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(TRIFLUOROMETHYL)GERMANES. PREPARATION AND PROPERTIES OF $(CF_3)_2GeHX$ (X = H, D, F, Cl, Br, I, CH_3) AND $CF_3GeH_nX_{3-n}$ (X = H, D, CF_2H, CH_3)

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Summary

The hydrogenation of $(CF_3)_nGeX_{4-n}$ (X = halogen, $n = 1$–3) with $NaBH_4$ in an acidic medium has been investigated. Deuteration with $NaBD_4$ and D_3PO_4 gave the partially deuterated species $CF_3GeH_nD_{3-n}$ and $(CF_3)_2GeH_nD_{2-n}$ in reasonable isotopic purity. The $(CF_3)_2GeHBr$ was isolated and converted into the halides $(CF_3)_2GeHX$ (X = F, Cl, I) by treatment with AgX or HX. Insertion of CF_2 into a Ge–H bond has been observed, and $(CF_3)(CF_2H)GeH_2$ has been characterized. Direct alkylation of Ge–H bonds was brought about by reaction with a mixture of RI and R'_2Zn (R, R' = CH_3, C_2H_5), and the methyl(trifluoromethyl)germanes $CF_3GeH_2(CH_3)$, $CF_3GeH(CH_3)_2$ and $(CF_3)_2GeH(CH_3)$ were isolated. For R = CD_3, R' = CH_3 the product distribution can be accounted in terms of two competing mechanisms.

Introduction

Of the trifluoromethyl derivatives of Main Group IV elements, germanium compounds have been most systematically studied [1–3]. Whereas trifluoromethylsilane, CF_3SiH_3, has been characterized recently [4], and some evidence has been presented for CF_3SnH_3 [5], the trifluoromethylgermanes, $(CF_3)_nGeH_{4-n}$ ($n = 1$–3), are readily accessible from the corresponding halides and $NaBH_4$ in an acidic medium [6]. Their bonding properties, which are dominated by a rather weak Ge–C bond, have been investigated by means of vibrational [7,8] and photoelectron [9] spectroscopy as well as by structural methods [10].

Because of its high electronegativity, the CF_3 group behaves like a halide, the basic difference from a halide being the inability to accept a negative charge and thus to act as a leaving group in S_N-type reactions. However, strong nucleophiles will eliminate the CF_3 group irreversibly, e.g. OH^- yields HCF_3 quantitatively. The electron-withdrawing power of the CF_3 group increases the acidity of the Ge–H bonds, leading to facile formation of rather stable CF_3-substituted germyl anions [11]. In this contribution we report the syntheses and properties of some CF_3-substituted germanes.

Results and discussion

Trifluoromethylgermanes are obtained in high yields (> 90%) from the corresponding halides and sodium tetrahydroborate in 30% phosphoric acid.

$$(CF_3)_nGe(Hal)_{4-n} \xrightarrow[5-20^\circ C]{NaBH_4/H_3PO_4} (CF_3)_nGeH_{4-n} \ (n = 1-3)$$

All the hydrides are colourless gases or liquids, and their vapour pressure data are listed in Table 1. ^1H, ^{19}F and ^{13}C NMR parameters including those of partly deuterated germanes are presented in Table 2.

The high electronegativity of the CF_3 group induces an increased acidity of the germanium bonded hydrogens with respect to GeH_4, e.g. slow H/D exchange is observed for $(CF_3)_3GeH$ in D_3PO_4 (5% in 24 h at 25°C). Since the exchange rate is greatly accelerated by the presence of a polarizable substituent such as iodine, the synthesis of distinct H/D isotopomers such as $(CF_3)_2GeHD$ becomes possible; for example, reaction of $(CF_3)_2GeI_2$ with $NaBD_4$ in H_3PO_4 yields $(CF_3)_2GeHD$:

$$(CF_3)_2GeI_2 \xrightarrow{BD_4^-} (CF_3)_2GeDI \underset{D^+}{\overset{H^+}{\rightleftharpoons}} (CF_3)_2GeHI \xrightarrow{BD_4^-} (CF_3)_2GeHD$$

The H/D exchange has been shown for pure $(CF_3)_2GeHI$ to be reversible and fast, the second hydrogenation step being much slower. The resulting $(CF_3)_2GeHD$ does not exchange under the conditions used. Similarly, CF_3GeH_2D and CF_3GeHD_2 may be obtained in reasonable isotopic purity by use of $NaBH_4/D_3PO_4$ or $NaBD_4/H_3PO_4$:

$$CF_3GeI_3 \xrightarrow{BD_4^-} CF_3GeDI_2 \underset{D^+}{\overset{H^+}{\rightleftharpoons}} CF_3GeHI_2 \xrightarrow{BD_4^-} CF_3GeHDI \xrightarrow{BD_4^-} CF_3GeHD_2$$

The H/D exchange is very rapid for CF_3GeHI_2 but slow for CF_3GeH_2I.

