Decomposition of 1f. The crude product mixture consists mainly (ca. 80%) of ketene **6f**. Kugelrohr distillation at 40 °C/0.5 Torr yields pure **6f** in 45% yield as a colorless oil. ^1H NMR and IR data agree with literature[6] values. ^{13}C NMR (C_6D_6): δ –3.2 ($C{=}C{=}O$), 0.3, 0.8 ($SiMe_3$ and $SiMe_2$), 49.7 (OMe), 168.1 ($C{=}O$).

X-ray Crystal Structure Analysis of (*E*)-2a. Crystal Data: $C_{12}H_{24}O_4Si_2$, molecular mass 288.5, orthorhombic, space group *Pbca*, $a = 8.987$ (1) Å, $b = 12.076$ (1) Å, $c = 15.329$ (7) Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, $d_{calcd} = 1.15$ g cm^{-3}.

Data Collection: crystal size 0.45 × 0.15 × 0.30 mm, monochromatized Mo Kα radiation, 1366 reflections measured in the range $4.0 \le 2\theta \le 46.0°$, 1153 unique reflections, $\omega/2\theta$ scan, scan width $(1.30 + 0.35(\tan\theta))°$.

Structure Solution and Refinement.[41] Structure solution was by direct methods (MULTAN) and refinement by a full-matrix least-squares method. H atoms were localized in a ΔF map and were refined (with B fixed) except for H3C and H4A. With 653 reflections ($I > 2.5\sigma(I)$) and 122 variables, refinement converged at $R = 0.062$, $R_w = 0.067$, $w = [\sigma(F_o)^2 + (0.04F_o)^2]^{-1}$ (shift/error ratio ≤0.75, residual electron density ≤0.58). Positional and thermal parameters for non-hydrogen atoms are given in Table III.

X-ray Crystal Structure Analysis of 4d. Crystal Data: $C_{24}H_{48}O_4Si_2$, molecular mass 456.8, monoclinic, space group $P2_1/c$, $a = 15.220$ (4) Å, $b = 8.503$ (3) Å $c = 22.247$ (3) Å, $\beta = 103.75$ (2)°, $Z = 4$, $d_{calcd} = 1.08$ g cm^{-3}.

Data Collection: crystal size 0.52 × 0.30 × 0.20 mm, monochromatized Mo Kα radiation, 2792 independent reflections in the range $4.0 \le 2\theta \le 41.0°$, $\omega/2\theta$ scan, scan width $(0.85 + 0.35(\tan\theta))°$.

Structure Solution and Refinement.[41] Structure solution was by direct methods (MULTAN) and refinement by a full-matrix least-squares method. H atoms were partly localized in a ΔF map and refined isotropically, and partly calculated and not refined. With 2169 reflections ($I > 2\sigma(I)$) and 463 variables, refinement converged at $R = 0.056$ and $R_w = 0.054$ (unit weights, shift/error ratio ≤1.60, residual electron density ≤1.06). Positional and thermal parameters for non-hydrogen atoms are given in Table IV.

Acknowledgment. Financial support of this work by the Volkswagen-Stiftung and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data, data collection, and structure solution and refinement, atomic and thermal parameters, and bond distances and angles for compounds (*E*)-**2a** and **4d** (9 pages). Ordering information is given on any current masthead page.

OM920337C

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(41) The program system Structure Determination Package (Enraf-Nonius, Delft, The Netherlands) was used. Plotting programs: Keller, E. SCHAKAL; University of Freiburg, Freiburg, Germany, 1990. Johnson, C. K. ORTEP-II; Report No. ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1975.

Hypervalent Monoorganyl- and Diorganyltin(IV) Fluoride Complexes: A ^{19}F and ^{119}Sn Study of Inter- and Intramolecular Dynamics in Solution

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Reactions of fluoride ion with diorganyltin(IV) dichlorides R_2SnCl_2 (R = Ph, Me, ^nBu, ^tBu) and monoorganyltin(IV) halides $RSnCl_3$ (R = Ph, Me, ^nBu) in dichloromethane solution have been studied using variable-temperature ^{19}F and ^{119}Sn NMR spectroscopy. A number of hypervalent tin species are identified in solution including $[Ph_2SnF_3]^-$, $[Ph_2SnClF_2]^-$, and $[Ph_2SnCl_2F]^-$, which are stereochemically rigid on the NMR time scale at –100 °C but fluxional at about –80 °C. The fluoride in $[Ph_2SnCl_2F]^-$ and $[Ph_2SnClF_2]^-$ shows a smaller apicophilicity than the chloride. Addition of fluoride ion causes appreciable R group migration for R = Ph.

Introduction

The poor solubility of organylfluorostannanes has largely restricted their study to investigations of solid compounds. A common feature of this class of compounds in the solid state is coordination expansion of the tin atom which is achieved by fluoride bridges which in turn often results in formation of polymeric materials. For example, dimethyldifluorostannane is a sheetlike polymer[1] containing six-coordinate tin whereas trimethylfluorostannane is probably a chain type polymer[2] containing five-coordinate tin. The crystal structure determination of triphenylfluorostannane has only recently been reported[3] and indicates a polymeric chain. Solid-state ^{119}Sn NMR studies have confirmed five coordination for trimethylfluorostannane, as well as for triisobutylfluorostannane and triphenylfluorostannane.[4] Trimesitylfluorostannane is monomeric in the solid state and contains four-coordinate tin,[5] presumably because the bulky organyl substituent prevents fluoride bridging. Vibrational and ^{119}Sn Mössbauer spectroscopies imply that methyltrifluorostannane contains both bridging and terminal fluorides such that the tin is six-coordinate.[6]

