Ligand exchange in adducts of triphenyltin fluoride

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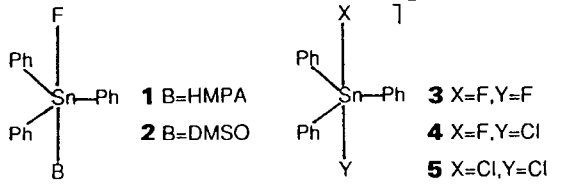
Abstract

A ^{19}F and ^{119}Sn NMR study of $Ph_3SnX_2^-$ (X=F, Cl) and Ph_3SnF:B (B=HMPA, DMSO) has shown that fluorine exchange occurs between four- and five-coordinate tin complexes, presumably via fluorine- and chlorine-bridged intermediates. The results point to a modified view of the isomerization and racemization of triorganoelement halides. Some reactions of $Ph_3SnF_2^-$ with tellurium and phosphorus compounds are described and the synthesis of $PhSnF_5^{2-}$ reported, but attempts to prepare six-coordinate adducts $Ph_3SnX_3^{2-}$ or Ph_3SnX_2:B^- were unsuccessful, although their presence in solution was indicated by NMR spectroscopy.

Introduction

Stereoselective synthesis, isomerization and ligand exchange processes of Main Group fluorides generally involve fluorine-bridged intermediates, as confirmed by synthetic and NMR studies [1] although, occasionally, these bridged intermediates are formed in a circuitous manner, involving common impurities and Lewis acids derived from the H_2O–HF–glass system [2]. As a continuation of our interest in fluorine-exchange processes, we decided to investigate triphenyltin(IV) adducts **1**–**5** by means of ^{19}F and ^{119}Sn NMR spectroscopy and analyze the role of bridged intermediates in the reaction of these adducts.



Experimental

NMR spectra were recorded on a Bruker AM300 spectrometer at 111.9 (^{119}Sn), 75.47 (^{13}C), 282.4 (^{19}F) and 94.76 (^{125}Te) MHz and chemical shifts were measured relative to external $SnMe_4$, external $SiMe_4$, internal C_6F_6 (−162.9 ppm with respect to $CFCl_3$) and external Ph_2Te (692 ppm with respect to Me_2Te), respectively. Mass spectra were obtained on a VG-7070-HF spectrometer.

Ph_3SnF was prepared from Ph_3SnCl and $KF\cdot 2H_2O$ in CH_2Cl_2 [3], or from Ph_3SnCl (258.5 mg, 0.67 mmol) and COF_2 (1.0 mmol) in CH_2Cl_2 (4 ml) in a glass tube [4]; MS (solid), *m/e*: 351 (M^+); 293 ($M^+ - Ph$). Ph_3SnF is insoluble in common organic solvents but was routinely identified by adding excess F^-, Cl^-, HMPA or DMSO to the solid and identifying $Ph_3SnX_2^-$ or Ph_3SnF:B in solution by ^{19}F and ^{119}Sn NMR spectroscopy. Ph_2SnF_2 was prepared from Ph_2SnCl_2 and $KF\cdot 2H_2O$ in CH_2Cl_2 [5]. Ph_3PF_2 was prepared from COF_2 and Ph_3P [4]; in a similar reaction, excess COF_2 was added to Ph_2TeCl_2 (103 mg, 0.29 mmol) in CH_2Cl_2 (10 ml) in a PTFE tube at −196 °C and the mixture warmed to 25 °C and stirred for 12 h. Removal of all volatile material gave Ph_2TeF_2 (12%), identified by ^{19}F NMR spectroscopy [6], and Ph_2TeFCl (78%). ^{19}F NMR (CD_3CN) of Ph_2TeFCl: δ −108.7 ppm, J(Te,F)=584.0 Hz., ^{125}Te NMR: δ 1068 ppm. The yield of Ph_2TeF_2 was increased by adding an excess of NaF to Ph_2TeClF or Ph_2TeCl_2 with stirring for 1 d. 4-Fluoro-2,2′-bipyridine was prepared as described earlier [2] and hexamethylphosphoric triamide (HMPA), dimethylsulfoxide (DMSO) and other chemicals were commercial samples used without further purification. The anions FHF^- and FDF^- were identified by ^{19}F NMR spectroscopy [7] at 25 °C or −50 °C, and F^- was observed at $\delta^{19}F$ −103 to −114 ppm.