The vibrational spectra of the partly deuterated species have been studied in detail and force constants have been derived [7,8].

Though CF_3 is a poor leaving group, some CF_3 elimination is observed in the

TABLE 1

VAPOUR PRESSURES ^{a} OF SOME (TRIFLUOROMETHYL)GERMANES

	B.p. (°C)	A	B	H_v^b	S_v^c
CF_3GeH_3	−22.1	1033	7.120	19.78	78.8
$(CF_3)_2GeH_2$	20.5	1424	7.855	27.26	92.8
$(CF_3)_3GeH$	31.7	1480	7.861	28.33	92.9
$(CF_3)_4Ge$	31.7	1505	7.942	28.81	94.5
$(CF_3)(CF_2H)GeH_2$	41.9	1685	8.355	32.26	102.4
$(CF_3)_2GeHBr$	48.6	1710	8.320	32.74	101.7

^{a} log p (mbar) = $-A/T + B$. ^{b} In kJ mol^{-1}. ^{c} In kJ mol^{-1} deg^{-1}.

TABLE 2

NMR DATA FOR THE (TRIFLUOROMETHYL)GERMANES $(CF_3)_nGe(H/D)_{4-n}$

	GeH_4	CF_3GeH_3	$(CF_3)_2GeH_2$	$(CF_3)_3GeH$
δ(H) [a]	3.30	4.27	5.05	5.65
δ(F) [a,e]	–	−49.2	−50.3	−50.1
Δδ(H) [b]	0.013	0.013	0.010	–
Δδ(F) [b]	–	0.033	0.032	0.027
^2J(HD) [c]	1.2	2.1	3.0	–
^3J(HF) [c]	–	8.7	7.8	6.7
^3J(DF) [c]	–	1.35	1.20	1.00
^4J(FF) [c]	–	–	4.72 [e]	4.10
δ(C) [d]	–	131.0	129.1	127.5
^1J(CF) [c]	–	331.7	330.7	329.5
^2J(CH) [c]	–	9.1	12.3	15.1
^3J(CF) [c]	–	–	5.3	4.8

[a] Internal TMS/$CFCl_3$ reference, $\delta = 10^6 \times (\nu - \nu_{Ref})/\nu_{Ref}$. [b] $\Delta\delta = \delta(GeH_n) - \delta(GeH_{n-1}D)$. [c] In Hz. [d] In C_6D_6, $\delta(C_6D_6)$ 127.0 ppm. [e] Ref. 3.

reaction with $NaBH_4$, giving the corresponding $(CF_3)_{n-1}$ germane, e.g. somewhat less than 5% $(CF_3)_2GeH_2$ is obtained in the preparation of $(CF_3)_3GeH$,

$$\mathrm{CF_3Ge}{\lessdot} \xrightarrow{\mathrm{BH_4}} {\gtrdot}\mathrm{Ge{-}H} + \mathrm{CF_3^-}$$

However, such elimination reduces the yield of CF_3GeH_3 from CF_3GeI_3 by as much as 50% at ambient temperature. The generated CF_3^- is not only protonated to form HCF_3, it also appears to eliminate F^- with concomitant formation of difluorocarbene. The latter, which may be trapped as HCF_2Br in hydrobromic acid, also inserts into a Ge–H bond yielding ca. 10% of $(CF_3)(CF_2H)GeH_2$ as well as small amounts of $(CF_3)(CF_2H)GeHX$ (1.5%) and $(CF_3)(CF_2H)GeX_2$ (< 0.5%), which were identified from their NMR spectra (Table 3):

$$\mathrm{HCF_3} \xleftarrow{\mathrm{H^+}} \mathrm{CF_3^-} \rightarrow \mathrm{CF_2} + \mathrm{F^-}$$

$$\mathrm{CF_2} + \mathrm{CF_3GeHX_2} \rightarrow \mathrm{(CF_3)(CF_2H)GeX_2}$$

If the hydrogenation is carried out in the corresponding HX acid the partially hydrogenated species may trapped, e.g. $(CF_3)_2GeHBr$ is obtained in a 10% yield when concentrated hydrobromic acid is used at ambient temperature. Conversion into other halides is readily brought about by AgX, to form the lighter halide (X = F, Cl), or with gaseous HI to form the iodide:

$$\mathrm{R_2GeHX} \xleftarrow{\mathrm{AgX}} \mathrm{R_2GeHY} \xrightarrow{\mathrm{HZ}} \mathrm{R_2GeHZ}\ (m_x < m_y < m_z)$$

The ^1H and ^{19}F NMR data of $(CF_3)_2GeHX$ (X = F, Cl, Br, I, CH_3) are given in Table 3. As in other (trifluoromethyl)fluorogermanes, no coupling to the Ge-bonded fluorine is observed, and fast fluorine exchange, possibly catalyzed by traces of HF, seems likely.