The Lewis acidity of organylfluorostannanes is demonstrated by their reaction with additional fluoride ion to

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(1) Schlemper, E. O.; Hamilton, W. C. *Inorg. Chem.* **1966**, *5*, 995.
(2) Clark, H. C.; O'Brien, R. J.; Trotter, J. *J. Chem. Soc.* **1964**, 2332.
(3) Tudela, D., Gutiérrez-Puebla, E., Monge, A. *J. Chem. Soc., Dalton Trans.* **1992**, 1069.
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form species such as $K_2Et_2SnF_4$,[7] $(NH_4)_2Me_2SnF_4$, and $(NH_4)Me_2SnF_3$, which have been isolated in the solid state.[8] Definitive structural data for these adducts are not available, although recently the X-ray crystal structure of $(Et_4N)(Me_4Sn_2F_5)$ was reported[9] and shows linear, fluoride-bridged units resulting in six-coordinate tin.

Much less is known about the nature of halide adducts of organylfluorostannanes in solution, there being only few reports of NMR investigations based on triorganylfluorostannane derivatives.[10-13] A recent report has demonstrated the utility of the hypervalent species $[Ph_3SnF_2]^-$ as a fluorinating agent.[14] As part of an ongoing study[15-18] of the Lewis acidity of compounds of main group elements and of the stereochemistry of hypervalent species, we now report results of investigation of the interaction of fluoride ion with monoorganylchlorostannanes and diorganyldichlorostannanes in solution.

Experimental Section

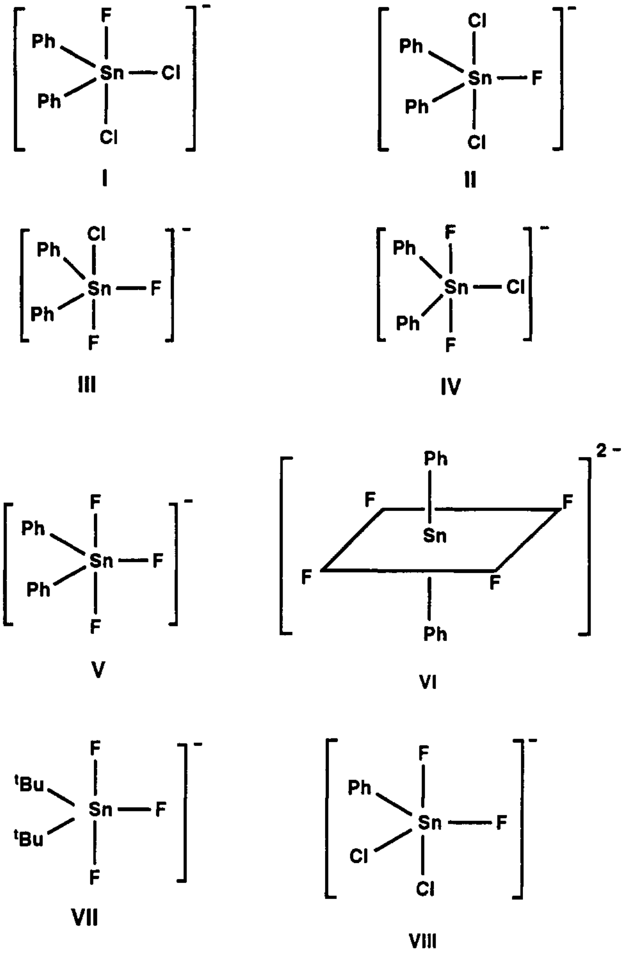
All tin-119 NMR spectra were recorded for sample solutions prepared from the appropriate molar ratios of tetrabutylammonium fluoride trihydrate ($Bu_4NF{\cdot}3H_2O$) and R_2SnCl_2 (R = Ph, Me ^{n}Bu, ^{t}Bu) or $RSnCl_3$ (R = Ph, Me, ^{n}Bu). Typically, the concentration of R_2SnCl_2 and $RSnCl_3$ was in the range 0.1–0.3 M. Solutions were diluted by a factor of 5–10 times to improve resolution of the ^{19}F spectra.

NMR spectra were recorded on a JEOL GX 270 spectrometer, ^{119}Sn at 100.75 MHz and ^{19}F at 254.19 MHz, using an external deuterium lock. Tin-119 chemical shifts were referenced against external Me_4Sn, and ^{19}F chemical shifts were referenced against external $CFCl_3$. Spectra generally were recorded with complete proton decoupling. Temperatures were maintained using a JEOL GVT3 temperature controller.

