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Synthesis and properties of trifluoromethylated stannanes. The formation and NMR spectra of the difluoromethylstannanes $(CF_3)_n(CF_2H)_mSn(CH_3)_{4-n-m}$

R. Eujen, N. Jahn and U. Thurmann

FB 9, Universität-GH Wuppertal, D-42097 Wuppertal (Germany)

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Abstract

Difluoromethylstannanes have been obtained by hydrogenation of $(CF_3)_4Sn$ with the hydrides $(CH_3)_3MH$ (M = Sn, Ge). The reaction is shown to proceed via attack of the hydride on the tin atom; transfer of fluoride from the CF_3 group to the MMe_3 group along with elimination of CF_2 yields the unstable $(CF_3)_3SnH$. Difluorocarbene is inserted quantitatively into Sn–H bonds, thus forming both Me_3SnCF_2H and $(CF_3)_3SnCF_2H$. The latter is subject to further formal replacements of CF_3 by CF_2H groups, finally yielding $Sn(CF_2H)_4$. For M = Sn, further methyl/trifluoromethyl exchanges lead to a variety of methyl-containing species, $(CF_3)_n(CF_2H)_mSnMe_{4-n-m}$. For M = Ge, insertion of CF_2 into the Ge–H bond is not observed; the lower reactivity of $GeMe_3H$ towards CF_2 is demonstrated independently by its reaction with such CF_2 sources as CF_3SiF_3 and $CF_2Br_2/C_2(NMe_2)_4$; trimethylgermyltin derivatives, $(CF_3)_n(CF_2H)_mSnGeMe_3$, are formed, with evolution of CF_2H_2. The compounds have been identified by their characteristic NMR spectra. Owing to Lewis acid/base interactions NMR chemical shifts and coupling constants are very sensitive to the choice of solvent. Linear correlations between the $^2J(SnF)$ couplings of CF_3 and CF_2H groups and between $^1J(SnC)$ and $^2J(SnF)$ are found.

Key words: Tin; Difluoromethyl; Group 14; Fluorine

1. Introduction

The properties of trifluoromethylated compounds such as $(CF_3)_4Ge$ or $(CF_3)_4Sn$ [1] are largely determined by the pseudohalide character of the CF_3 group. Its high electronegativity results in a high Lewis acidity of the central atom, though the bulk and the hardness of the fluorine sphere may oppose the tendency towards complex formation [2]. Compared with a halide, the CF_3 group is less sensitive towards replacement by nucleophiles. Whereas hydroxide cleaves the M–CF_3 bond quantitatively with formation of HCF_3, decomposition with less nucleophilic donors is slow, *e.g.* adducts of $(CF_3)_4Ge$ with NH_3 have been isolated [3]. The displacement of a CF_3 group, however, may proceed via a rather complex reaction mechanism; *e.g.*, the removal of a CF_3 group of $(CF_3)_4Sn$ with HI involves a carbene mechanism, HCF_2I being the final elimination product [4]. With hard hydrides such as $LiAlH_4$ complete destruction of the CF_3–Sn unit is observed even below −40°C, whereas with the milder hydride Bu_3SnH the halogens of $(CF_3)_nSnX_{4-n}$ are displaced selectively with formation of the corresponding trifluoromethyltin hydrides [5]. In this paper we report the formation of difluoromethylstannanes by attack of metal hydrides on trifluoromethylstannanes.

2. Results and discussion

The highly electrophilic character of the tin atom in $(CF_3)_4Sn$ implies that it will interact even with very weak nucleophiles. Such interactions can lead to complex formation or even cause displacement of the CF_3 group. The nucleophilicity of the methyl group in $SnMe_4$ is so high that a slow exchange of methyl and

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Correspondence to: Prof. Dr. R. Eujen.

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trifluoromethyl groups is observed even below room temperature [5]:

$$(CF_3)_4Sn + SnMe_4 \longrightarrow (CF_3)_3SnMe + CF_3SnMe_3 \quad (1)$$

This reaction is suitable for the preparation of $(CF_3)_3SnMe$, which owing to the reduced electrophilicity of the tin atom, exchanges much more slowly than $(CF_3)_4Sn$. The amount of CF_3SnMe_3 formed, however, is lower than expected, which is explained by competitive fluoride abstraction and precipitation of $SnMe_3F$, eqn. (2a). In absence of a CF_2 trap the eliminated difluorocarbene forms C_2F_4 and c-C_3F_6 (eqn. (2b)) (c = *cyclo*):

$$(CF_3)_4Sn + SnMe_4 \longrightarrow (CF_3)_3SnMe + SnMe_3F + \{CF_2\} \quad (2a)$$

$$(n+m)\{CF_2\} \longrightarrow n/2C_2F_4 + m/3c\text{-}C_3F_6 \quad (2b)$$

On the other hand the much stronger nucleophile $SnMe_3H$ reacts vigorously. When a mixture of $(CF_3)_4Sn$ with an excess of $SnMe_3H$ is allowed to warm from −196°C to ambient temperature, almost complete destruction of the CF_3Sn moieties takes place. If a 1:1 molar ratio is used, however, the reaction proceeds more smoothly, and after separation from the nonvolatile material ($SnMe_3F$ and some mixed methyl(trifluoromethyl)tin fluorides) the components of the complex mixture can be identified by NMR spectroscopy. A typical final product mixture contained, along with traces of other compounds containing CF_2H–Sn (Table 1), the compounds