Mixed methyl(trifluoromethyl)germanes are accessible by several methods including partial methylation of the iodide followed by hydrogenation. Thus treatment of

TABLE 3

NMR DATA[a] FOR $(CF_3)_2GeHX$ (X = F, Cl, Br, I) AND $(CF_3)(CF_2H)GeX_2$ (X = H, Cl, Br, I)

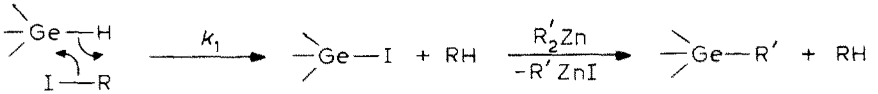
	δ(GeH)	δ(CF_3)	^3J(HF)	^1J(CF)[b]	^4J(FF)[b]					
$(CF_3)_2GeHF$[c]	6.52	−56.8	7.7	330(1)	3.9		δ(GeF)	−222		
$(CF_3)_2GeHCl$	6.20	−56.5	7.4	330.5	4.3					
$(CF_3)_2GeHBr$	5.97	−55.9	7.6	332.5	4.5					
$(CF_3)_2GeHI$	5.57	−54.9	7.9	335.9	4.8					
	δ(Ge*H*)	δ(CF_2*H*)	δ(C*F*$_3$)	δ(C*F*$_2$H)	^3J(HF)[d]	^2J(HF)	^4J(FF)	^3J(HH)	^3J(HF)[e]	^4J(HF)
$(CF_3)(CF_2H)GeH_2$	4.83	6.48	−49.9	−125.3	7.8	46.0	4.1	2.1	9.9	0.6
$(CF_3)(CF_2H)GeHCl$	6.09	6.34	−56.2	−128.6[f]	7.3	46.7	3.6	3.0	6.3	0.7
$(CF_3)(CF_2H)GeHBr$	5.83	6.43	−55.2	127.2	7.4	46.3	3.6	2.6	7.5	0.8
$(CF_3)(CF_2H)GeHI$	5.37	6.30	54.6	−125.4	7.5	46(1)	3.8	3.0	[g]	0.8
$(CF_3)(CF_2H)GeCl_2$	–	[g]	58.6	127.6	–	46.6	2.9	–	–	[g]
$(CF_3)(CF_2H)GeBr_2$	–	[g]	−59.2	−125.7	–	47.3	3.3	–	–	[g]
$(CF_3)(CF_2H)GeI_2$			−59.2	−123.9		47(1)	3.9(5)			[g]

[a] Shifts in ppm, coupling constants in Hz (see Table 2). [b] From ^{13}C satellites. [c] ^2J(HF) is not observed due to intermolecular fluorine exchange. [d] $J(F_3CGeH)$. [e] $J(F_2CGeH)$. [f] A shift difference of 0.40 ppm is observed for the AB system of the diastereotopic fluorines of the CF_2 group. [g] Not observed.

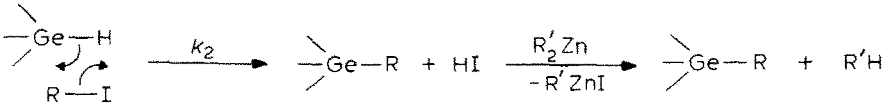
$(CF_3)_2GeI_2$ with $(CH_3)_2Cd$ yields $(CF_3)_2GeI(CH_3)$, which was converted into $(CF_3)_2GeH(CH_3)$ with $NaBH_4$. An alternative route to methyl(trifluoromethyl)germanes, $(CF_3)_n(CH_3)_mGeH_{4-n-m}$ ($n = 1, 2$), is the methylation of the corresponding trifluoromethylgermane CF_3GeH_3 or $(CF_3)_2GeH_2$ with a mixture of CH_3I and $(CH_3)_2Zn$ at or below ambient temperature; e.g.,

$$CF_3GeH_3 + CH_3I + (CH_3)_2Zn \rightarrow (CF_3)(CH_3)GeH_2 + CH_4 + CH_3ZnI$$

The ^1H and ^{19}F NMR spectra of some methyl(trifluoromethyl)germanes are listed in Table 4. The reaction proceeds smoothly until all the methyl iodide is consumed. With an excess of CH_3I germanium iodides such as CF_3GeI_3 are formed in addition to the partially methylated species. Use of a 1/1 $CD_3I/(CH_3)_2Zn$ mixture gives both CH_3- and CD_3-containing products; infrared analysis of the evolved methane confirms the presence of both CD_3H and CH_4 species. Methyl exchange between CD_3I and $(CH_3)_2Zn$ under these conditions is excluded since hydrolysis of the residual $(CH_3)_2Zn$ and CH_3ZnI yields CH_4 exclusively. These results may be accounted for by two alternative mechanisms which may be represented schematically as a "head-to-head" and a "head-to-tail" exchange; viz.

