Reactions of Bis(trifluoromethyl)mercury: The Synthesis and Properties of Methyl(trifluoromethyl)-stannanes and -plumbanes

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The reactions of $Hg(CF_3)_2$ with Group 4 organometallic compounds MMe_4 (M = Si, Ge, Sn, or Pb), $MMe_3(CF_3)$ (M = Sn or Pb), and M_2R_6 (M = Si or Sn, R = Me; M = Ge, Sn, or Pb, R = Ph) have been investigated. Exchange of one CF_3 group with a methyl group occurs for $SnMe_4$, $SnMe_3(CF_3)$, and $PbMe_4$; the lead derivative reacts much more readily than the tin compound. Cleavage of the metal–metal bond with formation of $MR_3(CF_3)$ has been achieved for Sn_2Me_6, but does not take place for Si_2Me_6 and the hexaphenyl derivatives. The reactions of $PbMe_3(CF_3)$ with bromine, hydrogen chloride, and water have been investigated together with its thermal stability. Spectroscopic properties are discussed for mixed trifluoromethyl–methyl derivatives of Group 4.

A VARIETY of exchange reactions between trifluoromethyl and methyl compounds is known. In Group 5 chemistry, the exchange of the methyl groups of MMe_3 with the trifluoromethyl group of CF_3I has been studied carefully.[1-4] The methyl derivatives of Group 4 are much less reactive, *e.g.* only trace amounts of $SnMe_2(CF_3)_2$ have been detected when heating CF_3I with $SnMe_3(CF_3)$.[5] The compounds $PbMe_3R_F$ (R_F = perfluoroalkyl group) have been synthesized by the reaction of perfluoroalkyl iodides with tetramethylplumbane,[6] but no data have been reported for the derivative $PbMe_3(CF_3)$.

Trifluoromethyl derivatives of mercury have been shown to react with organomercury compounds[7] according to equation (1), but it was not clear whether

$$HgX(CF_3) + HgR_2 \longrightarrow HgR(CF_3) + HgX(R) \quad (1)$$

migration of CF_3 or of X occurred. When methyl derivatives of tin or platinum were used instead of HgR_2, exchange of X (Cl or F_3CCO_2) with a methyl group was observed.[8] However, bis(trifluoromethyl)mercury readily transfers CF_3 groups to germanium halides. The exchange of trifluoromethyl and methyl groups has also been studied in the system $Hg(CF_3)_2$–$CdMe_2$ by means of n.m.r. spectroscopy.[9]

The mixed methyl–trifluoromethyl derivatives of germanium are thermally more stable than other Ge(CF_3) derivatives.[5] Therefore, compounds of the general type $M^{IV}Me_{4-n}(CF_3)_n$ might be sufficiently stable to permit the transfer of CF_3 groups at elevated temperatures.

EXPERIMENTAL

All the volatile materials were manipulated in a standard vacuum system. Air-sensitive involatile compounds were handled in an inert-atmosphere glove-bag. Starting materials were obtained from commercial sources and were purified by standard methods or used as received. Products were purified by trap-to-trap condensation and by gas chromatography using a Bendix 2 300 gas chromatograph equipped with an automatic temperature programmer. Infrared spectra were obtained with Beckman IR-20A or Beckman IR-12 spectrometers, utilizing 10-cm gas cells with KBr windows. Raman spectra were recorded on a Cary 82 spectrometer with a Kr^+ laser operating at 647.1 nm. N.m.r. spectra were obtained on a Perkin-Elmer R20B spectrometer (60.0 MHz for ^1H, 56.46 MHz for ^{19}F). Chemical shifts are related to CF_3CO_2H (^{19}F) and $SiMe_4$ (^1H); positive signs correspond to high-field (^{19}F) and low-field shifts (^1H). Coupling constants were determined with a Takeda-Riken TR 3824 X frequency counter. Mass spectra were recorded on a Hitachi RMU 6e mass spectrometer operating at room temperature. The elemental analyses were by Schwarzkopf Laboratories, Woodside, New York. Bis(trifluoromethyl)mercury was obtained by decarboxylation of the trifluoroacetate in the presence of $K_2[CO_3]$.[10]