$(CF_3)_3SnMe$	47%	$(CF_3)_2(CF_2H)SnMe$	9%
$(CF_3)_2SnMe_2$	9%	$(CF_3)(CF_2H)_2SnMe$	1.5%
$(CF_3)SnMe_3$	17%	$(CF_3)(CF_2H)SnMe_2$	18%

In principle, the distribution reflects a competition between methyl transfer, eqns. (1) and (2a), and a formal hydrogenation of a CF_3 group, eqn. (3):

$$(CF_3)_nSnMe_{4-n} + mSnMe_3H \longrightarrow (CF_3)_{n-m}(CF_2H)_mSnMe_{4-n} + mSnMe_3F \quad (3)$$

The typical CF_2 oligomerization products, tetrafluoroethylene and c-C_3F_6, are not formed. Instead, after a short reaction time a large amount of $(CF_2H)SnMe_3$ is observed, but upon prolonged standing at ambient temperature this disappears completely. The high efficiency of $SnMe_3H$ as a CF_2 trap was independently demonstrated by reaction with the CF_2 precursor systems CF_3SiF_3 [6] and $CF_2Br_2/(Me_2N)_2C{=}C(NMe_2)_2$ [7] which both yield $(CF_2H)SnMe_3$ along with some CF_3SnMe_3.

$$CF_3SiF_3 \xrightarrow{100°C} \{CF_2\} + SiF_4 \quad (4a)$$

$$CF_2Br_2 + (Me_2N)_2C{=}C(NMe_2)_2 \xrightarrow{20°C} \{CF_2\} + [(Me_2N)_2C{=}C(NMe_2)_2]^{2+} + 2Br^- \quad (4b)$$

$$H\text{-}SnMe_3 + \{CF_2\} \longrightarrow (CF_2H)SnMe_3 \quad (4c)$$

The reactivity of the Sn–H bond clearly contrasts with that of the Si–H bond; *e.g.* CF_2 does not react with $SiMe_3H$ [6]. The corresponding germane $GeMe_3H$

TABLE 1. NMR data [a] for the compounds $(CF_3)_n(CF_2H)_mSn(CH_3)_{4-n-m}$, observed in the reaction of $(CF_3)_4Sn$ with $SnMe_3H$

	$\delta(^{19}F)$		$\delta(^{1}H)$		$\delta(^{119}Sn)$	$2J$(SnF) [b]		^2J(HF) (CF_2H)	^4J(FF) (CF_3/CF_2H)
	(CF_3)	(CF_2H)	(CH_3)	CF_2H)		(CF_3)	(CF_2H)		
$(CF_3)_4Sn$	−38.7	–	–	–	−350.1	542/518	–	–	–
$(CF_3)_3SnMe$	−42.4	–	1.03	–	−182.1	441/422	–	–	–
$(CF_3)_2SnMe_2$	−46.4	–	0.69	–	−57.9	348/333	–	–	–
CF_3SnMe_3	−49.1	–	0.35	–	+8.5	266/254	–	–	–
$(CF_3)_3(CF_2H)Sn$	−39.0 (t)	−113.8 (dct)	–		[c]	468/447	486/464	44.3	2.2
$(CF_3)_2(CF_2H)_2Sn$	−39.2 (qt)	−115.5 (spt)	–		[c]	412/394	429/410	44.3	2.4
$(CF_3)(CF_2H)_3Sn$	−39.3 (spt)	−116.9 (qt)	–		[c]	[c]	385/368	44.4	2.4
$(CF_3)_2(CF_2H)SnMe$	−42.5 (t)	−120.3 (spt)	0.90	6.69	−177.9	389/372	389/373	44.6	2.6
$(CF_3)(CF_2H)_2SnMe$	−42.7 (qt)	−121.1 (q)	[c]	6.65	[c]	353/337	351/335	44.8	2.5
$(CF_2H)_3SnMe$	–	−121.6 (s)	[c]	6.65	[c]	–	315/301	45.0	–
$(CF_3)(CF_2H)SnMe_2$	−46.1 (t)	−124.4 (q)	0.57	6.52	−282.2	305/292	317/303	44.7	2.7
$(CF_2H)SnMe_3$	–	−125.5 (s)	0.24	6.33	−14.2	–	256/245	45.2	–
$(CF_3)_3SnH$ [d,e]	−40.5	–	–	–	−309.8 [g]	456/436	–	–	–
$(CF_3)_2(CF_2H)SnH$ [d,f]	−40.1 (t)	−117.4 (spt)	–	[c]	[c]	400/382	405/385	44.6	2.6

[a] Chemical shifts in ppm with reference to external $CFCl_3$, TMS, and $Sn(CH_3)_4$, without solvent; coupling constants in Hz; multiplicities from proton-decoupled spectra: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, spt = septet; dct = dectet. [b] $^2J(SnF) \triangleq {}^2J(^{119}SnF/^{117}SnF)$. [c] Not observed. [d] Observed among the volatile material after short reaction at −30°C. [e] $^3J(F_3CSnH)$ 8.3 Hz. [f] $^3J(F_3CSnH)$ 7.5 Hz; $^3J(F_2CSnH)$ 10.0 Hz. [g] Ref. 5.

shows an intermediate reactivity; thus reaction with CF_3SiF_3 yields a complex mixture that contains considerable amounts of CF_3GeMe_3, $(CF_2H)SiF_3$, C_2F_4 and its hydrogermylation product $HCF_2CF_2GeMe_3$, in addition to $(CF_2H)GeMe_3$. The outstanding ability of the Sn–H bond to trap CF_2 was furthermore demonstrated by addition of cyclohexene, which adds CF_2 very efficiently to give 7,7-difluoronorcarane. With the system $(CF_3)_4Sn/GeMe_3H/c\text{-}C_6H_{10}$, the formation of the $Sn\text{–}CF_2H$ derivatives was unaffected; 7,7-difluoronorcarane was observed only at temperatures of 120°C or above, when extensive decomposition of the $Sn\text{–}CF_3$ moieties takes place. Furthermore, the competitive formation of a $(CF_2H)Ge$ unit by insertion of CF_2 into the Ge–H bond was not observed at all.