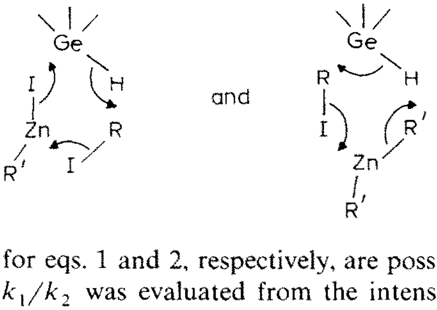


(1)



(2)

It should be noted that neither CH_3I nor $(CH_3)_2Zn$ reacts with CF_3GeH_3 at room temperature. Activation of the methyl iodide is required, and transition states such as:



for eqs. 1 and 2, respectively, are possible. For $R = CD_3$, $R' = CH_3$ the relative rate k_1/k_2 was evaluated from the intensities of the corresponding ^{19}F NMR signals, which show a well resolved CH_3/CD_3 isotopic shift for the CF_3 resonances (Table 4). For the first step of the reaction with CF_3GeH_3 a value of 2.5 is obtained, and this increases to 3.2 ± 0.3 for the second and third H/CH_3 substitution steps, whereas for $(CF_3)_2GeH_2$ the ratio decreases from 2.0 to 1.2. Use of C_2H_5I and $(C_2H_5)_2Zn$ yields the corresponding ethyl derivatives. Use of a mixture of $C_2H_5I/(CH_3)_2Zn$, however, yields C_2H_6 with traces of CH_4, and the ^{19}F NMR spectrum confirms the formation of methylated products only, indicating that k_1 is $\gg k_2$ for C_2H_5I. Presumably, the greater bulk of the ethyl group than of the methyl group

TABLE 4

NMR DATA[a] FOR SOME METHYL(TRIFLUOROMETHYL)GERMANES

	$\delta(CF_3)$	$^{1}J(CF)$	$\Delta\delta(CF_3)$[b]	$\delta(GeH)$	$\delta(CH_3)$	$^{3}J(FH)$	$^{3}J(HH)$	$^{4}J(FF)$
CF_3GeH_3	−49.2	331.7		4.27	–	8.70		–
$CF_3GeH_2(CH_3)$	−53.9	333.3	−0.053	4.39	0.61	7.75	3.75	
$CF_3GeH(CH_3)_2$	−58.2	335.6	−0.040	4.53	0.52	6.85	3.37	–
$CF_3Ge(CH_3)_3$	61.8	336.8[c]	−0.027	–	0.44	–		–
$CF_3GeI(CH_3)_2$	−62.4	338.5	[d]	–	1.24	–		
$CF_3GeI_2(CH_3)$	−64.7	340.8	[d]	–	2.03		–	
$CF_3GeHI(CH_3)$	−59.4	[d]	–	[d]	1.30	7.0	2.8	
$(CF_3)_2GeH_2$	−50.3[c]	330.7	–	5.05	–	7.8		4.72[c]
$(CF_3)_2GeH(CH_3)$	−54.4	331.6	−0.038	5.08	0.79	6.8	3.4	4.3
$(CF_3)_2Ge(CH_3)_2$	57.9	333.0	0.026		0.70	–		3.93[c]
$(CF_3)_2GeI(CH_3)$	58.2	336.2	[d]		1.4		–	4.3

[a] Chemical shifts in ppm, coupling constants in Hz. [b] $\Delta\delta(CF_3) = \delta(CF_3Ge(CH_3)R_2) - \delta(CF_3Ge(CD_3)R_2)$. [c] Ref. 3. [d] Not observed.

TABLE 5

VIBRATIONAL FUNDAMENTALS (cm^{-1}) OF $(CF_3)_2GeHX$ (X = F, Cl, Br, I, CH_3)

	X =	F	Cl	Br	I	CH_3 [b]	Intensity (IR/Ra) [c]
$\nu(GeH)$	a'	2162	2152	2145	2135	2133	m-s/s,p
$\rho(GeH)$	a'/a''	682	693/680	682	672	684/662	s/m
$\nu_s(CF_3)$	a'	1201	1194	1190	1184	1199	vs/w, (p)
	a''	1177	1165	1164	1158	1173	vvs/w
$\nu_{as}(CF_3)$	a'	1144	1144	1144	1143	1136	vvs/w,b
	a''	(1120)	1121/1117	1117	1117	1098	s/w,b
$\delta_s(CF_3)$	a'	732	732	731	731	727	m/s,p
$\delta_{as}(CF_3)$	a'	527	524	524	522	518	w/w
	a''	515	511	511	–	(510)	vw/-
$\rho(CF_3)$	a'	321	313	309	295	308	m/m,p
	a'	280	268	255	253	276	w/w, (p)
	a''	238	230	230	225	235	vw/w
	a''	–	202	202	–	200	vw/-
$\nu_s(GeC_2)$	a'	249	250	241	212 [d]	247	-/s,p
$\nu_{as}(GeC_2)$	a''	338	332	332	325	323	s/w
$\nu(GeX)$	a'	700	451	347	348 [d]	619	s/m,p
$\delta(GeC_2)$	a'	82	78	77	75	78	n.o./w-m
$\delta(CGeX)$	a'/a''	–	108	98/87	85	129	n.o./m