Results and Discussion

Reaction of Fluoride with Diorganyltin(IV) Dichlorides. No ^{119}Sn NMR resonance can be observed at room temperature for a dichloromethane solution containing equimolar quantities of fluoride ion and Ph_2SnCl_2 although the mixture is soluble. As the solution is cooled to −60 °C a broad ^{119}Sn singlet resonance appears near −250 ppm with further detail becoming apparent at −80 °C. At −100 °C the ^{119}Sn NMR spectrum comprises an intense singlet at −250 ppm, a doublet at −291 ppm [J(Sn–F) = 2360 Hz], a weak doublet at −269 ppm [J(Sn–F) = 2410 Hz], a triplet at −331 ppm [J(Sn–F) = 2370 Hz], and a weak singlet at −425 ppm. The singlet at −250 ppm is assigned as due to $[Ph_2SnCl_3]^-$,[16] while that at −425 ppm is attributed to $[Ph_2SnCl_4]^{2-}$. These latter assignments were subsequently confirmed by comparison with the ^{119}Sn NMR spectrum at −100 °C of a solution containing Ph_2SnCl_2 and chloride in the molar ratio 2:3 in which both $[Ph_2SnCl_3]^-$ and $[Ph_2SnCl_4]^{2-}$ singlets are observed simultaneously. Addition of further chloride causes the singlet due to $[Ph_2SnCl_3]^-$ to disappear. Somewhat curiously, the resonance for $[Ph_2SnCl_4]^{2-}$ cannot be observed in concentrated solutions (i.e., greater than about 25 mg/cm^3 of Ph_2SnCl_2). An earlier study[16] failed to detect $[Ph_2SnCl_4]^{2-}$ probably because the system was not studied at sufficiently low temperature.

Chart I



The chemical shift positions and multiplicities of the remaining ^{119}Sn resonances indicate that they arise from five-coordinate tin species which contain fluoride. The doublets at −291 and −269 ppm (relative intensity 4:1) are assigned to isomeric forms of $[Ph_2SnCl_2F]^-$ (structures I and II in Chart I). It was earlier shown that the ^{119}Sn chemical shift of five-coordinate trigonal bipyramidal tin complexes is influenced more by the groups occupying the equatorial positions than by the nature of groups occupying the apical positions.[18] A comparison of the $\delta(^{119}Sn)$ values for $[Ph_2SnCl_2F]^-$ with those for $[Ph_2SnCl_3]^-$ (−250 ppm) and $[Ph_2SnClF_2]^-$ (−331 ppm; see below) indicates that the ^{119}Sn resonance at −269 ppm could be assigned to isomer I and the resonance at −291 ppm to isomer II in Chart I. It is interesting to note that the concentration of these isomers is not the same but that isomer II dominates.

The triplet ^{119}Sn resonance at −331 ppm is assigned as due to $[Ph_2SnClF_2]^-$. In a more dilute solution the latter ^{119}Sn resonance remains a triplet down to −90 °C, but at −100 °C it resolves clearly into a doublet of doublets. The ^{19}F NMR spectrum of this solution at −100 °C contains two resonances each with $^{117/119}Sn$ satellites consistent with the two isomers of $[Ph_2SnCl_2F]^-$ described above (Table I). Also present are two equal intensity doublet resonances (J(F–F) = 15 Hz), each with $^{117/119}Sn$ satellites, and these resonances are assigned to $[Ph_2SnClF_2]^-$, which has the

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(16) Colton, R., Dakternieks, D. *Inorg. Chim. Acta* **1988**, *481*, 31.

(17) Colton, R., Dakternieks, D. *Inorg. Chim. Acta* **1988**, *143*, 151.

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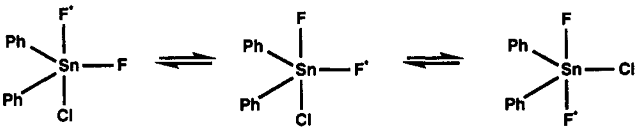
Table I. NMR Data for Species Formed from Reaction of Fluoride with Diphenyltin(IV) Dichloride or Phenyltin(IV) Trichloride in Dichloromethane Solution at -100 °C

species	$\delta(^{119}Sn)$, ppm	J(Sn–F), Hz	$\delta(^{19}F)$, ppm	J(F–F), Hz
$[Ph_2SnCl_3]^-$	-250			
$[Ph_2SnCl_4]^{2-}$	-425			
$[PhSnCl_4]^-$	-323			
$[PhSnCl_5]^{2-}$	-552			
$[Ph_2SnCl_2F]^-$	-291 (d)	2365	-139.7	
$[Ph_2SnCl_2F]^-$	-269 (d)	2410	-147.2	
$[Ph_2SnClF_2]^-$	-331 (d of d)	2420	-159.1 (d)	15
		2360	-159.7 (d)	15
$[Ph_2SnF_3]^-$	-402 (d of t)	2310 (d)	-173.8 (t)	28
		2250 (t)	-156.8 (d)	28
$[Ph_2SnCl_3F]^{2-}$	-464 (d)	2624	-140.3	
trans-$[Ph_2SnF_4]^{2-}$	-592 (quint)	2695	-125.0	
$[PhSnCl_2F_2]^-$	-503 (d of d)	2255	-79.4	
		2415	-55.6	
$[PhSnCl_3F_2]^{2-}$	-563 (d of d)	2560	-120.0 (d)	40
		1760	-74.0 (d)	40
trans-$[PhSnCl_4F]^{2-}$	-532 (d)	1825	-52.97	
$[PhSnF_5]^{2-}$	-692 (d of quint)	2430 (quint)	-140.0 (d)	20
		1180 (d)	-140.4 (quint)	20
$[SnF_6]^{2-\,a}$	-803 (sept)	1625	-152.6	

[a] Reference 21 quotes $\delta(^{119}Sn)$ -810 ppm at 30 °C.