The CH_3/CF_3 exchange reaction (eqn. (1)) of $SnMe_3H$ with $(CF_3)_4Sn$ would lead to CF_3SnMe_2H. While the latter hydride, which had been prepared by another route, is known to be a stable compound [8], it was not detected in the reaction mixture at any time. In principle, insertion of CF_2 into the Sn–H bond of CF_3SnMe_2H might account for the relatively large amount of $(CF_3)(CF_2H)SnMe_2$ produced, but it seems more likely that the latter is the result of CF_3/CH_3 exchange between $(CF_3)_4Sn$ and $(CF_2H)SnMe_3$, a product which is known to be formed but later consumed during the course of the reaction.

Evidence for the reaction pathway can be gained (a) by reducing the reactivity of the central atom; *e.g.* by using the corresponding germane $(CF_3)_4Ge$, (b) by reducing the nucleophilicity of the hydride, and (c) by carrying out the reaction under kinetic control at low temperature. Indeed, the more sterically-shielded $(CF_3)_4Ge$ is much less reactive towards $SnMe_3H$, and no CH_3/CF_3 exchange occurs at all. After one hour at 50°C less than 5% of the starting material is consumed, and the distribution of product is well reflected by eqn. (5):

$$(CF_3)_4Ge + 2Me_3SnH \xrightarrow{1\text{ h, }50°C} (CF_3)_3GeH + (CF_2H)SnMe_3 + SnMe_3F \quad (5)$$

The reaction of $(CF_3)_4Sn$ with the milder hydrogenation source $GeMe_3H$ proceeds slowly at room temperature but, it is complete within 100 min at 60°C. The methylation corresponding to eqn. (1) plays only a minor role, CF_3GeMe_3 being the only detectable CF_3Ge derivative (5% yield). The main reaction is now hydrogenation at the CF_3 group, eqn. (3), yielding compounds $(CF_3)_n(CF_2H)_{4-n}Sn$ ($n = 0\text{–}3$). Trimethylgermane is mainly converted into $GeMe_3F$ which is the major volatile product. The typical difluorocarbene elimination products C_2F_4, $c\text{-}C_3F_6$ or $(CF_2H)GeMe_3$ are not observed. In addition, the ^{19}F NMR spectra reveal the presence of another series of compounds, the much less volatile $(CF_3)_n(CF_2H)_{3-n}SnR$, for which the chemical shifts and especially the coupling constants are indicative of the presence of a strongly electron-donating group R. Comparison of the data with independently prepared $(CF_3)_3SnGeMe_3$ suggests that R is $GeMe_3$. Their formation can be explained by the displacement of a CF_2H group as CF_2H_2, which is evolved in an approximately equimolar amount, followed by addition of a $GeMe_3$ moiety to tin (eqn. (6)):

$$(CF_3)_n(CF_2H)_{4-n}Sn + GeMe_3H \longrightarrow (CF_3)_n(CF_2H)_{3-n}SnGeMe_3 + CF_2H_2 \quad (6)$$

TABLE 2. ^{19}F, ^1H and ^{119}Sn NMR data [a] for the compounds $(CF_3)_n(CF_2H)_mSnR_{4-n-m}$ (R = Me, $GeMe_3$), observed in the reaction of $(CF_3)_4Sn$ with $GeMe_3H$

	$\delta(^{19}F)$		$\delta(^1H)$ (CF_2H)	$\delta(^{119}Sn)$	$^2J(SnF)$ [b]		$^2J(SnH)$ (CF_2H)	$^2J(FH)$ (CF_2H)	$^4J(FF)$ (CF_3/CF_2H)
	(CF_3)	(CF_2H)			(CF_3)	(CF_2H)			
$(CF_3)_4Sn$ [d]	−48.5	–	–	−498.0	518/495	–	–	–	–
$(CF_3)_3(CF_2H)Sn$ [d]	−46.3 (t)	−119.8 (dzt)	6.46	−443.7	417/398	557/532	215.8/206.2	45.6	2.7
$(CF_3)_2(CF_2H)_2Sn$ [d]	−44.5 (qt)	−119.9 (spt)	6.49	−402.3	314/300	468/447	189.4/181.1	45.6	2.7
$(CF_3)(CF_2H)_3Sn$ [d]	−43.3 (spt)	−120.4 (q)	6.52	−367.0	258/247	392/375	159.0/152.5	45.5	2.5
$(CF_2H)_4Sn$ [d]	–	−120.9 (s) [e]	6.53	−337.3	–	325/310	[c]	45.5	2.2
$(CF_3)_3SnMe$ [d]	−46.8	–	–	[c]	403/385	–	[c]	–	–
$(CF_3)_3SnGeMe_3$	−42.6	–	–	[c]	305/291	–	–	–	–
$(CF_3)_2(CF_2H)SnGeMe_3$	−41.7 (t)	−119.0 (spt)	[c]	[c]	257/246	[c]	[c]	45.3	3.0
$(CF_3)(CF_2H)_2SnGeMe_3$	−40.7 (qt)	−119.1 (q)	[c]	[c]	222/212	305/291	[c]	45.4	2.9
$(CF_2H)_3SnGeMe_3$	–	−119.1 (t)	[c]	[c]	–	281/268	[c]	45.8	–

[a] See Table 1. [b] $^nJ(SnE) \triangleq {}^nJ(^{119}SnE/^{117}SnE)$. [c] Not observed. [d] In THF-d_8. [e] Appears as pseudo-triplet with $^4J(CF_2H/CF_2H) = 2.2$ Hz, see text.