Preparation of $Bu_4N^+Ph_3SnF_2^-$ (3) and $Et_4N^+Ph_3SnFCl^-$ (4)

Following the procedure reported for $Et_4N^+Ph_3SnF_2^-$ [3], a slight excess of $Bu_4NF\cdot 2H_2O$

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(0.40 mmol) was added to a suspension of Ph_3SnF (120 mg, 0.33 mmol) in CH_2Cl_2 (4 ml) with continuous shaking until a clear solution was formed. Evaporation of the solvent gave colourless crystals of $Bu_4N^+Ph_3SnF_2^-$, identified by ^{19}F and ^{119}Sn NMR spectroscopy (Table 1) and by ^{13}C NMR spectroscopy. ^{13}C NMR ($CDCl_3$): δ C1 146.9 ppm [J(C1, F) = 24.9 Hz, J(C1, ^{119}Sn) = 920 Hz]; δ C2 136.1 ppm [J(C2, F) = 3.0 Hz, J(C2, ^{119}Sn) = 47.5 Hz]; δ C3 125.6 ppm [J(C3, F) = 2.0 Hz, J(C3, ^{119}Sn) = 70.9 Hz]; δ C4 126.1 ppm [J(C4, F) ~ 0 Hz, J(C4, ^{119}Sn) = 15.1 Hz]. The compound dissolves appreciably in common organic solvents, m.p. 155 °C. MS (solid), *m/e*: 370 (Ph_3SnF^+).

Attempts to prepare six-coordinate $Ph_3SnX_3^{2-}$ salts were unsuccessful. Crystallization from mixtures of $Ph_3SnF_2^-$ and excess fluoride in various solvents produced only crystals of $Bu_4N^+Ph_3SnF_2^-$. In a typical experiment, KF (46.5 mg, 0.80 mmol), dried at 100 °C for 1 h, and 18-crown-6 ether (211 mg, 0.80 mmol) in a 1:1 molar ratio in CH_3CN was stirred until a clear solution formed which was added to recrystallized and vacuum-dried $Bu_4N^+Ph_3SnF_2^-$ in CH_3CN (10 ml) under nitrogen. The solution was stirred overnight and its ^{19}F NMR spectrum examined, but mainly $Ph_3SnF_2^-$ plus some SnF_6^{2-} was identified. Reactions with CsF, NaF, $Bu_4NF \cdot 2H_2O$ and K^+FHF^- were also unsuccessful. Attempts to prepare $Ph_3SnFCl_2^{2-}$ or $Ph_3SnF_2Cl^{2-}$, by adding varying amounts of Et_4NCl to Ph_3SnFCl^- or $Ph_3SnF_2^-$, were also unsuccessful. Addition of excess Cl^- to $Ph_3SnF_2^-$ resulted in the formation of Ph_3SnFCl^-, $Ph_3SnCl_2^-$ and F^-, as well as an unknown species, $\delta^{119}Sn$ −405 ppm [(quartet), $J(^{19}F-^{119}Sn)$ = 2480 Hz], tentatively identified as $Ph_2SnF_3^-$.

$Et_4N^+Ph_3SnFCl^-$ (**4**) was prepared from a 1:1 stirred mixture of Ph_3SnF and Et_4NCl in acetonitrile, according to the method of Holmes and co-workers [3]. ^{13}C NMR ($CDCl_3$): δ C1 145.3 ppm; δ C2 134.4 ppm, [J(C2, ^{119}Sn) = 49 Hz]; δ C3 124.9 ppm [J(C3, ^{119}Sn) = 72 Hz]; δ C4 125.5 ppm [J(C4, ^{119}Sn) = 17 Hz].