Reactions of Bis(trifluoromethyl)mercury.—With $PbMe_4$. A solution of tetramethylplumbane (350 mg, 1.3 mmol) in toluene (*ca.* 40%) and a two-fold excess (based on complete substitution) of bis(trifluoromethyl)mercury were sealed in a 4-mm glass tube. The tube was heated to 70 °C and the progress of the reaction was followed by ^{19}F and ^1H n.m.r. spectroscopy. After 2 weeks the signal for $PbMe_4$ had disappeared and absorptions due to $HgMe(CF_3)$ and $PbMe_3(CF_3)$ with their characteristic isotope satellites had appeared in a mol ratio of 1 : 1. The reaction mixture was separated by repeated gas chromatography. Toluene, excess of $Hg(CF_3)_2$, and $HgMe_2$ (2% yield) were removed by means of a column (24 ft × 0.375 in) of 10% SE-30 on Chromosorb P; separation of $HgMe(CF_3)$ and $PbMe_3(CF_3)$ was achieved on a column (7 ft × 0.25 in) of Carbowax on Chromosorb P at 80 °C, yields 350 (94) and 390 mg (93%) respectively.

Methyl(trifluoromethyl)mercury is a colourless liquid, b.p. 130 and m.p. −13.8 °C. Its ^{19}F and ^1H n.m.r. spectra show quartets under high resolution which are accompanied by ^{199}Hg satellites: $\delta(CH_3)$ 1.24 [$^2J(HgH)$ 139.3] and $\delta(CF_3)$ − 42.2 p.p.m. [$^2J(HgF)$ 940, $^4J(HF)$ 0.45, and $^1J(^{13}CH)$ 134 Hz]. The mass spectrum consists of peaks with the appropriate isotope pattern of Hg: *m/e* 286

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$[HgMe(CF_3)]^+$ (18), 271 $[Hg(CF_3)]^+$ (24), 267 $[HgMe(CF_2)]^+$ (10), 217 $[HgMe]^+$ (100), 202 Hg^+ (55), and 69 $[CF_3]^+$ (90%). The gas-phase i.r. spectrum reveals absorptions at 2 910w, 1 180m, 1 150vs, 1 080vs, 1 045m, 770w, and 550s cm^{-1}, whereas the Raman spectrum of the liquid shows bands at 2 995vw, 2 912m,p, 2 802vw,p, 1 414vw, 1 200m,p, 1 140m,p, 1 110vw,p, 1 035w, 776vw, 742vw,p, 705s,p, 553vs,p, 515w, 243sh, 240vs,p, and 117s cm^{-1}.

Trimethyl(trifluoromethyl)lead is a colourless liquid which melts at −31 °C and boils at 128 °C with slow decomposition. Its n.m.r. spectrum consists of singlets with ^{207}Pb satellites ($I = \frac{1}{2}$, natural abundance 22.6%); $\delta(CH_3)$ 1.20 [$^2J(^{207}PbH)$ 71.8, $^1J(^{13}CH)$ 138.2 Hz] and $\delta(CF_3)$ −35.6 p.p.m. [$^2J(PbF)$ 240.6 Hz]. The gas-phase i.r. spectrum shows major bands at 3 020w, 2 940m, 1 175m, 1 153m, 1 123vs, 1 073vs, 1 046(sh), 776s, 734m, and 487s cm^{-1}. Raman absorptions are observed at 3 020vw, 2 935w,p, 1 410vw, 1 182m,p, 1 168w, 1 116vw,p, 698w,p, 489m, 469vs,p, 205m,p, 126m, and 96m cm^{-1}. The mass spectrum shows an $[M - F]^+$ peak (see Table 1) (Found: C, 14.55; H, 3.05; F, 17.0. Calc. for $C_4H_9F_3Pb$: C, 14.95; H, 2.80; F, 17.75%).