A typical product distribution for the tin-containing material as determined by their ^{19}F NMR spectra (Table 2) was:

$(CF_3)_4Sn$	10%	$(CF_3)_3SnMe$	2%
$(CF_3)_3(CF_2H)Sn$	18%	$(CF_3)SnMe_3$	4%
$(CF_3)_2(CF_2H)_2Sn$	15%	$(CF_3)_2(CF_2H)SnGeMe_3$	11%
$(CF_3)(CF_2H)_3Sn$	13%	$(CF_3)(CF_2H)_2SnGeMe_3$	16%
$(CF_2H)_4Sn$	6%	$(CF_2H)_3SnGeMe_3$	5%

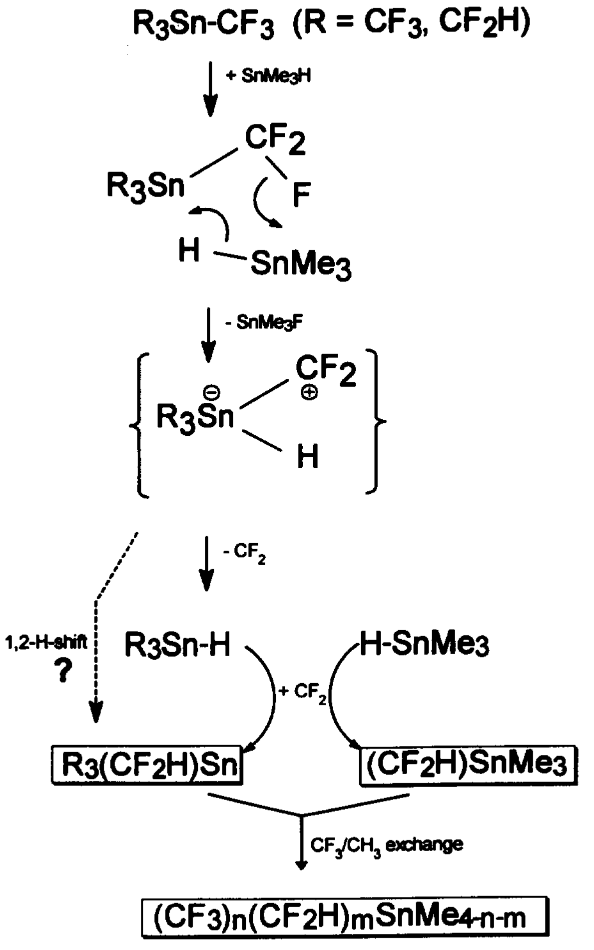
With the even less reactive silane $SiMe_3H$ no reaction takes place below 60°C. At higher temperatures, there is extensive decomposition of $(CF_3)_4Sn$, and among the volatile decomposition products small amounts of $SiMe_3F$ and $(CF_3)_3(CF_2H)Sn$ are clearly discernible.

When the reaction of $(CF_3)_4Sn$ with $SnMe_3H$ was carried out at -30°C, the initial formation of $(CF_3)_3$-SnH was confirmed by gas phase IR spectroscopy, its ν(SnH) band at 1946 cm^{-1} being characteristic [5]. If the volatile material is removed after 20 min at -30°C, the following product distribution is observed for the fluorine-containing material:

$(CF_3)_4Sn$	14%	$(CF_3)_3SnMe$	11%
$(CF_3)_3(CF_2H)Sn$	11%	$(CF_3)_2(CF_2H)SnMe$	2%
$(CF_3)_2(CF_2H)_2Sn$	4%	$(CF_3)(CF_2H)SnMe_2$	3%
$(CF_3)(CF_2H)_3Sn$	1%	$(CF_2H)SnMe_3$	23%
$(CF_3)_3SnH$	20%	$(CF_3)_2(CF_2H)SnH$	5%

After one hour at ambient temperature the Sn–H functional compounds have disappeared.