Reactions of Ph_2SnF_2 and Ph_2SnCl_2

No reaction occurred and no new NMR signals were observed if fluorides CsF, KF, NaF, $Bu_4NF \cdot 2H_2O$ and K^+FHF^- were added to a suspension of insoluble Ph_2SnF_2 in CH_2Cl_2 or CH_3CN at temperatures of 10 °C to 35 °C with vigorous stirring for 7 d. After further stirring for 1 month at 25 °C, the ^{19}F and ^{119}Sn NMR spectra revealed the formation of $PhSnF_5^{2-}$ and $Ph_3SnF_2^-$, as well as impurities such as SiF_6^{2-} and BF_4^-. Removal of $Ph_3SnF_2^-$ by crystallization increased the concentration of $PhSnF_5^{2-}$; however, the latter could not be isolated but was identified by ^{19}F and ^{119}Sn NMR spectroscopy (Table 1).

$PhSnF_5^{2-}$ was prepared more readily by adding $Bu_4N^+Ph_3SnF_2^-$ (409 mg, 0.65 mmol) to a solution of Ph_2SnCl_2 (107 mg, 0.31 mmol) in CH_2Cl_2 (4 ml). After shaking for 2 min, an insoluble solid (~500 mg) was formed; the filtrate did not exhibit any ^{19}F NMR signal but addition of $Bu_4NF \cdot 2H_2O$ to the solid mixture in CH_2Cl_2 revealed the presence of $PhSnF_5^{2-}$ and $Ph_3SnF_2^-$. Because of the unreactivity of solid Ph_2SnF_2, its presence in the solid mixture could not be confirmed by NMR spectroscopy.

Ph_2SnCl_2 (δSn −26.1 ppm) interacted readily with halide or base, as demonstrated by NMR changes in the following samples: Ph_2SnCl_2: Bu_4NF, δSn ($CDCl_3$)

TABLE 1. ^{19}F and ^{119}Sn NMR data for phenyltin(IV) adducts

Sample	δSn (ppm)	δF (ppm)	$J(^{119}Sn-F)$ (Hz)	Solvent
$Ph_3SnF \cdot HMPA$ (**1**)	−272	−174.2	2040	HMPA/$CDCl_3$
$Ph_3SnF \cdot DMSO$ (**2**)	−271	−178.2	2090	DMSO-d_6
$Et_4N^+Ph_3SnFCl^-$ (**4**)	−293	−159.0	1916	$CDCl_3$
$Et_4N^+Ph_3SnCl_2^-$ (**5**)	−253.7[a]			$CDCl_3$
$Bu_4N^+Ph_3SnF_2^-$ (**3**)[b]	−345.9	−160.9	2010	CD_2Cl_2
3/DMSO = 1:3.5	−346.6		2025	CD_2Cl_2
3/DMSO = 1:10	−347.9		2027	CD_2Cl_2
3/DMSO = 1:20	−349.1		2033	CD_2Cl_2
3/DMSO = 1:30	−349.7		2037	CD_2Cl_2
$(Bu_4N^+)_2PhSnF_5^{2-}$	−406	−140.4(F^A) −141.2($4F^B$)	1107(Sn-F^A) 2484(Sn-F^B) 17.9(F^A-F^B)	CD_2Cl_2

[a]Lit. value [29]: $\delta^{119}Sn$ −257.2 ppm in CD_3NO_2.
[b]NMR spectra in various solvents: $\delta^{19}F$ ($CDCl_3$) −160.6 ppm, J(F, ^{119}Sn) = 1944 Hz; $\delta^{19}F$ (acetone-d_6) −160.9 ppm, J(F, ^{119}Sn) = 1959 Hz; $\delta^{19}F$ (CD_3CN) −160.8 ppm, J(F, ^{119}Sn) = 2000 Hz; $\delta^{19}F$ (HMPA/$CDCl_3$) −168.1 ppm, J(F, ^{119}Sn) = 2013 Hz; $\delta^{19}F$ (CD_3CN + KF in 18-crown-6) −163.4 ppm, J(F, ^{119}Sn) = 1975 Hz.

−220.8 (br); Ph_2SnCl_2:2Bu_4NF, δSn (DMSO-d_6) −352.0 (br); Ph_2SnCl_2:2HMPA, δSn ($CDCl_3$) −280.7 (br); Ph_2SnCl_2:2Ph_3PO, δSn ($CDCl_3$) −135.5 (br), but ligand exchange in these systems was not investigated further.