Scheme I



static five-coordinate geometry shown in structure III. The inter- and intramolecular dynamics have been revealed by results of variable-temperature measurements of the ^{19}F spectra (Figure 1). As the temperature is raised, the two doublet resonances of $[Ph_2SnClF_2]^-$ broaden and coalesce near -60 °C. The two resonances for $[Ph_2SnCl_2F]^-$ also coalesce at -60 °C. Above -60 °C two broad singlet resonances appear and these sharpen with increasing temperature, and at -35 °C each resonance again has clear $^{117/119}Sn$ satellites. Above -20 °C both the resonances again broaden, and at 0 °C there is no longer evidence for tin–fluorine coupling. Adding about 30% ethanol to the mixture does not change the spectrum but allows study at higher temperature. At 45 °C the ^{19}F resonances for $[Ph_2SnCl_2F]^-$ and $[Ph_2SnClF_2]^-$ are extremely broad, and at 60 °C they coalesce indicating rapid intermolecular fluoride exchange between $[Ph_2SnCl_2F]^-$ and $[Ph_2SnClF_2]^-$.

These NMR spectral data are consistent with static trigonal bipyramidal geometries at -100 °C for both $[Ph_2SnCl_2F]^-$ and $[Ph_2SnClF_2]^-$. In the case of $[Ph_2SnCl_2F]^-$ there is evidence that both isomers I and II exist, while for $[Ph_2SnClF_2]^-$ only isomer III appears to exist at low temperature. Structures II and III are unusual in that electronegative fluorides would normally be expected to occupy axial positions.[20] At -60 °C both $[Ph_2SnCl_2F]^-$ and $[Ph_2SnClF_2]^-$ become fluxional, probably via a Berry pseudorotation mechanism. A single pseudorotation between structures I and II is sufficient to bring about equivalence of the axial and equatorial fluorines in $[Ph_2SnCl_2F]^-$. However, two such processes could operate to bring about equivalence of the axial and equatorial fluorines in $[Ph_2SnClF_2]^-$ (Scheme I). The rate of intermolecular fluoride exchange only becomes significant above about 45 °C.

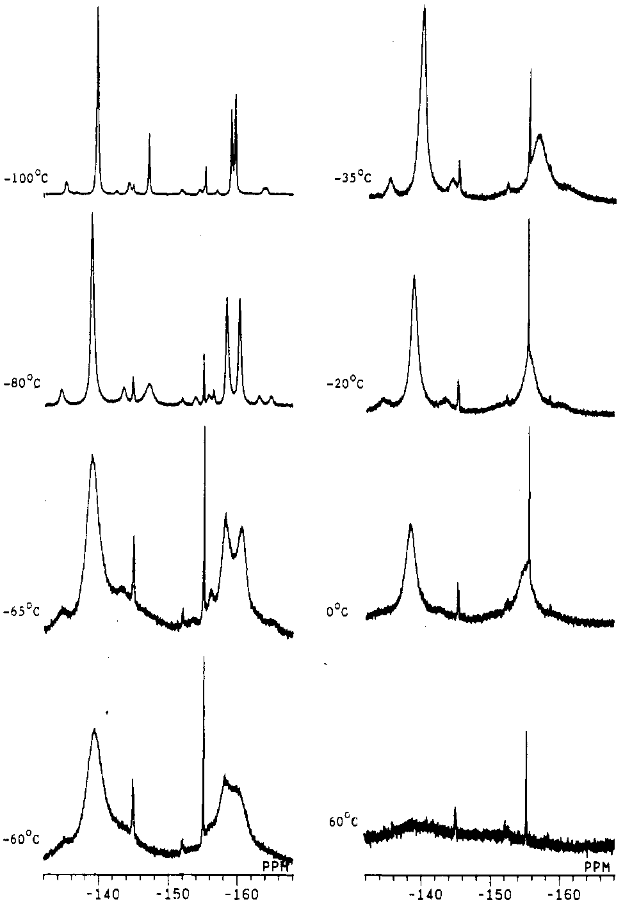


Figure 1. Portion of ^{19}F spectra indicating behavior of species $[Ph_2SnClF_2]^-$ and $[Ph_2SnCl_2F]^-$ at various temperatures.

Addition of a second mole equivalent of fluoride ion causes the ^{119}Sn NMR spectrum of the solution to change, and at -100 °C there are resonances consistent with the presence of $[Ph_2SnClF_2]^-$, $[Ph_2SnF_3]^-$, and $[Ph_2SnCl_4]^{2-}$. There is a singlet resonance at -250 ppm which could be either $[Ph_2SnCl_3]^-$ or $[Ph_3SnCl_2]^-$. There is also a doublet at -464 ppm (Table I), the origin of which is unclear, but on the basis of its chemical shift position, it may be due to one of the possible isomers of the six-coordinated species $[Ph_2SnCl_3F]^{2-}$. The ^{19}F NMR spectrum of this solution at -100 °C contains triplet and doublet resonances (J(F–F) = 28 Hz), indicating nonequivalent fluorine atoms consistent with the trigonal bipyramidal structure V for $[Ph_2SnF_3]^-$. Raising the temperature from -100 °C causes the ^{119}Sn doublet of triplets resonance of $[Ph_2SnF_3]^-$ to broaden, and at -80 °C the resonance appears as a quartet, which indicates the onset of intramolecular fluxionality.

The ^{119}Sn NMR spectrum after addition of a third mole equivalent of fluoride is simpler and indicates $[Ph_2SnF_3]^-$ is now the major tin species in solution. There are also weak ^{119}Sn resonances at chemical shift positions previously assigned to $[Ph_3SnClF]^-$[13] and $[Ph_3SnCl_2]^-$.[16] The singlet at -251 ppm was assigned as due to $[Ph_3SnCl_2]^-$ on the basis of the stoichiometry of the solution, even though the chemical shift position cannot distinguish it from $[Ph_2SnCl_3]^-$. More importantly, the appearance of these two minor species indicates phenyl group migration has occurred.