[a] Gas phase IR or liquid phase Raman (< 300 cm^{-1}) frequencies. [b] $\nu_{as}(CH_3)$ 3011 (w/w), $\nu_s(CH_3)$ 2940 (w/m,p), $\delta_{as}(CH_3)$ 1423 (m/vw), $\delta_s(CH_3)$ 1267 (w/w,p), $\rho(CH_3)$ 858 (m-s/w) and 820 (s/vw). [c] s = strong, m = medium, w = weak, p = polarized, n.o. = out of range of the spectrometer. [d] The lines at 212 and 348 cm^{-1} are strongly mixed in Ge–C and Ge–X characters.

prevents the direct formation of a Ge–C_2H_5 unit. In contrast, for the combination $CH_3I/(C_2H_5)_2Zn$ all possible products $CF_3GeH_a(CH_3)_b(C_2H_5)_cI_d$ are evident from the NMR spectra.

Vibrational spectra

Except for some characteristic Ge–X features the vibrational spectra of the compounds $(CF_3)_2GeHX$ (X = F, Cl, Br, I, CH_3), Table 5, are very similar, and are readily assigned by comparison with the spectra of $(CF_3)_2GeH_2$ and $(CF_3)_3GeH$ [8]. Thus, the skeleton vibrations of $(CF_3)_2GeHBr$ are almost identical to those of $(CF_3)_3GeH$ owing to the similarity of the Br and CF_3 masses and the Ge–Br and Ge–CF_3 bond strengths [12], whereas the internal CF_3 vibrations are characteristic for a $(CF_3)_2Ge$ unit [8].

Similarily the spectra of $(CF_3)(CF_2H)GeH_2$ strongly resemble those of $(CF_3)_2GeH_2$ with the exception of the C–H stretching, the C–H rocking mode with

TABLE 6

VIBRATIONAL SPECTRA AND ASSIGNMENTS FOR $(CF_3)(CF_2H)GeH_2$

IR_{gas}	$Ra_{liq.}$	Assignment
	82w	$\delta(GeC_2)$
207w	212w, (p)	$\rho(CF_3)$
250sh	253s,p	$\nu_s(GeC_2)$
262m	265vw	$\rho(CF_3, CF_2)$
305sh	303w-m,p	
323s	320m,p	$\nu_{as}(GeC_2)$
441m-s	442w,p	$\delta(CGeH)$
517vw	512w	$\delta_{as}(CF_3)$
538vw	552w-m,p	
610m	614m,p	$\delta(CF_2)$
642m	653w	twist (CGeH)
691m-s	700w	wag (CGeH)
729vs	726s,p	$\delta_s(CF_3)$
809vw		729 + 82 = 811
849s	843m	$\delta(GeH_2)$
935vw		729 + 207 = 936
1055vs	1030vw	$\nu(CF_2)$
1093sh		
1118vvs	1090w,b	$\nu_{as}(CF_3)$
1184vs	1182w, (p)	$\nu_s(CF_3)$
1311s	1312w,p	$\rho(CH)$
1338sh	1337vw	
1385vw		1118 + 262 = 1380
1837vw		1118 + 729 = 1847
1909vw		1184 + 729 = 1913
2131s	2137s,p	$\nu_s(GeH_2)$
2150s	2155w	$\nu_{as}(GeH_2)$
2205vw		1118 + 1093 = 2211
2230vw		2 × 1118 = 2236
2298w		1184 + 1118 = 2302
2360w		2 × 1184 = 2368
2396vw		2150 + 250 = 2400
2951m	2965w,p	$\nu(CH)$

its two components at 1311 and 1338 cm^{-1}, and the CF_2 deformation at 610 cm^{-1} (Table 6). Conclusions about the geometry of $(CF_3)(CF_2H)GeH_2$ may be drawn from the Raman polarization spectra. The highest possible symmetry for this molecule is C_s, with the C–H bond located in the mirror plane. The skeleton vibrations of the molecule $(CF_3)_2GeH_2$, which have been analyzed in terms of C_{2v} symmetry, correlate as $a_1 \rightarrow a'$, $a_2 \rightarrow a''$, $b_1 \rightarrow a''$, and $b_2 \rightarrow a'$. Inspection of Table 6, however, shows that the GeH_2 rocking mode (a'' for C_s symmetry) at 440 cm^{-1} is clearly polarized; that is, the symmetry must be lower than C_s, with the C–H bond rotated out of the GeC_2 plane.