Reaction of Ph_2SnCl_2 with XeF_2

Solid XeF_2 (15.2 mg, 0.09 mmol) was added slowly with stirring to a solution of Ph_2SnCl_2 (30.9 mg, 0.09 mmol) and Et_4NCl (1.49 mg) in CH_2Cl_2 (4 ml). The reaction was exothermic and the solution turned dark green within 2–3 min. Eventually, a white solid formed which was insoluble in common organic solvents but addition of excess $Bu_4NF \cdot 2H_2O$ to the solid mixture gave a solution containing SnF_6^{2-} (54%), $ClSnF_5^{2-}$ (38%), *cis*-$Cl_2SnF_4^{2-}$ (7%) and *trans*-$Cl_2SnF_4^{2-}$ (1%), identified by ^{19}F NMR spectroscopy [8]. If excess DMSO was added to the solid mixture, $SnF_5(DMSO)^-$ [8] was identified in solution by ^{19}F NMR spectroscopy.

$Ph_3SnF_2^-$ and phosphorus compounds

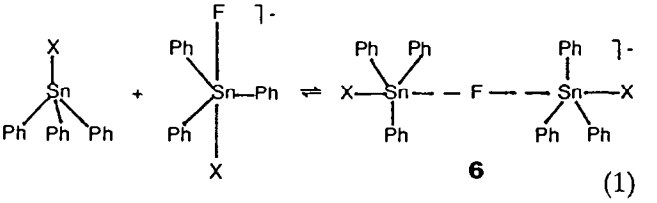
A slight excess of Cl_3PO was added to a solution of $Bu_4N^+Ph_3SnF_2^-$ in CH_2Cl_2 in a glass tube and the formation of $P(O)FCl_2$ and $P(O)F_2Cl$ confirmed by ^{19}F NMR spectroscopy. On standing in solution, hydrolysis gave mainly $P(O)F(OH)_2$. In a similar reaction, Cl_3PO (0.20 mmol) in CH_2Cl_2 (2 ml) was added to solid Ph_3SnF (60.0 mg, 0.16 mmol) and the products $P(O)FCl_2$ and $P(O)F_2Cl$ were identified by ^{19}F NMR spectroscopy. After 7 d in solution, hydrolysis gave mainly $P(O)F(OH)_2$. No reaction and no intermolecular fluorine exchange occurred between $Ph_3SnF_2^-$ and Ph_3PF_2 and the ^{19}F NMR spectrum of a 1:1 molar mixture showed only unreacted starting compounds.

Reaction of $Ph_3SnF_2^-$ with Ph_2TeCl_2

$Bu_4N^+Ph_3SnF_2^-$ (81.9 mg, 0.13 mmol) in CH_2Cl_2 (2 ml) was added to Ph_2TeCl_2 (21.2 mg, 0.06 mmol) in CH_2Cl_2 (2 ml) in a 2:1 molar ratio. The solution turned cloudy and a white precipitate (~30 mg) was removed by filtration and identified as Ph_3SnF by the method described above. Examination of the filtrate by ^{19}F and ^{125}Te NMR spectroscopy revealed the formation of Ph_2TeF_2 and Ph_2TeFCl, as well as some unreacted Ph_2TeCl_2 (<10%). A similar result was obtained when $Ph_3SnF_2^-$ and Ph_2TeCl_2 was mixed in a 1:1 molar ratio.

Results and discussion

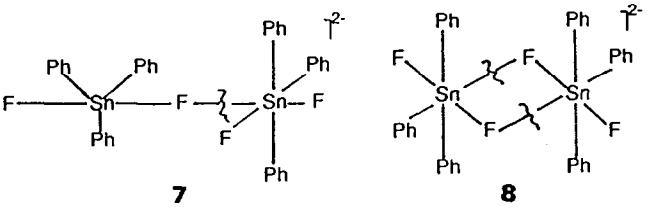
Fluorine exchange in the Ph_3SnX–Ph_3SnFX^- system is compatible with a rapid equilibrium involving four- and five-coordinate tin species and a fluorine-bridged intermediate **6**, i.e.



(1)

and the following experimental results were found to be in agreement with the proposed mechanism of eqn. (1).