The ^{19}F NMR spectrum at -100 °C of a dichloromethane solution made by mixing Ph_2SnCl_2 and 3 mol equiv of fluoride clearly shows the expected doublet and triplet resonances corresponding respectively to axial and equatorial fluorides in $[Ph_2SnF_3]^-$ (structure V). As the tem-

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(20) Reference 19, however, does indicate that for hypervalent silicon compounds fluorine can be less apicophilic than chlorine.

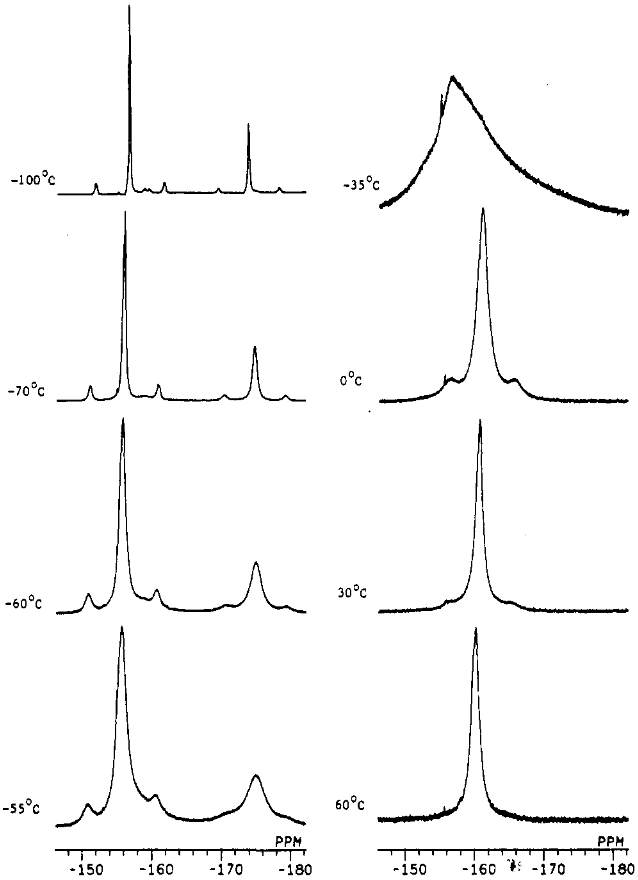
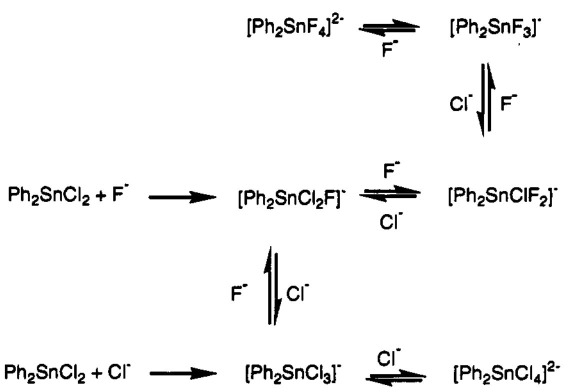


Figure 2. Portion of ^{19}F spectra indicating behavior of species $[Ph_2SnF_3]^-$ at various temperatures.

Scheme II



perature is raised the resonances broaden such that J(F–F) is no longer seen, although both resonances still clearly have $^{117/119}$Sn satellites (Figure 2). Both ^{19}F resonances are very broad at −55 °C, and at −45 °C they coalesce. At −35 °C there is a single broad ^{19}F resonance with no evidence of $^{117/119}$Sn satellites. At 0 °C the ^{19}F resonance begins to sharpen and $^{117/119}$Sn satellites are again apparent. Above 15 °C the $^{117/119}$Sn satellites broaden, and J(Sn–F) coupling is lost at 30 °C. These data are indicative of intramolecular exchange of axial and equatorial fluorine atoms followed by intermolecular fluoride exchange at higher temperature.

The ^{119}Sn spectrum of the above solution after the addition of a further 1 mol equiv of fluoride ion shows a weak resonance at the position assigned to $[Ph_3SnF_2]^-$ [10,13] and a much more intense resonance due to $[Ph_2SnF_3]^-$. Also present is a quintet resonance at −592 ppm, which is assigned to the six-coordinate species *trans*-$[Ph_2SnF_4]^{2-}$ (structure VI). The corresponding ^{19}F spectrum shows a singlet resonance (with $^{117/119}$Sn satellites) which confirms assignment to the *trans*-$[Ph_2SnF_4]^{2-}$ isomer. There is no evidence for the *cis*-$[Ph_2SnF_4]^{2-}$ isomer nor is there evidence for formation of any of the remaining possible six-coordinate species having the stoichiometry $[Ph_2SnCl_2F_2]^{2-}$ and $[Ph_2SnClF_3]^{2-}$. Addition of a fifth equivalent of fluoride to the above solution results in observation of *trans*-$[Ph_2SnF_4]^{2-}$ as the only diphenyltin-containing species in solution. The reactions of fluoride with Pn_2SnCl_2 are summarized in Scheme II.