With methyl derivatives of tin. (*a*) Tetramethylstannane (245 mg, 1.37 mol) and $Hg(CF_3)_2$ (187 mg, 0.55 mol) were sealed in a 4-mm glass tube and heated to 80 °C for 2 weeks. Periodic ^{1}H and ^{19}F n.m.r. measurements indicated slow formation of $HgMe(CF_3)$ and $SnMe_3(CF_3)$ in the mol ratio *ca.* 1 : 1. After reaction of *ca.* 20% of $Hg(CF_3)_2$ no further reaction was observed. Increasing temperatures did not improve the yield but rather led to slow decomposition and the formation of C_3F_6. Attempts to improve the yield by employing an excess of the mercury compound or by using different solvents (diethyl ether or benzene) were not successful. The resulting $SnMe_3(CF_3)$ was separated by g.c. It's spectroscopic properties were in good agreement with those reported earlier.[11]

TABLE 1

Mass spectra of $M^{IV}Me_3(CF_3)$ compounds (M = Ge, Sn, or Pb) *

Ion	M Ge	 Sn	 Pb
$[MMe_2(CF_3)]^+$	2.9	4.0	6.5
$[M(CF_3)]^+$	<0.5	<0.5	0.8
$[MFMe_2]^+$	28.4	23.5	15.3
$[MMe_3]^+$	36.4	36.4	26.0
$[MFMe]^+$	1.5	1.1	0.5
$[MMe_2]^+$	4.7	8.7	3.4
$[MF]^+$	8.0	5.5	5.7
$[MMe]^+$	12.7	12.7	21.3
$[MH]^+$	2.5	1.5	
M^+	2.9	5.8	19.7
$[CF_3]^+$	<0.5	<0.5	0.8

* Intensities are given as percentages of the total ionization.

(*b*) In a closed tube, $SnMe_3(CF_3)$ (0.52 g, 2.25 mol) and $Hg(CF_3)_2$ (1.84s, 5.45 mol) were heated to 75 °C. The ampoule was opened after 5 d, and trap-to-trap condensation was used to remove excess of $Hg(CF_3)_2$. The fraction which passed through the trap at −96 °C was identified by its i.r. spectrum as perfluorocyclopropane (0.15 mol), contaminated with a trace of fluoroform. The remaining liquid was separated by g.c. on a column (24 ft × 0.375 in) of 10% Chromosorb P. Besides unchanged $SnMe_3(CF_3)$ (2.0 mmol), $HgMe(CF_3)$ (0.23 mol) and $SnMe_2(CF_3)_2$ (0.09 mmol) were obtained. Increase of the reaction temperature beyond 80 °C led to more extensive decomposition of $SnMe_2(CF_3)_2$ thus lowering the yield. Longer reaction times did not result in a marked increase in the extent of conversion.

The ^{1}H and ^{19}F n.m.r. spectra consist of singlets with $^{119}Sn-^{117}Sn$ satellites: $\delta(CH_3)$ 0.65 [$^2J(^{119/117}SnH)$ 66.4/63.6] and $\delta(CF_3)$ −31.5 p.p.m., [$^2J(^{119/117}SnF)$ 346.0/330.4 Hz]. Major bands were observed in the gas-phase i.r. spectrum at 3 010w, 2 925m, 1 163vs, 1 139vs, 1 094vs, 1 074vs, 775s, 735m, 713m, 552s, and 528s cm^{-1}. The mass spectrum consisted almost entirely of peaks with the characteristic tin isotope pattern at *m/e* (referred to ^{120}Sn, intensities corrected for overlapping peaks): 273 $[SnMe(CF_3)_2]^+$ (5), 269 $[SnMe_2(CF_2)(CF_3)]^+$ (2), 223 $[SnFMe(CF_3)]^+$ (27), 219 $[SnMe_2(CF_3)]^+$ (100), 189 $[Sn(CF_3)]^+$ (6), 185 $[SnMe(CF_2)]^+$ (2), 173 $[SnF_2Me]^+$ (26), 169 $[SnFMe_2]^+$ (92), 154 $[SnFMe]^+$ (12), 150 $[SnMe_2]^+$ (8), 139 $[SnF]^+$ (43), 135 $[SnMe]^+$ (29), 120 Sn^+ (21), 100 $[C_2F_4]^+$ (2), 81 $[C_2F_3]^+$ (3), and 69 $[CF_3]^+$ (3%) (Found: C, 17.5; H, 2.25; F, 39.85. Calc. for $C_4H_6F_6Sn$: C, 16.75; H, 2.10; F, 39.75%).