(a) All fluorine exchange and cleavage of Sn–F bonds in $Ph_3SnF_2^-$ is stopped if samples of $Ph_3SnF_2^-$ are purified by crystallization, presumably because crystallization removes any four-coordinate tin species from solution, including the sparingly soluble Ph_3SnF, thus preventing the formation of a fluorine-bridged intermediate **6**. This result eliminates simple ionization of $Ph_3SnF_2^-$ and loss of F^- as a mechanism for fluorine exchange. Dimerization of $Ph_3SnF_2^-$ is a reasonable process because fluorine bridging is a common feature of tin fluorides [9]; nevertheless, the fact that purified $Ph_3SnF_2^-$ does not undergo fluorine exchange implies that dimers such as **7** or **8** do not lead to Sn–F bond cleavage, e.g.



probably because selective cleavage of the weakest bonds does not lead to the loss of Sn–F coupling in $Ph_3SnF_2^-$. Unequal bridging bonds in dimeric tin fluorides containing the $Sn(\mu\text{-}F)_2Sn$ unit have been identified by X-ray crystallography [10], and selective cleavage of fluorine-bridged intermediates has been observed in related Main Group fluorides [1, 11].

(b) The five-coordinate 1:1 adducts Ph_3SnF:HMPA (**1**), Ph_3SnF:DMSO (**2**) and Ph_3SnFCl^- (**4**) undergo rapid fluorine exchange and loss of Sn–F coupling, and this result suggests that partial dissociation of the adducts ensures that four-coordinate tin species are present, as required by eqn. (1). Consistent with this view was the finding that addition of a five-fold excess of HMPA to **1**, a five-fold excess of DMSO to **2** or a 20-fold excess of Cl^- to **4** stops fluorine exchange in these adducts, as the concentration of the four-coordinate species is decreased by the excess Lewis base. The NMR data for non-exchanging **1**–**5** are given in Table 1.

(c) Equation (1) implies that halogen redistribution in five-coordinate tin halides is catalyzed by four-coordinate tin species and, indeed, we find only broad ^{19}F and ^{119}Sn NMR peaks in mixtures of fluoride and chloride adducts. The addition of a 20-fold excess of Et_4NCl, however, slows down the rate of eqn. (2),

$$Ph_3SnF_2^- + Ph_3SnCl_2^- \rightleftharpoons 2Ph_3SnFCl^- \quad (2)$$

and well-resolved NMR spectra for all three species depicted in eqn. (2) can be observed by ^{119}Sn NMR spectroscopy, as shown in Fig. 1.

(d) Several reactions of $Ph_3SnF_2^-$ were carried out in order to test its ability as a fluoride donor. If, during the course of the reaction, a four-coordinate tin compound was introduced, then Sn–F coupling in $Ph_3SnF_2^-$ was lost. For example, a 2:1 reaction of 'rigid' $Ph_3SnF_2^-$ with Ph_2TeCl_2 gave 'rigid' Ph_2TeF_2 and Ph_2TeFCl [eqn. (3)]:

$$Ph_3SnF_2^- + Ph_2TeCl_2 \rightleftharpoons Ph_2TeF_2 + Ph_2TeFCl + Ph_3SnFCl^- + Ph_3SnCl_2^- \quad (3)$$

but unreacted $Ph_3SnF_2^-$ then underwent rapid intermolecular fluorine exchange, presumably because $Ph_3SnCl_2^-$ or Ph_3SnFCl^- is in equilibrium with a four-coordinate tin compound. In a similar reaction, exchange and Sn–F bond cleavage was initiated in 'rigid' $Ph_3SnF_2^-$ by the addition of Ph_3TeCl.

In all these rapidly exchanging systems, it was possible to stop fluorine exchange at the completion of an experiment and identify triphenyltin species in solution via NMR spectroscopy by adding $Bu_4NF \cdot 2H_2O$ or excess Et_4NCl. Chlorine exchange via bridged intermediates such as $FPh_3Sn--Cl--SnPh_3Cl^-$ or $B{:}Ph_3Sn--Cl--SnPh_3Cl$ is also to be expected, but chlorine exchange was not directly observable in our NMR experiments.

