the sublimate (IR spectroscopy), the unambiguous characterization of the primary “sublimate” (Me₃SnF or Me₃SnOH + KF) was hindered by particles drawn along from the solution. A similar observation was reported by H. C. Clark et al. [4]; on heating a mixture of dry KF and Me₃SnBr to 170 °C, a white sublimate of the correct composition of Me₃SnF was formed. Since Me₃SnF de-composes at ~360 °C without subliming, the authors assumed the intermediate formation of a thermally unstable salt, “[K(Me₃SnF₂)]”.

On addition of PhPF₄, Me₃SnF dissolved in MeCN. This indicates a transfer of fluoride ions to phosphorus and the intermediate formation of [Me₃Sn]⁺ [PhPF₃]−. Since this product could not be isolated (only Me₃SnF was recovered) and the ³¹P NMR signals of PhPF₄ were extraordinarily broad, a rapid fluorine exchange is assumed.

The reaction product of Me₃SnF and PF₅ in CH₂CN, a colourless, very hygroscopic solid (m.p.: ~65 °C (dec.)), was isolated simply by removing the solvent in vacuo at room temperature. The ¹⁹F and ³¹P NMR spectra showed the expected sharp resonances of the [PF₅]− anion and of traces of [(O):PF₃O]−. These features are in accord with a slow fluorine exchange. A complete removal of acetoniitrile, probably due to its coordination to the cationic tin atom, was not achieved. Analysis of a sample, taken after approximately 5 hours of
evacuation, indicated a composition \([\text{Me}_3\text{Sn}-0.17 \text{NCCH}_3]^+\text{[PF}_6^-].\)

Conclusions

Triorganofluorostannanes behave not only as easily recycleable potent fluorinating agents, but are also valuable precursors in the preparation of organotin compounds. Contrary to the behaviour typical of almost insoluble compounds, these fluorostannanes show high reactivity as fluoride donors towards any compound which is capable of forming stable fluorine compounds (e.g. adducts) by ion-transfer-reactions. In analogy to Ph$_3$SnF, Me$_3$SnF shows a weak tendency to form anionic fluoride adducts.

Experimental Section

All experiments, except for the reaction with CaBr$_2$, were performed in an atmosphere of dry nitrogen, using Schlenk techniques. The solvents were dried using standard procedures [19]. Me$_3$SnF was prepared by the method of E. Krause [14].

\(^1\)H, \(^{13}\)C, \(^{19}\)F and \(^{31}\)P NMR shift values are given in ppm, downfield from TMS, CFCI$_3$ and H$_3$PO$_4$ (85%), respectively. NMR spectra were recorded on a Bruker AC 200 spectrometer. IR spectra were recorded on a Beckman IR 4260 instrument. Microanalyses were performed in this laboratory.

\((\text{CICH}_2)_2\text{MeSiF}_2\)

To 4.5 g (24.6 mmol) of Me$_3$SnF in a nitrogen-flushed heavy-wall glass tube, 2.01 g (12.3 mmol) of \((\text{ClCH}_2)\text{MeSiCl}_2\) were quickly added and the stopcock was closed immediately. An exothermic reaction was observed and within 10 min a homogeneous liquid phase was formed. By a direct trap to trap vacuum condensation 1.32 g (10.1 mmol, 82%) \((\text{ClCH}_2)\text{MeSiF}_2\) was isolated. \(^1\)H NMR (CDCI$_3$): \(\delta 3.36\) (t, \(^3\)J(FH) = 3.26 Hz, Si-CH$_2$is); \(\delta 0.50\) (t, \(^3\)J(FH) = 5.97 Hz, Si-CH$_3$is); \(^{13}\)C NMR (CDCI$_3$): \(\delta 28.19\) (t, \(^3\)J(FC) = 21.70 Hz, Si-CH$_2$Cl) [20]; \(\delta -6.67\) (t, \(^3\)J(FC) = 15.57 Hz, Si-CH$_3$) [20]; \(^{19}\)F NMR (CDCI$_3$): \(\delta -138.49\) (s) [20].