With Sn_2Me_6. Hexamethyldistannane (444 mg, 1.35 mmol) and $Hg(CF_3)_2$ (397 mg, 1.19 mmol) were enclosed in a glass tube and heated to 75 °C. Elemental mercury was formed, and after 1 week the n.m.r. signal for Sn_2Me_6 [δ 0.18 p.p.m., $J(^{119}SnH)$ 48.8 Hz] had almost disappeared. New peaks were observed due to $SnMe_4$ [δ 0.04 p.p.m., $J(^{119}SnH)$ 54.5 Hz] and $SnMe_3(CF_3)$ [0.32 p.p.m., $J(^{119}SnH)$ 59.2 Hz]. The volatile material was passed through a slush kept at −20 °C to remove the mercury and less volatile compounds. The liquid obtained consisted of $SnMe_3(CF_3)$ (0.096 mmol, 36%), $SnMe_4$ (0.38 mmol, 14%), $SnMe_2(CF_3)_2$ (0.027 mmol, 1%), and C_3F_6 (0.41 mmol).

Hexamethyldisilane did not show any reactions with $Hg(CF_3)_2$ below 130 °C.

With M_2Ph_6 (M = Ge, Sn, *or* Pb). The hexaphenyldimetal compound (*ca.* 0.1 mmol) was dissolved in benzene and together with $Hg(CF_3)_2$ (0.2 mmol) this solution was transferred to a sealed tube. The temperature was increased to 125 °C over a period of 3 weeks. No reaction was observed for the digermane at 110 °C. Further increase of the temperature led to decomposition with formation of a black tar and a small amount of perfluorocyclopropane. Similar results were obtained for the distannane. Hexamethyldiplumbane became slightly yellow at 110 °C; the only product containing a CF_3 group was $HgPh(CF_3)$ [$J(^{199}HgF)$ 1 000 Hz], but no $Pb(CF_3)$ derivative could be detected by n.m.r. spectroscopy.

Reactions of Trimethyl(trifluoromethyl)lead.—With $Hg(CF_3)_2$. The compound $PbMe_3(CF_3)$ was heated in a sealed tube with an excess of $Hg(CF_3)_2$ to 60, 80, and 100 °C, keeping the mixture at each temperature for 1 week. No formation of $PbMe_2(CF_3)_2$ could be detected. Instead, the re-formation of some $PbMe_4$ was observed, followed by slow formation of $HgMe(CF_3)$. No perfluorocyclopropane, which could be expected as a decomposition product, was obtained. Solutions in toluene or benzene gave the same results.

With HCl. The compound $PbMe_3(CF_3)$ was dissolved in dry diethyl ether and stirred for 2 min under an atmosphere of dry hydrogen chloride. The mixture was cooled to −78 °C, and the volatile components were removed and shown by i.r. spectroscopy to consist of HCl and CHF_3. The liquid was transferred to a n.m.r. tube attached to the reaction bulb. The tube was sealed and allowed to warm

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[11] R. Eujen and H. Bürger, *J. Organometallic Chem.*, 1975, **88**, 165; R. Eujen, Dissertation, Braunschweig, 1974.