The presence of excess halide or base in the above experiments raises the possibility that six-coordinate adducts are formed; however, our attempt to prepare stable adducts such as $Ph_3SnX_3^{2-}$ or $Ph_3SnX_2{:}B^-$ from the reactions of $Ph_3SnF_2^-$ or Ph_3SnFCl^- with F^-, Et_4NCl, HMPA or DMSO were unsuccessful. Sources of fluoride ion included CsF, NaF, K^+FHF^-, KF in 18-crown-6 ether and $Bu_4NF \cdot 2H_2O$. Furthermore, adding the ligand 4-fluoro-2,2'-bipyridine (fbpy), which is a sensitive indicator of adduct formation [2], to $Ph_3SnF_2^-$ in a 1:1 ratio gave ^{19}F NMR spectra characteristic of $Ph_3SnF_2^-$ and uncomplexed fbpy. Attempts by others to prepare $Ph_3SnClX_2^{2-}$ have also been unsuccessful [12].

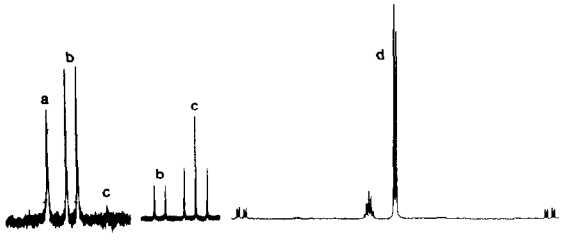
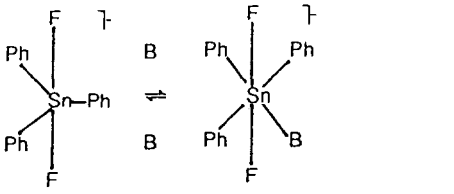


Fig. 1. Typical ^{119}Sn NMR spectra of mixtures of (a) $Ph_3SnCl_2^-$ (**5**), (b) Ph_3SnFCl^- (**4**) and (c) $Ph_3SnF_2^-$ (**3**) in the presence of excess Et_4NCl; ^{19}F NMR spectrum of (d) $PhSnF_5^{2-}$. Chemical shifts and coupling constants are listed in Table 1.

Small changes in chemical shifts and coupling constants were detected if the NMR spectrum of $Ph_3SnF_2^-$ was recorded in basic solvents (Table 1); for example, $\delta^{119}Sn$ in CD_2Cl_2 (−345.9 ppm) changes to −349.7 ppm, in the direction of higher coordinate tin, as a 30-fold excess of DMSO is added, and it is reasonable to ascribe such modest changes to the presence of small amounts of the six-coordinate adduct **9** in solution [eqn. (4)]:



(4)

3 *mer*-**9** B = DMSO, HMPA

We assume that base enters the equatorial plane of **3** to give *mer*-(**9**) because the isoelectronic cation $Ph_3TeF_2^+$ reacts exclusively at an equatorial site [11]; moreover, the addition of fluoride ion to Ph_3AsF_2 and Ph_3SbF_2 gives only *mer*-$Ph_3EF_3^-$ [13].

The addition of fluoride ion to $Ph_3SnF_2^-$ leads to small changes in chemical shift and coupling constants, but does not result in the loss of Sn–F or C–F coupling in $Ph_3SnF_2^-$ as demonstrated by ^{19}F, ^{119}Sn and ^{13}C NMR spectroscopy. A small equilibrium concentration of six-coordinate $Ph_3SnF_3^{2-}$ appears reasonable, but the retention of Sn–F coupling eliminates a *fac*-$Ph_3SnF_3^{2-}$ structure (C_{3v}). On the other hand, a *mer*-$Ph_3SnF_3^{2-}$ isomer is compatible with retention of Sn–F coupling because selective cleavage of a fluorine ligand F^a which is *trans* to phenyl is not expected to cleave the original Sn–F bonds [eqn. (5)]; just such an effect has been observed in the analogous *mer*-$Ph_3TeX_3^-$/$Ph_3TeX_2^+$ (X = F, Cl, OH) system [1, 11].