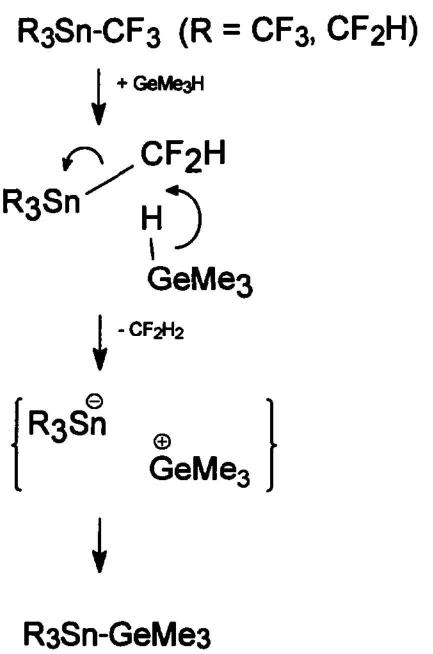
In principle, the formation of a difluoromethyl group could be explained by S_N2 displacement of a fluoride from the CF_3 group. However, attack on the well screened carbon of the CF_3 group, even by a hydride, is not very likely. Instead, addition of hydride to the tin atom, with increase of the coordination number, followed by transfer of fluoride to the $GeMe_3$ or $SnMe_3$ group seems to be more reasonable (Scheme 1). Loss of a CF_3 group due to CF_3H formation does not occur to a significant extent. The resulting "difluorocarbene adduct" could react in two ways. First, a 1,2-hydride shift might occur, which would directly account for the formation of the CF_2H group. However, in the reaction of $(CF_3)_4Ge$, such a hydride shift, with formation of $(CF_3)_3(CF_2H)Ge$, does not take place. Instead, a second pathway is followed, in which the hydride $(CF_3)_3GeH$ is formed by loss of CF_2 which subsequently undergoes insertion into the more reactive Sn–H bond of $SnMe_3H$. Though the hydride shift cannot be excluded in the case of the reaction with $(CF_3)_4Sn$, the observation of the intermediates $(CF_3)_3$ SnH and $(CF_3)_2(CF_2H)SnH$ suggests a CF_2 elimination/reinsertion mechanism. The competitive insertion into the Sn–H bonds of $(CF_3)_3SnH$ and $SnMe_3H$ leads to both $(CF_3)_3(CF_2H)Sn$ and the initially observed $(CF_2H)SnMe_3$. The electrophilicity of the tin atom is not greatly reduced by replacement of a CF_3 with a CF_2H group, and in a second cycle $(CF_3)_2$-$(CF_2H)SnH$ and $(CF_3)_2(CF_2H)_2Sn$ are formed from $(CF_3)_3(CF_2H)Sn$. Further scrambling of the methyl groups, following eqn. (1), yields the final product distribution.



Scheme 1. Reaction pathway for the formation of mixed (difluoromethyl)(trifluoromethyl)(methyl)stannanes from $(CF_3)_4Sn$ and $SnMe_3H$.

The product distribution of the reaction of $(CF_3)_4Sn$ with $GeMe_3H$ is consistent with the same mechanism as that in Scheme 1. In accordance with the higher affinity of the Sn–H bond towards CF_2, $(CF_2H)Ge$ derivatives are not observed.

The replacement of a further fluorine atom of the CF_2H group by hydrogen does not occur. Instead, elimination of CF_2H_2 is observed. Presumably, the reduced steric shielding of the carbon atom allows a direct transfer of hydride to the CF_2H group. Furthermore, the reaction is favoured by the relatively high stability of a fluorinated stannyl anion [9], which acts as



Scheme 2. Reaction pathway for the formation of trimethylgermyl derivatives $(CF_3)_n(CF_2H)_{3-n}SnGeMe_3$.

a leaving group (Scheme 2). The formulation of an ionic intermediate is backed by the observation that independently prepared $(CF_3)_3SnSnMe_3$ is dissociated, at least in polar solvents, to the ions, $(CF_3)_3Sn^{\ominus}$ and $SnMe_3^{\oplus}$ [13]. Recombination with the $GeMe_3$ unit gives the (trimethylgermyl)stannanes. The amount of CF_2H_2 evolved is consistent with the sum of the Sn–$GeMe_3$ derivatives formed.

3. NMR spectra

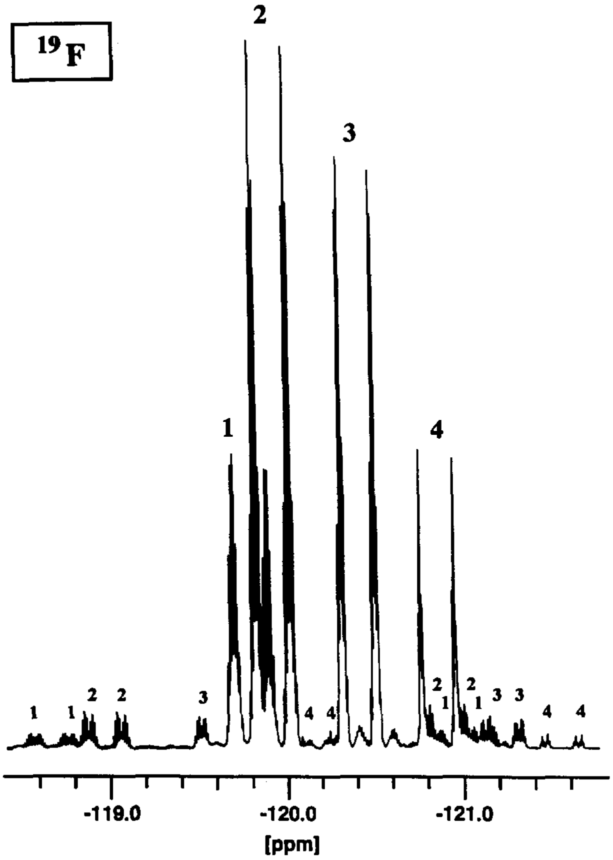


Fig. 1. ^{19}F NMR spectrum of the CF_2H part of $(CF_3)_{4-n}(CF_2H)_nSn$. The main signals and their $^{119/117}Sn$ satellites are denoted by the number, n, of CF_2H groups.