up. After some minutes a white solid precipitated. The n.m.r. spectrum of the solution showed peaks due to unchanged $PbMe_3(CF_3)$, CHF_3, and some CHF_2Cl. After 24 h the $PbMe_3(CF_3)$ had disappeared completely and an equimolar amount of CHF_3 had been formed. The ^1H n.m.r. spectrum of the precipitate dissolved in MeOH consisted of a singlet at 1.37 p.p.m. with a PbH coupling constant of 78 Hz, which is in good agreement with the value reported for $PbClMe_3$ in methanol.[12]

With Br_2. Bromine (80 mg, 0.50 mmol) was condensed on to $PbMe_3(CF_3)$ (180 mg, 0.56 mmol), sealed, and warmed slowly to room temperature. After the bromine had reacted completely, the tube was opened, and the volatile products were transferred to a vacuum line and separated by passing through a slush at −60 °C. The volatile fraction consisted of MeBr (0.42 mmol) and a trace amount of CF_3Br. The remaining fraction was sealed in a capillary. N.m.r. and Raman spectra showed bands due to MeBr (0.04 mmol), $PbMe_3(CF_3)$ (0.04 mmol), and a new $Pb(CF_3)$ compound (0.02 mmol), containing CF_3 and Me in a mol ratio of 1 : 1 {$\delta(CF_3)$ −39.0 [$^2J(PbF)$ 379], and $\delta(CH_3)$ 1.65 p.p.m. [$^2J(PbH)$ 84.9 Hz]}.

Thermal decomposition. The compound $PbMe_3(CF_3)$ decomposes slowly at the boiling point. Some decomposition was also observed when the compound was stored in glass ampoules, especially capillaries, although the glass was flamed very carefully at 10^{-4} mmHg.* When heated to 150 °C in a sealed ampoule, 40% of the compound was recovered after 3 d. The volatile decomposition products were shown by i.r. spectroscopy to consist almost quantitatively of perfluorocyclopropane with only trace amounts of fluoroform.

RESULTS AND DISCUSSION

Bis(trifluoromethyl)mercury was treated with methyl derivatives of Group 4 elements to form $M^{IV}(CF_3)$ compounds by reaction (2). The ease of this reaction

$$MMeR_3 + Hg(CF_3)_2 \longrightarrow MR_3(CF_3) + HgMe(CF_3) \quad (2)$$

increases with decreasing M–C bond strength: whereas no reaction was observed for $SiMe_4$ and $GeMe_4$, tetramethylstannane exchanged one methyl group at 80—120 °C. Tetramethylplumbane was converted quantitatively into $PbMe_3(CF_3)$ at 70 °C (see Scheme). Starting with $SnMe_3(CF_3)$ a second methyl group could be exchanged: the yield of $SnMe_2(CF_3)_2$ was limited by low conversion and by extensive decomposition at the reaction temperature. Surprisingly, a second trifluoromethyl group could not be transferred to lead by this method. However, some $PbMe_4$ was reformed when heating $PbMe_3(CF_3)$ with $Hg(CF_3)_2$. On the other hand, n.m.r. and Raman spectral evidence for $PbMe_2(CF_3)_2$ was obtained when $PbMe_3(CF_3)$ was treated with bromine (see below).

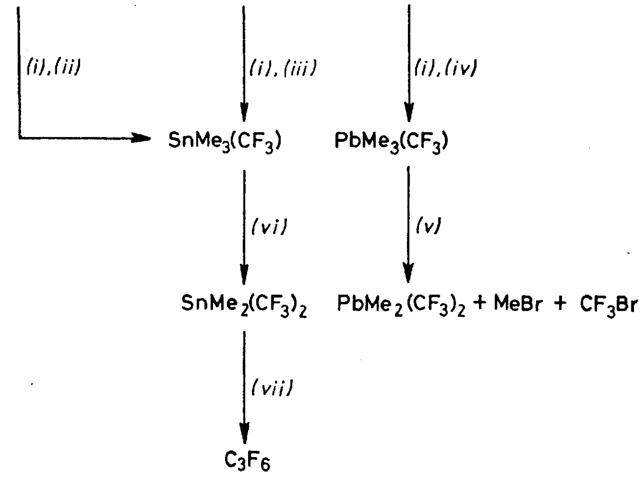
The low conversion rates in the case of the reaction of $Hg(CF_3)_2$ with both $SnMe_4$ and $SnMe_3(CF_3)$ could be due either to an equilibrium in (2) or to the formation of an inhibitor. The first possibility could be excluded by treating pure $SnMe_3(CF_3)$ with $HgMe(CF_3)$; no formation of $SnMe_4$ or $Hg(CF_3)_2$ but rather trace amounts of $SnMe_2(CF_3)_2$ and some decomposition were observed. Additionally, attempts to increase the effective concentration of $Hg(CF_3)_2$ by the use of solvents did not lead to any improvement of yields or conversion rates.