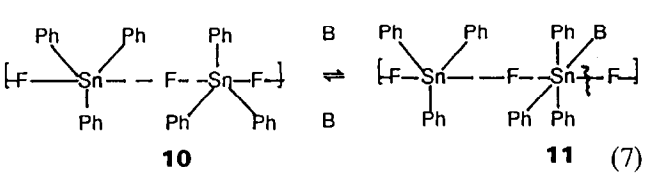
$$Ph_3SnF_2^- \overset{F^-}{\rightleftharpoons} \textit{mer}\text{-}Ph_3SnF_2F^{a2-} \overset{Ph_3SnF_2^-}{\rightleftharpoons} Ph_3SnF_2--F^a--SnF_2Ph_3^{3-} \quad (5)$$

We suggest, therefore, that small amounts of six-coordinate *mer* isomers are present in solution, as well as fluorine-bridged species; in fact, higher coordinate tin species cannot be excluded, given the tendency of tin compounds to form six- and even seven- or eight-coordinate adducts [14]. However, three phenyl substituents must strongly shift the equilibrium towards the pentacoordinate state, in agreement with the decreasing acceptor strength of tin as halogens are replaced by bulky organic substituents.

The fact that $R_4N^+Ph_3SnF_2^-$ is soluble in organic solvents and can be purified and recrystallized with ease, combined with the insolubility of Ph_3SnF, makes $Ph_3SnF_2^-$ a potentially useful fluoride-ion donor, and it was possible to verify by ^{19}F NMR spectroscopy that an excess of chloride ion or base such as DMSO or pyridine liberates fluoride ion [eqn. (6)]. In acetonitrile or dichloromethane as solvents, the formation of F^- was accompanied by the formation of FHF^- and FDF^-, a known reaction [7].

$$Ph_3SnF_2^- \xrightleftharpoons{Cl^- \text{ (or B)}} Ph_3SnFCl^- \text{ (or } Ph_3SnF{:}B) + F^- \quad (6)$$

Ph_2SnF_2 is insoluble in common organic solvents and the solid does not interact with F^-, Cl^-, DMSO or other bases under mild conditions. This insolubility must reflect the presence of six-coordinate tin, as pointed out by Holmes and co-workers [3]. However, Ph_3SnF is five-coordinate in the solid state [15], and its solid–solution equilibria and interaction with bases or halide ions to give adducts **1–5** can be explained by the same mechanistic features [eqn. (7)] as postulated for the equilibria in solution.



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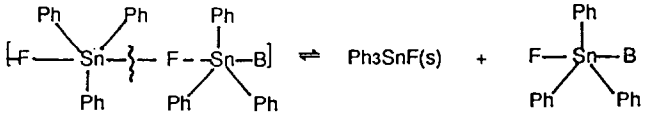
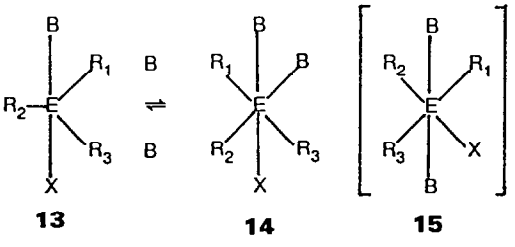


Thus, exclusive attack of B at an equatorial site of **10** gives a six-coordinate tin species **11**; cleavage of a bridging fluorine bond in **11** followed by cleavage of a second bridging bond in **12** then liberates soluble $Ph_3SnF{:}B$.

Ligand exchange and racemization of triorganoelement halides

The reaction conditions employed in this study closely resemble those under which trisubstituted halides of tin, as well as of silicon, undergo halide- and base-catalyzed isomerization and racemization. Indeed, two of the mechanistic details discussed above, viz. fluorine transfer via bridged intermediates and selective attack of a sixth ligand at an equatorial site, have a direct bearing on the mechanism of racemization. For example, isomer **15** has been postulated as an intermediate in racemization [16], but our analysis suggests that equatorial attack of base on **13** leads only to isomer **14**, rather than **15**; however, an equilibrium between **13** and **14** as depicted in eqn. (8) does not lead to racemization.

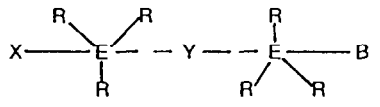


(8)

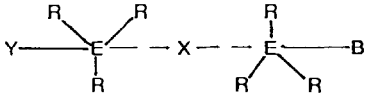
Pseudorotation of **13** has been postulated [17], but this postulate is unnecessary. Instead, loss of fluorine or chlorine ligands via halogen-bridged intermediates, accompanied by addition and removal of base molecules to give ionic and neutral intermediates such as $R_3SnF_2^-$, $R_3SnCl_2^-$, R_3SnFCl^-, $R_3SnF{:}B$, $R_3SnCl{:}B$, R_3SnB^+ and $R_3SnB_2^+$, as discussed by Corriu *et al.* [18], Chojnowski *et al.* [19], Bassindale *et al.* [20] and others [21], provides a unified view of ligand exchange, as well as of halide- and base-catalyzed isomerization and racemization. Cations such as $R_3Sn(base)_2^+$ [22], as well as anions $R_3SnX_2^-$ [23] and neutral adducts $R_3SnX{:}base$ [24], have all been identified by X-ray crystallography.