The NMR data for the volatile compounds, recorded after separation from the non-volatile material, such as $SnMe_3F$ and some decomposition products, are presented in Table 1 for the reaction of $(CF_3)_4Sn$ with $SnMe_3H$, and Tables 2 and 3 display the corresponding data for the reaction with $GeMe_3H$. The CF_2H part of the ^{19}F NMR spectrum of a product mixture containing the species $(CF_3)_n(CF_2H)_{4-n}Sn$ ($n = 0$–3) is displayed in Fig. 1. Inspection of the data reveals that some chemical shifts and coupling constants are highly dependent on the media. For example the $\delta(^{19}F)$ value of -38.7 ppm for neat $(CF_3)_4Sn$ [4] is shifted by almost 10 ppm to high field in the $GeMe_3H$ reaction mixture, and this shift is accompanied by a decrease in the $^2J(SnF)$ coupling constant. This shift appears to be connected to the large amount of $GeMe_3F$ formed. In contrast to $SnMe_3F$, $GeMe_3F$ is volatile and co-con-

TABLE 3. ^{13}C NMR data for the compounds $(CF_3)_n(CF_2H)_mSn$ [a], observed in the reaction of $(CF_3)_4Sn$ with $GeMe_3H$

	δ ^{13}C		$^1J(SnC)$ [b]		$^1J(CF)$		$^1J(CH)$	$^3J(CF)$ [d]		$^3J(CH)$	
	(CF_3)	(CF_2H)	(CF_3)	(CF_2H)	(CF_3)	(CF_2H)		(CF_3)	(CF_2H)	(CF_3)	(CF_2H)
$(CF_3)_4Sn$	137.6	–	1198/1145	–	358.5	–	–	5.9	–	–	–
$(CF_3)_3(CF_2H)Sn$	137.8	129.2	902/862	1222/1168	357.8	287.3	190.3	5.5	3.8	2.1	–
$(CF_3)_2(CF_2H)_2Sn$	138.2	129.3	619/591	1022/977	358.2	285.4	189.1	4.5	4.1	2.4	0.8
$(CF_3)(CF_2H)_3Sn$	138.4	129.7	478/459	808/774	356.4	283.6	186.2	4.1	3.9	2.3	1.3
$(CF_2H)_4Sn$	–	130.2	–	[c]	–	282.1	183.8	–	4.0	–	1.2

[a] See Table 1, solvent THF-d_8. [b] $^nJ(SnE) \triangleq {}^nJ(^{119}SnE/^{117}SnE)$. [c] Not observed. [d] The couplings to the fluorines of the CF_3 and CF_2H groups are equal within the given resolution.

denses with the CF_3Sn containing compounds. The Lewis acidity increases with increasing number of CF_3 groups attached to tin, and consequently $(CF_3)_4Sn$ is most susceptible towards complexation or interaction with a base, *e.g.*:

$$(CF_3)_4Sn + F\text{-}GeMe_3 \rightleftharpoons (CF_3)_4Sn \cdots F \cdots GeMe_3 \qquad (7)$$

Such an interaction is confirmed by the observation that upon addition of KF to $(CF_3)_4Sn$ a stable *cis*-oriented octahedral complex is formed. The average CF_3 resonance of this fluoro complex is shifted to high-field, −51.5 ppm, and the $^2J(SnF)$ coupling is reduced to *ca.* 400 Hz [8]. If no donor is present, the ^{19}F resonance of $(CF_3)_4Sn$ is found at the high frequency end of the scale for $CF_3Sn(IV)$ derivatives [4], whereas in a fluoride-containing medium it appears at the low-frequency end. The lower Lewis acidity of the methyl and also of the difluoromethyl-substituted stannanes reduces their tendency towards complexation analogous to that shown in eqn. (7) so this exhibits a smaller high-field shift of the ^{19}F signal. As a consequence, the "normal" sequence of resonances for these compounds is exactly reversed in the presence of $GeMe_3F$.

The identification of the mixed $CF_3/CF_2H/CH_3$ stannanes on the basis of characteristic chemical shifts, coupling patterns, intensities, and selective decoupling experiments is straightforward. Furthermore, the presence of ^{119}Sn and ^{117}Sn isotopes with relative abundances of 8.6% and 7.6%, respectively, gives rise to satellite spectra with $^2J(SnF)$ couplings that are very sensitive towards the specific electronic environment of the tin atom [4].

Whereas the ^{19}F signal of a CF_3Sn group resonates at *ca.* −40 to −50 ppm, that of the tin-bonded CF_2H groups is found at *ca.* −120 ppm as a characteristic doublet ($^2J(HF) = 45 \pm 1$ Hz), which shows further fine structure due to the $^4J(FF)$ coupling with the CF_3 group. The multiplicities of the proton noise-decoupled CF_2H resonances are given in the Tables. Coupling between two CF_2H groups becomes evident only upon decoupling of the CF_3 group or for $(CF_2H)_4Sn$, whose signal appears as a pseudo-triplet with $^4J(C\mathit{F}_2H/C\mathit{F}_2H) \cong 2$ Hz. Coupling of the $CF_2\mathit{H}$ proton to the $C\mathit{F}_3$ group is not observed. The $^2J(SnF)$ couplings of the CF_3 and CF_2H groups follow essentially the same pattern. While a linear correlation between the $\mathit{Sn}\text{-}C\mathit{F}_3$ and $\mathit{Sn}\text{-}C\mathit{F}_2H$ couplings is evident from Fig. 2, this correlation depends on the medium and is clearly displaced for the fluoride-containing solution.

The lower electronegativity of the CF_2H group relative to a CF_3 group leads to a higher covalent character of the $Sn\text{-}CF_2H$ bond and thus a stronger demand for 5s(Sn) character. Thus both $^2J(SnF)$ coupling constants decrease as n increases from 1 to 4 for the $(CF_3)_{4-n}(CF_2H)_nSn$ derivatives. In accordance with the higher covalency, and thus 5s(Sn) demanding character, of the $Sn\text{-}CH_3$ bond, a further decrease of $^2J(SnF)$ occurs upon replacement of CF_3 moieties by CH_3 groups.