Unlike Ph_2SnCl_2, addition of 1 mol equiv of fluoride to a dichloromethane solution of Me_2SnCl_2 results in considerable precipitation and no ^{119}Sn NMR signals were observed for the temperature range +25 to −100 °C. The situation is unchanged on the addition of a second mole equivalent of fluoride. However, on the addition of a third mole equivalent of fluoride the precipitate dissolves and a broad quintet resonance ($w_{1/2}$ approximately 100 Hz) at −390 ppm is observed at −100 °C, which is consistent with formation of *trans*-$[Me_2SnF_4]^{2-}$. The quintet broadens as the temperature is increased and coalesces at −80 °C. The solution is completely clear after addition of the fourth mole equivalent of fluoride, but the ^{119}Sn quintet resonance remains broad at temperatures down to −110 °C. The ^{19}F NMR spectra of all of these solutions are broad and could not be clearly assigned. Similarly the addition of fluoride to $^nBu_2SnCl_2$ is accompanied by extensive precipitation and the only ^{119}Sn resonances observed are for the 1:1 solution and comprise a broad singlet at −112 ppm due to $[^nBu_2SnCl_3]^-$ and a broad doublet at −150 ppm, J(Sn–F) = 2600 Hz, possibly arising from formation of $[^nBu_2SnCl_2F]^-$. No ^{119}Sn resonances could be detected for other fluoride to $^nBu_2SnCl_2$ ratios.

Interestingly, addition of fluoride to $^tBu_2SnCl_2$ does not cause precipitation and a 1:1 solution in dichloromethane is clear. The ^{119}Sn NMR spectrum of this solution at −100 °C contains resonances consistent with formation of $[^tBu_2SnCl_3]^-$, $[^tBu_2SnCl_2F]^-$, and $[^tBu_2SnClF_2]^-$. The solution remains clear after the addition of a second mole equivalent of fluoride, and the ^{119}Sn NMR spectrum then shows only the triplet resonance due to $[^tBu_2SnClF_2]^-$. The ^{19}F resonances for $[^tBu_2SnCl_2F]^-$ and $[^tBu_2SnClF_2]^-$ could not be unequivocably assigned because the resonances were broad in dichloromethane. However, in acetone solution the ^{19}F resonances were sharper and assignments were made on the basis of the magnitude of the J(Sn–F) coupling (Table II). There was no clear evidence for J(F–F) coupling of the resonance attributed to $[^tBu_2SnClF_2]^-$, which might result either from poor resolution of a small J(F–F) value or from the fact that $[^tBu_2SnClF_2]^-$ may still be fluxional at −100 °C.

The ^{119}Sn NMR spectrum after addition of a third mole equivalent of fluoride shows the resonance due to $[^tBu_2SnClF_2]^-$ and an apparent quartet which is assigned to $[^tBu_2SnF_3]^-$ (Table II). Adding a fourth equivalent of fluoride leaves the ^{119}Sn NMR spectrum with only the quartet resonance of $[^tBu_2SnF_3]^-$. The ^{19}F spectrum of this solution at −100 °C shows two resonances (relative intensity 2:1) each with $^{117/119}$Sn satellites which is consistent with the static trigonal bipyramidal geometry shown in VII. No J(F–F) could be resolved. Two ^{19}F resonances broaden with increasing temperature and coalesce at about −60 °C. The resonance does not sharpen with increasing temperature, which indicates the presence of rapid intermolecular fluoride exchange. The similarity of coupling between axial and equatorial fluorine-to-tin coupling seen in the ^{19}F NMR spectrum indicates that the apparent quartet seen in the corresponding ^{119}Sn NMR spectrum could in fact

Table II. NMR Data for Species Formed from Reaction of Fluoride with Diorganyltin(IV) Dichlorides or Organyltin(IV) Trichloride in Dichloromethane Solution at −100 °C

species	$\delta(^{119}\mathrm{Sn})$, ppm	J(Sn–F), Hz	$\delta(^{19}\mathrm{F})$, ppm	J(F–F), Hz
$[{}^t\mathrm{Bu_2SnCl_3}]^-$	−143			
$[{}^t\mathrm{Bu_2SnCl_2F}]^-$	−202 (d)	2625	−141.9[a]	
$[{}^t\mathrm{Bu_2SnClF_2}]^-$	−279 (t)	2690	−161.3[a]	
$[{}^t\mathrm{Bu_2SnF_3}]^-$	−350 (quart)	2720	−153.2[b]	
			−181.2[c]	
$[\mathrm{Bu_2SnCl_3}]^-$	−112			
$[\mathrm{BuSnCl_4}]^-$	−255			
$[\mathrm{BuSnCl_5}]^{2-}$	−485			
$[\mathrm{Bu_2SnCl_2F}]^-$	−150 (d)	2600	−167.0	
$[\mathrm{MeSnCl_4}]^-$	−252			
$[\mathrm{MeSnCl_5}]^{2-}$	−505			
$[\mathrm{MeSnF_5}]^{2-}$	−616 (d of quint)	1160 (d)	−136.4 (quint)	15
		2595 (quint)	−125.5 (d)	15
trans-$[\mathrm{Me_2SnF_4}]^{2-}$	−390 (quint)	2260		
trans-$[\mathrm{MeSnCl_4F}]^{2-}$	−490 (d)	1750	−54.8	
$[\mathrm{MeSnCl_3F_2}]^{2-}$	−512 (d of d)	2690	−103.8	
		1655	−79.0	
trans-$[\mathrm{BuSnCl_4F}]^{2-}$	−479 (d)	1750	−58.8	
mer-$[\mathrm{BuSnCl_3F_2}]^{2-}$	−500 (d of d)	2880	−113.7 (d)	32
		1660	−75.2 (d)	32
$[\mathrm{BuSnF_5}]^{2-}$	−635 (d of quint)	2840 (quint)	−132.9 (d)	6
		1180 (d)	−136.0 (quint)	6

[a] Measured in acetone solution at −100 °C. [b] J(Sn–F) = 2735 Hz measured from ^{19}F spectrum. [c] J(Sn–F) = 2560 Hz measured from ^{19}F spectrum.