Because of their importance for the determination of reliable force constants, especially in the direct comparison of $Ge-CF_3$ and $Ge-CH_3$ bond strengths, the vibrational spectra of $CF_3GeH_2(CH_3)$ and $CF_3GeH(CH_3)_2$ including both GeD and CD_3 containing isotopomers will be subject of a separate study [13].

Experimental

(Trifluoromethyl)iodogermanes, $(CF_3)_nGeI_{4-n}$, were obtained from GeI_4 and $(CF_3)_2Hg$ [6]. Dimethyl zinc was prepared from CH_3I, Cu, Zn and catalytic amounts of I_2 at 120°C, sealed in a glass ampoule. D_3PO_4 was made from P_4O_{10} and D_2O.

Manipulations were carried out under dry nitrogen or on a vacuum line equipped with greaseless stopcocks. Reaction mixtures for NMR analysis were sealed in 4 mm glass tubes. ^1H and ^{19}F NMR spectra were recorded on a Varian EM 390 spectrometer operating at 90.00 and 84.67 MHz, respectively, and ^{13}C NMR spectra on a Varian FT 80A spectrometer at 20.0 MHz. Positive chemical shifts refer to high frequencies relative to the standards, TMS (^1H, ^{13}C) and $CFCl_3$ (^{19}F). Infrared spectra of volatile compounds were recorded in 20 cm gas cells equipped with KBr or polyethylene windows on a Perkin–Elmer 580B instrument between 180 and 4000 cm^{-1}. Raman spectra were taken on the liquids sealed in 1 mm capillaries with a Cary 82 spectrometer with Kr^+ laser excitation at 647.1 nm. Mass spectra were obtained with a Varian MAT 311 spectrometer. Masses of isotopic clusters refer to the most abundent isotope (e.g. ^{74}Ge). Vapour pressure data were obtained with a MKS Baratron BHS 315 manometer and a Pt 100 resistance thermometer.

Synthesis of trifluoromethylgermanes

$(CF_3)_3GeH$. A 500 ml flask equipped with a magnetic stirrer, a septum and a dropping funnel was charged with 100 ml of 30% phosphorous acid and connected to a vacuum line via a reflux condenser kept at −20°C. After degassing and venting with nitrogen, 20.3 g (50 mmol) of $(CF_3)_3GeI$ were added from a syringe to the ice-cooled acid. While a pressure of ca. 600 mbar was maintained, a solution of 8 g $NaBH_4$ in 80 ml H_2O was added during 1 h, and the evolved condensable gases were collected in two −196°C traps. Fractional condensation followed by isothermal distillation at 0°C using a slit tube column yielded 11.3 g $(CF_3)_3GeH$, unreacted $(CF_3)_3GeI$ (4 g), and small amounts of $(CF_3)_3GeH_2$.

MS: 263 $(CF_3)_2(CF_2)GeH$ (10), 213 $(CF_3)_2GeH$ (60), 181 CF_3GeF_2 (5), 163 CF_3GeHF (90), 143 CF_3Ge (20), 119 C_2F_5 (7), 113 F_2GeH (68), 101 C_2F_4H (20), 93 GeF (100), 75 GeH (6), 74 Ge (15), 69 CF_3 (60), 51 CF_2H (90).

$(CF_3)_2GeH_2$ and CF_3GeH_3 were obtained by a similar procedure with yields exceeding 90%.

$(CF_3)_2GeH_2$. MS: 195 $(CF_3)(CF_2)GeH_2$ (10), 163 CF_3GeHF (11), 145 CF_3GeH_2 (95), 143 CF_3Ge (25), 113 F_2GeH (25), 95 $FGeH_2$ (55), 93 GeF (100), 83 C_2F_3H, 75 GeH (50), 74 Ge (30), 69 CF_3 (8), 51 CF_2H (20).

CF_3GeH_3. MS: 145 CF_3GeH_2 (10), 144 CF_3GeH (15), 143 CF_3Ge (20), 93 GeF (80), 77 GeH_3 (100), 75 GeH (25), 74 Ge (20), 69 CF_3 (25), 51 CF_2H (25).

The partly deuterated compounds $(CF_3)_2GeHD$, contaminated with 24% $(CF_3)_2GeH_2$ and 2% $(CF_3)_2GeD_2$ were obtained from $(CF_3)_2GeI_2$, H_3PO_4 and $NaBD_4$. The corresponding reaction of CF_3GeI_3 with $NaBD_4/H_3PO_4$ yielded a sample containing 35% CF_3GeH_3, 50% CF_3GeH_2D and 15% CF_3GeHD_2, whereas use of $NaBH_4/D_3PO_4$ resulted in 16% CF_3GeH_2D, 72% CF_3GeHD_2 and 12% CF_3GeD_3, the compositions being determined by NMR analysis.