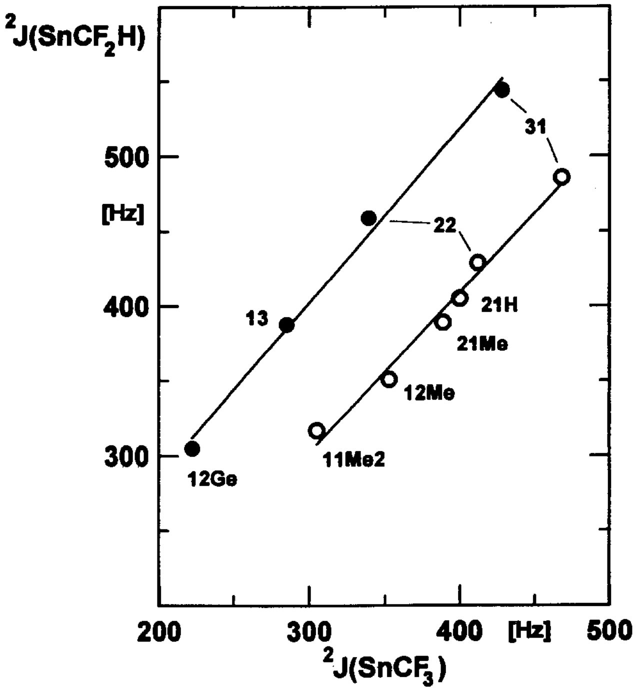


Fig. 2. Correlation of the $^2J(SnF)$ coupling constants of $SnCF_2H$ and $SnCF_3$ groups in mixed (trifluoromethyl)(difluoromethyl)stannanes, $(CF_3)_n(CF_2H)_mSnR_{4-n-m}$. The digits in the figure give the values of n and m, and the R groups are designated explicitly (Ge ≙ $GeMe_3$). Solid circles (●) refer to solutions containing fluoride ($GeMe_3F$).

Inspection of the corresponding data points for $(CF_3)_3(CF_2H)Sn$ and $(CF_3)_2(CF_2H)_2Sn$, denoted by 31 and 22, respectively, in Fig. 2, shows that the addition of $GeMe_3F$ lowers $^2J(\mathit{Sn}C\mathit{F}_3)$ but raises $^2J(\mathit{Sn}C\mathit{F}_2H)$. Such a splitting of coupling constants has been found for many static CF_3Sn complexes; *e.g.*, the ^{119}SnF couplings to the various CF_3 groups in the 1,10-phenanthroline complex of $(CF_3)_4Sn$ are 603 and 342 Hz [8] for the groups in axial and equatorial positions, respectively, the average value of 473 Hz being lower than that for the free species (542 Hz). If similar behaviour is assumed for the mixed CF_3/CF_2H stannanes, it follows that the CF_3 group preferentially takes the position associated with the small coupling constant. As the number of CF_2H groups increases, the CF_2H groups also have to adopt these positions. Consequently, the largest decrease of $^2J(SnCF_3)$ upon complexation or solvation will arise for the compound with the minimum number of CF_3 groups, $CF_3(CF_2H)_3Sn$. This consideration is confirmed by the observation that

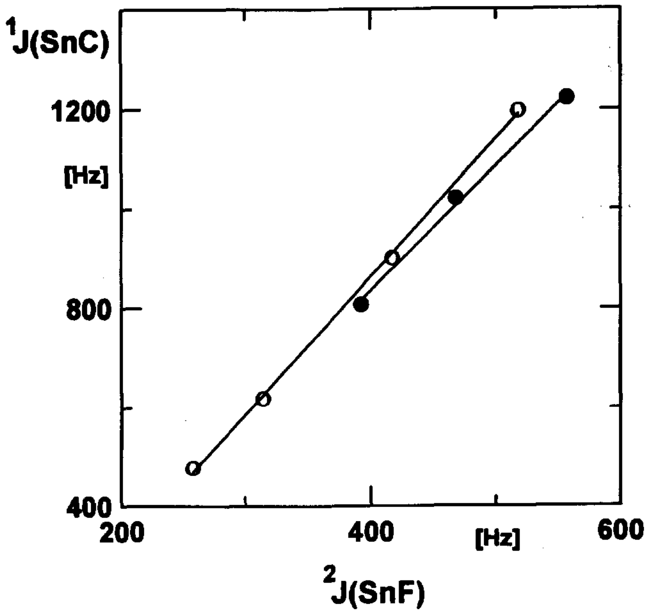


Fig. 3. Correlation of ^1J(SnC) *vs.* ^2J(SnF) coupling constants of $SnCF_2H$ (●) and $SnCF_3$ (○) groups.

the largest increase in $^2J(SnCF_2H)$ occurs for $(CF_3)_3(CF_2H)Sn$, and there is no increase in the case of $CF_3(CF_2H)_3Sn$.

A pronounced solvent dependence is also observed for the $\delta(^{119}Sn)$ values of the series $(CF_3)_n(CF_2H)_{4-n}$: in the presence of Me_3GeF the ^{119}Sn resonance of $(CF_3)_4Sn$ is shifted by 150 ppm to high fields with respect to those for uncomplexed species. Replacement of CF_3 by CF_2H causes an average low-field shift of 40 ppm (Table 2).