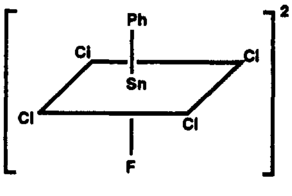
be a poorly resolved doublet of triplets. Attempts at isolation of pure, crystalline samples containing $[{}^t\mathrm{Bu_2SnF_3}]^-$ have so far been unsuccessful.

Reaction of Fluoride with Organyltin(IV) Trichlorides. The ^{119}Sn NMR spectrum at −60 °C of a dichloromethane solution prepared by mixing 1:1 molar equivalents of fluoride and $\mathrm{PhSnCl_3}$ contains considerable amounts of precipitate but shows two intense singlet resonances at −248 and −550 ppm which have previously been assigned to $[\mathrm{Ph_2SnCl_3}]^-$ and $[\mathrm{PhSnCl_5}]^{2-}$, respectively.[16,17] There is an additional broad singlet resonance at −323 ppm which arises from $[\mathrm{PhSnCl_4}]^-$[17] and a weak doublet of doublets at −503 ppm (J(Sn–F) = 2415, 2255 Hz) tentatively assigned as due to $[\mathrm{PhSnCl_2F_2}]^-$, which has structure VIII. The corresponding ^{19}F resonances (Table I) show no J(F–F) coupling.

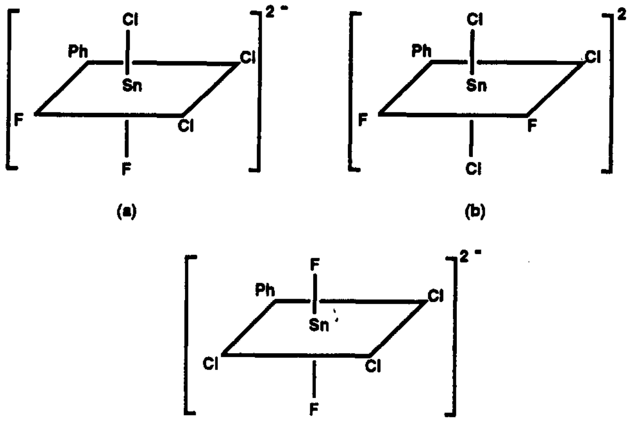
Addition of a second mole equivalent of fluoride results in the appearance of a singlet at −425 ppm due to $[\mathrm{Ph_2SnCl_4}]^{2-}$. There is also an intense doublet at −532 ppm, which is assigned to *trans*-$[\mathrm{PhSnCl_4F}]^{2-}$ (structure IX in Chart II), and a weak doublet of doublets at −563 ppm, which may be assigned to an isomer of $[\mathrm{PhSnCl_3F_2}]^{2-}$ (structure X). At −100 °C the resonances are unchanged with the exception that the singlet at −425 ppm has sharpened considerably. Apparently the equilibrium is effected by precipitation of insoluble fluoride complexes of tin thus leaving a higher chloride-to-tin ratio in solution which leads to the formation of the more soluble chloride complexes observed.

The ^{119}Sn NMR spectrum at −100 °C after addition of a third equivalent of further fluoride shows an intense singlet at −425 ppm, a doublet of quintets assigned to $[\mathrm{PhSnF_5}]^{2-}$ and a septet at the chemical shift position previously assigned to $[\mathrm{SnF_6}]^{2-}$,[21] as well as weak resonances for species already described above.

Chart II



IX



(a) (b)

(c)

X

Addition of a fourth mole equivalent of fluoride moves the equilibrium towards formation of fluoride-rich species. After addition of 6 mol equiv of fluoride there is no longer evidence for tin species containing chloride and the only species seen in the ^{119}Sn NMR spectrum are $[\mathrm{Ph_2SnF_3}]^-$, *trans*-$[\mathrm{Ph_2SnF_4}]^{2-}$, $[\mathrm{PhSnF_5}]^{2-}$, and $[\mathrm{SnF_6}]^{2-}$. Clearly, phenyl group migration has taken place. Phenyl group migration at room temperature has previously been observed for the reaction $[\mathrm{SnCl_6}]^{2-} + \mathrm{Ph_2SnCl_2} \rightleftharpoons [\mathrm{PhSnCl_4}]^-$ and for the reaction $\mathrm{PhSnCl_3} + \mathrm{PBu_3} \rightleftharpoons \mathrm{SnCl_4(PBu_3)_2} + \mathrm{Ph_2SnCl_2(PBu_3)}$.[17] Phenyl group migration is usually associated with high temperature, and indeed reactions between various stoichiometries of $\mathrm{SnX_4}$ and $\mathrm{Ph_4Sn}$ are used synthetically to yield the series $\mathrm{Ph}_n\mathrm{SnX}_{3-n}$.