In the established synthesis[13] of $SnMe_3(CF_3)$ the Sn–Sn bond in the Sn_2Me_6 is cleaved; this may also be affected with $Hg(CF_3)_2$ as in (3). The Si–Si bond of

$$Me_3Sn{-}SnMe_3 + Hg(CF_3)_2 \longrightarrow 2\,SnMe_3(CF_3) + Hg \quad (3)$$

Si_2Me_6 is not affected by $Hg(CF_3)_2$. Phenyl groups stabilize the metal–metal bond sufficiently to prevent its cleavage, even in the case of Pb_2Ph_6.

Dimethylbis(trifluoromethyl)tin is thermally less stable than $SnMe_3(CF_3)$. Decomposition takes place at as low as 80 °C, the only volatile product being C_3F_6 in a mol ratio corresponding to elimination of difluorocarbene from both CF_3 groups. Trimethyl(trifluoromethyl)lead is about as stable as its tin analogue. At 150 °C, *ca.* 60% of the compound was decomposed within 3 d, the major product being C_3F_6.



SCHEME Reactions of $Hg(CF_3)_2$ with methyl derivatives of tin and lead: (*i*) + $Hg(CF_3)_2$; (*ii*) 80 °C; (*iii*) 80—100 °C, 20% yield; (*iv*) 70 °C, 95% yield; (*v*) Br_2; (*vi*) 75 °C, 10% yield; (*vii*) >80 °C

It was shown by analysis of the vibrational spectra of related compounds[14] that the bond between the central atom and the CF_3 group is considerably weaker than that to a methyl group. In this respect it is interesting that almost no products are observed which are due to the formation of free trifluoromethyl radicals. Cleavage of the $M{-}CF_3$ bond is accompanied by concerted transfer of a fluorine atom to the metal. However, both processes are observed in the mass spectra. The characteristic step following ionization is loss of a CF_3 radical. As a consequence the mass spectra of the trimethyl(trifluoromethyl) compounds (Table 1) closely resemble those of

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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[13] H. C. Clark and C. J. Willis, *J. Amer. Chem. Soc.*, 1960, **82**, 1888.

[14] H. Bürger and R. Eujen, *Spectrochim. Acta*, 1975, **A31**, 1645, 1655.

other trimethyl compounds. CF_n^+ fragments which are typical of perfluoroalkyl derivatives are almost absent. The total amount of fragments containing fluorine decreases in the order Ge > Sn > Pb, thus indicating the more pronounced tendency for the heavier homologues to undergo cleavage of the M–CF_3 bond. Three-co-ordinate ions containing a CF_3 group decompose by elimination of CF_2. The base peak in the spectra of the bis(trifluoromethyl) derivatives can be attributed to loss of a CF_3 radical followed by CF_2 elimination.

TABLE 2

N.m.r. parameters of $MMe_{4-n}(CF_3)_n$ (M = Sn or Pb) [a]

Compound	$\delta(CF_3)$ [b]	$\delta(CH_3)$ [c]	^2J(MF) [d]	^2J(MH) [d]
$SnMe_4$		0.05		54.1
$SnMe_3(CF_3)$	−29.2	0.41	270	59.7
$SnMe_2(CF_3)_2$	−31.5	0.65	346	66.4
$Sn(CF_3)_4$	39.7		531	
$PbMe_4$		0.92		61.3
$PbMe_3(CF_3)$	−35.6	1.20	240	71.8
$PbMe_2(CF_3)_2$	−39.0	1.65	379	84.9

[a] For M = Ge see ref. 1. [b] In p.p.m. relative to external CF_3CO_2H. [c] In p.p.m. relative to $SiMe_4$. [d] In Hz; M = ^{119}Sn or ^{207}Pb.