\(\text{F}_2\text{PCH}_2\text{PF}_2\)

The experimental details of the preparation of this compound resembled those of the synthesis of \((\text{CICH}_2)_2\text{MeSiF}_2\). As a result of the absence of a solvent, the considerable heat of reaction was immediately transferred to the highly volatile and pyrophoric F$_2$PCH$_2$PF$_2$. For that reason it was essential to prevent any contact of the educts, e.g. by inclination of the tube, before the stopcock was closed. For the preparation of larger quantities of F$_2$PCH$_2$PF$_2$ the use of solvents is advised. 9.0 g (49.3 mmol) of Me$_3$SnF and 2.7 g (12.4 mmol) of Cl$_2$PCH$_2$PCl$_2$ yielded 1.78 g of a colourless and extremely pyrophoric condensate. The \(^1\)H NMR integration revealed a content of \(-33\%\) (0.6 g) of Me$_3$SnCl and 1.2 g (7.74 mmol, \(-67\%\)) of F$_2$PCH$_2$PF$_2$ (yield: \(-63\%\)). The spectra were in agreement with literature reports [11]. \(^1\)H, \(^{13}\)C, \(^{19}\)F and \(^{31}\)P NMR.

\(\text{PF}_5\)

In a 50 ml three-necked flask 5.0 g (27.4 mmol) of Me$_3$SnF was dispersed and magnetically stirred in 5 ml of xylene. Through a septum a saturated solution of PCl$_5$ in xylene (1.14 g, 5.47 mmol) was added, and the temperature was raised to 80 °C. A slow stream of nitrogen carried the gaseous products to a trap cooled with liquid N$_2$. The recondensation of the product into a heavy-wall glass tube yielded 0.57 g (4.5 mmol, 83%) of PF$_5$ (characterized by IR-spectroscopy [21]).

\(\text{Me}_3\text{SnPF}_5\cdot\text{CH}_3\text{CN}\)

A mixture of PF$_5$ and N$_2$ was slowly passed through a magnetically stirred suspension of 0.5 g (2.7 mmol) of Me$_3$SnF in 5 ml of CH$_3$CN. After a few minutes, without heating, the fluorostannane was dissolved completely. Vacuum (2mm Hg) was applied to the reaction mixture for 5 h. The residue consisted of 0.78 g of a colourless, extremely hygroscopic solid (m.p. \(-65\) °C), soluble in CH$_3$CN, CHCl$_3$ and DMSO. \(^1\)H NMR (CDCI$_3$): \(\delta 0.59\) (s, \(^3\)J(\(^{119}\)Sn-H)=69.8 Hz, \(^3\)J(\(^{117}\)Sn-H)=66.7 Hz). \(^{13}\)C NMR (CDCI$_3$): \(\delta 0.56\) (s, \(^3\)J(\(^{119}\)Sn,\(^{13}\)C)= 490.5 Hz, \(^3\)J(\(^{117}\)Sn-\(^{13}\)C)=468.6 Hz). \(^{31}\)P NMR (CDCI$_3$): \(\delta -138.7\) (sept., \(^3\)J(\(\text{PF}\)=707.0 Hz). \(^{19}\)F NMR (CDCI$_3$): \(\delta -71.8\) (d, \(^1\)J(\(\text{PF}\)=709.0 Hz).

\(\text{C}_3\text{H}_9\text{SnPF}_6\) (308.78)

\begin{align*}
\text{Caled} & \quad C 11.67 \quad H 2.94 \quad N 0.00\% \\
\text{Found} & \quad C 12.60 \quad H 3.02 \quad N 0.78\% \\
\text{but C}_3\text{H}_9\text{SnPF}_6\cdot0.17\text{CH}_3\text{CN} (315.76) \\
\text{Caled} & \quad C 12.70 \quad H 3.10 \quad N 0.75\% \\
\text{Found} & \quad C 12.60 \quad H 3.02 \quad N 0.78\% \\
\end{align*}

\(\text{Ph}_3\text{SnBr}\)

To a stirred dispersion of 2.0 g (5.4 mmol) of Ph$_3$SnF in 5 ml of a 1:1-mixture of methanol and water, 0.8 g of CaBr$_2$-hydrate (\(-80\%\) CaBr$_2$, 3.2 mmol) was added. After 20 min the reaction mix-
ture was filtered, dried in vacuo, dissolved in 5 ml of CH$_2$Cl$_2$, refiltered and dried in vacuo again. 1.76 g (4.1 mmol, 76%) of Ph$_3$SnBr (m.p. 117 °C) were isolated (mass spectrum, $^{13}$C NMR [22], $^1$H NMR).

**n-Bu$_3$SnBr**

The analogous reaction of 3.4 g (11.0 mmol) of n-Bu$_3$SnF with 1.65 g of CaBr$_2$-hydrate (6.6 mmol) yielded 2.97 g (73%) of liquid n-Bu$_3$SnBr (b.p. 230 °C) (mass spectrum, $^{13}$C NMR [23,24], and $^1$H NMR spectrum).

**Acknowledgements**

We are grateful to BASF AG, BAYER AG and HOECHST AG for supplying chemicals used in this research, and to the Fonds der Chemischen Industrie for financial assistance.