The ^{13}C shifts of the CF_3 and CF_2H groups, Table 3, are almost constant. In contrast, the ^1J(SnC) couplings span a wide range from *ca.* 500 to 1200 Hz, despite the rather small electronic changes. These changes are well correlated with those of the corresponding ^2J(SnF) couplings (Fig. 3). It should be noted, however, that this correlation deviates somewhat from that given in ref. 4; *e.g.*, the decrease of *ca.* 25 Hz in ^2J(SnF) upon complexation of $(CF_3)_4Sn$ contrasts with the increase in ^1J(SnC) of almost 200 Hz. Nevertheless, the general correlation shows that both ^1J(SnC) and ^2J(SnF) couplings are negative [4].

The ^1H triplet of the CF_2H group is found near 6.5 ppm. The ^2J(SnH) coupling increases with the increasing number of electronegative CF_3 groups. Decoupling and 2D experiments on CF_2HSnMe_3 have shown that $^2J(SnCHF_2)$ is negative; that is, the sign is opposite to that for a $Sn-CH_3$ group.

The evidence for the trimethylgermyltin derivatives that are much less volatile is mainly based on their NMR spectra. In general, the presence of a MMe_3 substituent (M = C, Si, Ge, Sn) in a CF_3Sn or CF_3Ge derivative leads to a high-frequency shift of the fluorine resonances. Furthermore, the +I effect of the electropositive $GeMe_3$ group gives rise to a very small ^2J(SnF) coupling constant.

3. Experimental section

Volatile material was handled on a vacuum line equipped with greaseless stopcocks. $(CH_3)_3SnH$ and $(CH_3)_3GeH$ were prepared from the corresponding chlorides and $LiAlH_4$ in di-n-butyl ether, $(CF_3)_4Sn$ from $SnBr_4$ and $(CF_3)_2Cd$ [4,10]. NMR spectra were recorded with a Bruker AC 250 instrument (^1H 250.13 MHz; ^{19}F 235.36 MHz; ^{119}Sn 93.28 MHz). IR spectra were recorded with a Bruker IFS 25 spectrometer with samples in 10 cm gas cells.

3.1. Reaction of $(CF_3)_4Sn$ with $SnMe_3H$ or $GeMe_3H$

(a) Trimethylstannane (1.2 mmol) was condensed on to 460 mg (1.17 mmol) of $(CF_3)_4Sn$ and the mixture allowed to warm slowly to ambient temperature. After stirring for two hours all volatile material was removed from the precipitated fluorides and transferred to a 4 mm glass ampoule for analysis by NMR spectroscopy (see Table 1). The signals due to $(CF_2H)SnMe_3$ had disappeared after 24 h, and a white solid had formed again. The ampoule was opened under vacuum and the volatile material transferred to a new ampoule and re-analyzed.

(b) In the corresponding reaction of 200 mg (1.7 mmol) of trimethylgermane with 170 mg (0.43 mmol) of $(CF_3)_4Sn$ the sealed ampoule was warmed to 60°C for 100 min because the reaction was very slow at ambient temperature. For NMR data see Table 2.

(c) In order to allow detection of intermediates, the reaction mixture was kept at −30°C for 20 min. The formation of $(CF_3)_3SnH$ was monitored by taking the IR spectra of the gas above the liquid reaction mixture (ν(SnH) at 1946 cm^{-1}, PQR). The volatile material was transferred to the vacuum line, diluted with C_6D_6, and sealed in a 4 mm glass ampoule for NMR analysis.

3.2. Reaction of $GeMe_3H$ with CF_3SiF_3

Trimethylgermane (1 mmol) was sealed with 0.5 mmol of CF_3SiF_3 in a 4 mm glass ampoule and the mixture kept at 100°C for 3 h. The volatile material was separated by fractional condensation and analyzed by ^{19}F and ^1H NMR spectroscopy. The fraction which passed a −126°C trap contained SiF_4 (45%), CF_2HSiF_3 [11] (15%), CF_3H (4.5%) along with traces of C_2F_4 (0.9%) and c-C_3F_6 (0.6%), whereas the fraction trapped at −126°C consisted of unchanged $GeMe_3H$ and CF_2HGeMe_3 (13%) ($\delta(CF_2H)$ −133.7 ppm, $\delta(CF_2H)$

5.89 ppm, $\delta(CH_3)$ 0.28 ppm, $^2J(FH)$ 47.0 Hz), CF_3GeMe_3 [12] (15%), $HC_2F_4GeMe_3$ (2.6%) ($\delta(CF_2H)$ −131.4 ppm, $\delta(CF_2Ge)$ −125.2 ppm, $\delta(CF_2H)$ 5.43 ppm, $^2J(FH)$ 55.7 Hz, $^3J(FH)$ 5.2 Hz), $(CF_2H)_2GeMe_2$ (1.8%) ($\delta(CF_2H)$ −135.5 ppm, $\delta(CF_2H)$ 6.03 ppm, $^2J(FH)$ 45.7 Hz; $^4J(FF)$ 2.7 Hz), and CFH_2GeMe_3 (1.8%), ($\delta(CFH_2)$ −265.9 ppm, $\delta(CFH_2)$ 4.48 ppm, $^2J(FH)$ 47.7 Hz).

3.3. Reaction of $SnMe_3H$ with CF_2Br_2 $(NMe_2)_2C=C(NMe_2)_2$

To 3.7 g (18 mmol) of CF_2Br_2 and 1.5 g (5.9 mmol) of $SnMe_3H$ in 4 ml of sulfolane, tetrakis(dimethylamino)ethylene (1.2 g, 5.9 mmol) was added dropwise from a syringe. After further stirring for 15 min the volatile material was transferred to the vacuum line and separated by fractional condensation to yield 0.85 g of an equimolar mixture of CF_3SnMe_3 and CF_2HSnMe_3.

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