Our analysis suggests that isomer **15** may be formed by an alternative route, as a result of equatorial attack of a halide ion on the intermediate $R_3E(base)_2^+$, but the rate of racemization would then be dependent on the formation of $R_3E(base)_2^+$ (D_{3h}).

The fact that some reactions of R_3EX compounds show an abrupt change from inversion to retention as the nature of the halide or solvent is changed [25], is readily explained by the selective cleavage of bridging halogen bonds in unsymmetrical intermediates such as **16** or **17**.



16



17

Cleavage of tin–phenyl bonds

Phenyl–tin bonds were not cleaved during any of the ligand-exchange studies described above, but loss of phenyl was observed under more vigorous reaction conditions. After stirring a mixture of insoluble Ph_2SnF_2 and excess $Bu_4NF \cdot 2H_2O$ in CH_2Cl_2 for 1 month, unreacted solid Ph_2SnF_2 (~40%) was filtered off and the filtrate contained $Ph_3SnF_2^-$ and a small amount of $PhSnF_5^{2-}$. It was also possible to identify $PhSnF_5^{2-}$ in mixtures of $Ph_3SnF_2^-$ and excess KF or NaF in acetonitrile. The anion $PhSnF_5^{2-}$ could be produced within several minutes by adding $Ph_3SnF_2^-$ to soluble Ph_2SnCl_2, which gave a mixture of insoluble phenyltin fluorides within several minutes [eqn. (9)]. Addition of excess $Bu_4NF \cdot 2H_2O$ to this solid mixture produced $Ph_3SnF_2^-$ and $PhSnF_5^{2-}$, but $Ph_2SnF_2(s)$ does not react with fluoride under moderate conditions and was not identified in the mixture.

$$Bu_4N^+Ph_3SnF_2^- + Ph_2SnCl_2 \overset{-Bu_4NCl}{\rightleftharpoons} \quad (9)$$

$$\begin{array}{ccccc} [Ph_3SnF(s)] & + & [Ph_2SnF_2(s)] & + & [PhSnF_3(s)] \\ \downarrow F^- & & \downarrow F^- & & \downarrow F^- \\ Ph_3SnF_2^- & & \text{No reaction} & & PhSnF_5^{2-} \end{array}$$

The anion $PhSnF_5^{2-}$ was characterized by NMR spectroscopy (Table 1) and the ^{19}F NMR spectrum is shown in Fig. 1. Its AB_4 spin pattern, with $^{117/119}Sn$ satellites and $J(F^a-F^b) = 17.9$ Hz establishes an octahedral $XSnF_5$ structure. The possibility that $XSnF_5$ might be $HOSnF_5^{2-}$ or $ClSnF_5^{2-}$ can be eliminated by comparison with published NMR spectra [8]. The trend in coupling constants $J(F^a-F^b)$ for the series $PhTeF_5$ (148 Hz) [26], $PhPF_5^-$ (38 Hz) [27] and $PhSiF_5^{2-}$ (11.0 Hz) [28] makes a value of $J(F^a-F^b) = 17.9$ Hz appear reasonable for $PhSnF_5^{2-}$.

Loss of phenyl substituents was also observed in the reaction of Ph_2SnCl_2 with XeF_2 in the presence of Et_4NCl, which gave a dark green solution and eventually a white solid mixture. On treatment with excess $Bu_4NF \cdot 2H_2O$, this was converted to soluble SnF_6^{2-}, SnF_5Cl^{2-}, and *cis*- and *trans*-$SnF_4Cl_2^{2-}$. If excess DMSO was added to the solid mixture, $SnF_5(DMSO)^-$ was also identified by NMR spectroscopy.

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