TABLE 3

Averaged M–CH_3 stretching frequencies (cm^{-1}) *

Compound	M Ge	Sn	Pb
MMe_4	590	521	470
$MMe_3(CF_3)$	605	534	482
$MMe_2(CF_3)_2$	618	542	490
$MMe(CF_3)_3$	628		

* $\nu_{av} = \frac{1}{n}\sum_i^n g_i\nu_i$ (g_i = degeneracy of the vibration ν_i).

The n.m.r. and vibrational spectra do not indicate any significant changes in the molecular framework. Increasing CF_3 substitution leads to deshielding of both hydrogen and fluorine atoms and to increasing M–H and M–F coupling constants (Table 2).

As can be derived from approximate normal-co-ordinate analysis, the M–CH_3 stretching frequencies are very characteristic and thus may be used as an indication of M–C bond strength. The averaged frequencies of the M–CH_3 stretching modes are given in Table 3. Increasing CF_3 substitution increases the strength of the bonds to the methyl groups. A parallel effect is observed for the C–H bonds in the methyl groups: going from $GeMe_4$ to $GeMe(CF_3)_3$ leads to a regular increase of the averaged ν(CH) (2 929 to 2 942 to 2 956 to 2 965 cm^{-1}). These tendencies can be attributed simply to the electron-withdrawing effect of the CF_3 group. Analogous considerations should not be extended to the M–CF_3 bonds because of strong coupling to other modes. A more sophisticated analysis of the vibrational spectra will be published elsewhere.[15]

In its chemical properties, $PbMe_3(CF_3)$ reveals some differences compared with its tin analogue. (*a*) The lead compound is readily attacked by moisture. Even carefully flamed glass surfaces caused some decomposition. The volatile products consisted mainly of fluoroform and trace amounts of $PbMe_4$. (*b*) Hydrogen chloride attacks $SnMe_3(CF_3)$ with elimination of methane.[6] When an ether solution of $PbMe_3(CF_3)$ was treated with dry hydrogen chloride, fluoroform was evolved and a white solid precipitated which was identified as $PbClMe_3$. Additionally some CHF_2Cl was observed indicating the formation of difluorocarbene. (*c*) Bromine reacts smoothly with excess of $PbMe_3(CF_3)$ and, similar to the tin analogue, a methyl group is split off. Among the volatile material another $PbCF_3$ compound was detected with spectroscopic properties which are in accordance with the formulation $PbMe_2(CF_3)_2$. The formation of this compound can be accounted for by sequence (4)—(5). Whereas transfer of a methyl

$$PbMe_3(CF_3) + Br_2 \longrightarrow PbBrMe_2(CF_3) + MeBr \quad (4)$$

group does not result in any change, transfer of a CF_3 group (5b) explains the observed product. The ability of $PbMe_3(CF_3)$ to transfer methyl as well as trifluoromethyl groups was demonstrated with $SnCl_4$. When $PbMe_3(CF_3)$ was allowed to warm up slowly with an excess of $SnCl_4$, an immediate reaction occurred with $SnCl_3Me$ as the major product. The ^{19}F n.m.r. spectrum of the reaction mixture indicated the formation of at least four compounds containing CF_3 groups attached to tin.

$$\begin{tikzcd}
 & PbMe_3(CF_3) + PbBrMe_2(CF_3) \quad (5a) \\
PbBrMe_2(CF_3) + PbMe_3(CF_3) \arrow[ur] \arrow[dr] & \\
 & PbMe_2(CF_3)_2 + PbBrMe_3 \quad (5b)
\end{tikzcd}$$

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