$(CF_3)_2GeHBr$. 2.3 g (6.2 mmol) $(CF_3)_2GeBr_2$ in 48% HBr solution were reacted with an excess of $NaBH_4$ as described above, solution and reflux condenser being kept at ambient temperature. After fractional condensation the products were separated by gas chromatography on a SE 30 1/4″ × 6′ column (gas chromatograph Varian 3700), yielding 0.48 mmol of $(CF_3)_2GeHBr$.

MS: 225 CF_3GeHBr (100), 175 FGeHBr (28), 155 GeBr (56), 113 F_2GeH (16), 93 GeF (64), 74 Ge (16), 69 CF_3 (22), 51 CF_2H (94).

$(CF_3)_2GeHCl$. 280 mg (0.96 mmol) $(CF_3)_2GeHBr$ were condensed on 2 g freshly prepared AgCl and the mixture was shaken at room temperature for 2 h, after which the process was repeated with a fresh charge of AgCl. Fractional condensation yielded 205 mg (86%) $(CF_3)_2GeHCl$.

MS: 229 $(CF_3)(CF_2)GeHCl$ (6), 179 CF_3GeHCl (100), 163 CF_3GeHF (20), 129 FGeCl (35), 109 GeCl (59), 93 GeF (68), 74 Ge (21), 69 CF_3 (39), 51 CF_2H (98).

$(CF_3)_2GeHF$. 180 mg (0.62 mmol) $(CF_3)_2GeHBr$ were condensed on 1.2 g freshly prepared AgF which had been dried and degassed at 50°C and 10^{-4} mbar for 24 h. After fractional condensation 120 mg (84%) $(CF_3)_2GeHF$ were obtained. Mol.weight (gas phase) 228.7 (calcd. 230.6).

MS: 213 $(CF_3)(CF_2)GeHF$ (6), 163 CF_3GeHF (100), 113 F_2GeH (46), 93 GeF (80), 74 Ge (12), 69 CF_3 (26), 51 CF_2H (62).

$(CF_3)_2GeHI$ was obtained from repeated cocondensation of 440 mg (1.5 mmol) $(CF_3)_2GeHBr$ and an excess of HI. Separation was achieved by trap-to-trap condensation yielding 330 mg (65%) $(CF_3)_2GeHI$.

MS: 340 $(CF_3)_2GeHI$ (71), 271 CF_3GeHI (100), 221 FGeHI (25), 220 FGeI (9), 201 GeI (50), 93 GeF (50), 74 Ge (10), 69 CF_3 (13), 51 CF_2H (47).

$(CF_3)(CF_2H)GeH_2$. The hydrogenation of CF_3GeI_3 (6.35 g, 12.2 mmol) was carried out as described above for $(CF_3)_3GeH$, however without cooling. Product separation was by fractional condensation. The −96°C trap retained CF_3GeH_2I, $(CF_3)(CF_2H)GeH_2$ and traces of $(CF_3)(CF_2H)GeHI$, $(CF_3)(CF_2H)GeI_2$ and CF_3GeHI_2.$(CF_3)(CF_2H)GeH_2$ was purified by GLC yielding 260 mg (11%).

MS: 177 $(CF_2)(CF_2H)GeH_2$ (0.7), 145 CF_3GeH_2 (98), 127 $(CF_2H)GeH_2$ (26), 93 GeF (100), 82 C_2F_3H (23), 75 GeH (30), 74 Ge (10), 69 CF_3 (5), 51 CF_2H (35).

$(CF_3)_2GeI(CH_3)$. To a stirred solution of 12 g (26 mmol) $(CF_3)_2GeI_2$ in 30 ml n-butyl ether, a solution of 1.8 g (12.6 mmol) $(CH_3)_2Cd$ in 20 ml n-butyl ether was added during 30 min. Distillation yielded 4.3 g (12.2 mmol, 47%) $(CF_3)_2GeI(CH_3)$.

MS: 354 $(CF_3)_2GeI(CH_3)$ (38), 339 $(CF_3)_2GeI$ (11), 285 $CF_3GeI(CH_3)$ (100), 235 $FGeI(CH_3)$ (60), 177 $CF_3GeF(CH_3)$ (27), 127 $GeF_2(CH_3)$ (28), 93 GeF (10). IR: 2970m, 2940m, 1417m, 1257m, 1189vs, 1164vs, 1130vs, 1106s, 816s, 728m, 617m, 525w, 320s.

Raman: 2930mp, 1415vwp, 1258wp, 1183wp, 1157w, 1120vw, 1105vw, 838vw, 813vwp, 724mp, 617mp, 523w, 318w, 289mp, 248mp, 237vw, 210vsp, 188vwp, 144m, 85sh, 73s.

$(CF_3)_2GeH(CH_3)$ was obtained in 85% yield from $(CF_3)_2GeI(CH_3)$ and $NaBH_4$ as described above.