The ^{119}Sn NMR spectrum of a solution made by mixing an equimolar ratio of fluoride to $\mathrm{MeSnCl_3}$ contains two singlet resonances (−252 and −505 ppm) which are attributed to $[\mathrm{MeSnCl_4}]^-$ and $[\mathrm{MeSnCl_5}]^{2-}$, respectively. Addition of a second mole equivalent of fluoride gives rise to a ^{119}Sn NMR spectrum which contains a doublet resonance, attributed to *trans*-$[\mathrm{MeSnCl_4F}]^{2-}$, and a doublet of doublets, assigned to $[\mathrm{MeSnCl_3F_2}]^{2-}$. The solution becomes clear after the addition of a third equivalent of fluoride, but no ^{119}Sn NMR signal could be detected for this solution or for a solution which contains 4 mol equiv of fluoride. The solution is still clear after addition of a fifth mole equivalent of fluoride, and the ^{119}Sn NMR spectrum now contains only a doublet of quintets which is assigned to $[\mathrm{MeSnF_5}]^{2-}$. Very similar results are obtained when $\mathrm{MeSnCl_3}$ is replaced by $\mathrm{BuSnCl_3}$. NMR details are summarized in Table II.

Summary

Addition of fluoride ion to diorganyltin(IV) dichloride or monoorganyltin(IV) trichloride leads to formation of several series of hypervalent tin complexes in solution. From these often complex mixtures, a variety of intra- and intermolecular processes can be defined. The diorganyltin(IV) precursors have lower Lewis acidity than the monoorganyltin(IV) compounds so that five-coordinate and six-coordinate species, respectively, dominate the two series. There is clear evidence that the fluorides in

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(21) Dillon, K. B.; Marshall, A. *J. Chem. Soc., Dalton Trans.* 1984, 1245.

$[Ph_2SnCl_2F]^-$ and $[Ph_2SnClF_2]^-$ have a lower apicophility than the chloride.

Addition of fluoride to Ph_2SnCl_2 or $PhSnCl_2$ causes phenyl group migration. The degree of phenyl group migration is larger for the monoorganyltin(IV) precursors. Interestingly, addition of other Lewis bases such as chloride on bromide ion or triorganylphosphine oxide does not promote such migration.

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Nature of the Stabilization of a Carbenium Ion Adjacent to Two Organometallic Groups. $[Mo_2Cp_2(CO)_4(\mu\text{-}FcCHC{\equiv}C(CH_2)_2CH_3)]^+BF_4^-$: X-ray Structure and NMR Dynamic Investigation

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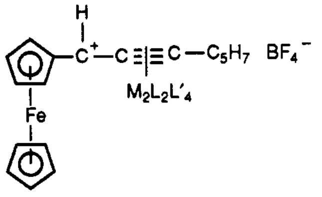
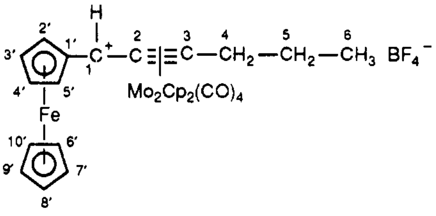
A variable-temperature ^{13}C NMR investigation in solution, complemented with a CPMAS experiment in the solid state, was performed on $[Mo_2Cp_2(CO)_4(\mu\text{-}FcCHC{\equiv}C(CH_2)_2CH_3)]^+BF_4^-$ (**1c**). In solution, the NMR spectra are highly temperature dependent. We describe fluxional behavior of this carbenium ion simultaneously adjacent to two organometallic groups; ferrocenyl and acetylenic dimolybdenum cluster. In addition, the X-ray structure of the complex **1c** was determined. This compound crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and cell dimensions $a = 7.972$ (2) Å, $b = 27.221$ (4) Å, and $c = 15.285$ (3) Å; the structure was refined to R and R_w values of 4.1 and 4.5, respectively, with the use of 2711 reflections. We demonstrate that the dimolybdenum cluster is mainly involved in the stabilization of the positive charge. The fluxional behavior together with molecular structure data shows an uncommon role of the ferrocenyl group in its interaction with the carbenium ion.

Introduction

We have previously described[1] the synthesis of carbenium ions **1a** and **1b** where the carbon atom bearing the positive charge is simultaneously adjacent to a ferrocenyl group and an acetylenic C_2M_2 cluster. Primary NMR studies have provided some evidence about the nonfluxionality of the cobalt species **1a** and on the contrary the fluxionality of the cation **1b** at room temperature, in solution. We had interpreted the behavior of **1b** as a competition between the two organometallic groups $FeCp_2$ and $C_2M_2L_6$ in stabilizing the C^+. In such a case, the stabilization mode of C^+ is not so easy to display. On the basis of our knowledge about structural properties and fluxionality for carbenium ions adjacent to the one organometallic group $C_2Mo_2Cp_2(CO)_4$, we will discuss the stabilization mode for **1c**. A variable-temperature NMR investigation, in solution, completed with a CPMAS and the molecular structure, in the solid state, has been performed on **1c** to explain the stabilization and dynamical behavior of this intricate carbenium ion.



1a: M = Co, L = L′ = CO
1b: M = Mo, L = Cp, L′ = CO



1c

Results

Description of the Structure. The X-ray crystal structure of $[Mo_2Cp_2(CO)_4(\mu\text{-}FcCHC{\equiv}C(CH_2)_2CH_3)]^+BF_4^-$ has been determined. The asymmetric unit consists of four discrete cations $[Mo_2Cp_2(CO)_4(\mu\text{-}FcCHC{\equiv}C(CH_2)_2CH_3)]^+$ and four BF_4^- anions. A solvent molecule, CH_2Cl_2, is enclosed in the unit cell, but has no direct interaction with

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