MS: 209 $(CF_3)(CF_2)GeH(CH_3)$ (1), 177 $CF_3GeF(CH_3)$ (6), 159 $CF_3GeH(CH_3)$ (55), 127 F_2GeCH_3 (16), 109 $FGeH(CH_3)$ (100), 93 GeF (35), 89 $GeCH_3$ (30), 74 Ge (4), 51 CF_2H (10).

Reactions of $(CF_3)_nGeH_{4-n}$ $(n = 1, 2)$ *with* $CH_3I/(CH_3)_2Zn$

To 1.15 mmol of CF_3GeH_3 were condensed 1.15 mmol CH_3I and 1.15 mmol $(CH_3)_2Zn$. A white solid separated when the mixture was warmed to room temperature. Analysis of the volatile materials yielded 1.3 mmol CH_4, 0.38 mmol unreacted CF_3GeH_3, 0.44 mmol $CF_3GeH_2(CH_3)$, 0.24 mmol $CF_3GeH(CH_3)_2$, 0.09 mmol $CF_3Ge(CH_3)_3$ and 0.17 mmol unreacted $(CH_3)_2Zn$. Hydrolysis of the non-volatile residue yielded 0.55 mmol CH_4. Separation was achieved by fractional condensation.

$CF_3GeH_2(CH_3)$. MS: 160 $CF_3GeH_2(CH_3)$ (4), 159 $CF_3GeH(CH_3)$ (5), 143 CF_3Ge (10), 109 $FGeH(CH_3)$ (42), 93 GeF (72), 89 $GeCH_3$ (100), 75 GeH (34), 74 Ge (44), 69 CF_3 (12).

$CF_3GeH(CH_3)_2$. MS: 159 $CF_3GeH(CH_3)$ (3), 158 CF_3GeCH_3 (2), 143 CF_3Ge (2), 123 $FGe(CH_3)_2$ (30), 109 $FGeH(CH_3)$ (33), 105 $GeH(CH_3)_2$ (100), 93 GeF (20), 89 $GeCH_3$ (45), 75 GeH (6), 74 Ge (8), 69 CF_3 (3). Utilizing $CD_3I/(CH_3)_2Zn$ yielded CD_3H/CH_4 (IR analysis), $CF_3GeH_2(CH_3)/CF_3GeH_2(CD_3)$ (0.72/0.28), $CF_3GeH(CH_3)_2/CF_3GeH(CH_3)(CD_3)/CF_3GeH(CD_3)_2$ (0.56/0.37/0.07) and $CF_3Ge(CH_3)_3/CF_3Ge(CH_3)_2(CD_3)/CF_3Ge(CH_3)(CD_3)_2/CF_3Ge(CD_3)_3$ (0.41/0.38/0.17/0.03), relative abundancies given in parentheses being determined by relative peak heights of the CF_3 NMR signals. Hydrolysis of the residue gave only CH_4.

Similarily, $(CF_3)_2GeH_2$, CD_3I and $(CH_3)_2Zn$ yielded $(CF_3)_2GeH(CH_3)/(CF_3)_2GeH(CD_3)$ (0.68/0.32) and $(CF_3)_2Ge(CH_3)_2/(CF_3)_2Ge(CH_3)(CD_3)/(CF_3)_2Ge(CD_3)_2$ (0.37/0.46/0.17).

A reaction mixture of 0.60 mmol CF_3GeH_3, 0.45 mmol CH_3I and only 0.10 mmol $(CH_3)_2Zn$ yielded iodogermanes, the product composition being $CF_3GeH_2(CH_3)$ (25%), CF_3GeH_2I (13%), $CF_3GeH(CH_3)_2$ (4.5%), $CF_3GeHI(CH_3)$ (5%), CF_3GeHI_2 (2.5%), $CF_3Ge(CH_3)_3$ (3%), $CF_3GeI(CH_3)_2$ (14%), $CF_3GeI_2(CH_3)$ (9%), and CF_3GeI_3 (24%).

Derivatization of CF_3GeH_3 with $(C_2H_5)_2Zn$ and slight excess of C_2H_5I yielded 35% of $CF_3GeH_2(C_2H_5)$ ($\delta(CF_3)$ −51.3 ppm, ^3J(HF) 7.3 Hz), 20% $CF_3GeH(C_2H_5)_2$ ($\delta(CF_3)$ −53.8 ppm, ^3J(HF) 6.8 Hz) and 30% CF_3GeI_3 ($\delta(CF_3)$ −68.5 ppm). The ^1H NMR spectrum showed the non-resolved ethyl resonances around 1.2 ppm as well as C_2H_6 at 0.87 ppm (referenced to $\delta(CF_3GeH_3)$ 4.27 ppm). With $CF_3GeH_3/(C_2H_5)_2Zn/CH_3I$ all above mentioned CF_3 resonances attributed to methyl- and ethyl-containing species were observed and both CH_4 and C_2H_6 were evolved. In contrast, use of the combination $CF_3GeH_3/(CH_3)_2Zn/C_2H_5I$ led only to methylated germanes.

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