δ 1.60. This peak disappeared as the ethyl peaks of C_2H_5OH and a small somewhat broad peak appeared (δ 3.14). That the latter peak is characteristic of the $(Ph_3P)_2CuH_3BCO_2H$ complex suggests that the overall reaction sequence is simply the hydrolysis of eq 6. This reaction may actually be an equilibrium although, under the described condition, it appears to proceed substantially to the right.

$$(Ph_3P)_2CuH_3BCOOC_2H_5 + H_2O \rightarrow (Ph_3P)_2CuH_3BCOOH + C_2H_5OH \quad (6)$$

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Registry No. $(Ph_3P)_3AgBH_4$, 68630-67-1; $(Ph_8P)_3AgH_3BCO_2C_2H_5$, 68630-68-2; $(Ph_3P)_3AgH_3BCO_2H$, 68630-69-3; $(Ph_3P)_2CuBH_4$, 16903-61-0; $(Ph_3P)_2CuH_3BCO_2C_2H_5$, 53395-65-6; $(Ph_3P)_2CuH_3BCO_2CH_3$, 68630-70-6; $(Ph_3P)_2CuH_3BCO_2H$, 68630-71-7; $K^+H_3BCO_2C_2H_5^-$, 33752-75-9; $(Ph_3P)_3CuCl$, 15709-76-9; $(Ph_3P)_4CuF$, 68630-72-8.

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Trifluoromethylthio and Trifluoromethylseleno Derivatives of Germane and Digermane[1]

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Reactions of halogenogermanes with $Hg(ECF_3)_2$ (E = S or Se) provide a route to the compounds GeH_3ECF_3 and $GeH_2(ECF_3)_2$. The latter in particular exhibit unusual thermal stability in comparison with related derivatives, as do the digermanes $Ge_2H_5ECF_3$ prepared by reaction of the mercury(II) salts in diethyl ether with digermanyl iodide in situ at −63 °C. IR, Raman, mass spectrometric, and ^1H and ^{19}F NMR data are reported and discussed for the new compounds.

Introduction

Questionable thermal stability has continued to be associated with derivatives of germane embodying germanium–chalcogen bonds since the classic difficulties encountered in isolating digermyl oxide,[2] a congener of dimethyl ether. While it has been reported that $O(GeH_3)_2$ and also methoxygermane, GeH_3OMe, undergo decomposition at 0 °C, sulfur- and selenium-containing analogues appear to be less thermally labile:[3] digermyl selenide[4] is said[5] to be unchanged after 6 days in the liquid phase at ambient temperature, although under similar conditions yellowing of a range of methylseleno species related to $Me_3GeSeMe$ has been noted.[6]

Our conclusion that the instability of digermyl oxide may have been overestimated[7] has provided a basis for a continuing interest in this area. In the present paper we report the synthesis of (trifluoromethylthio)germane and its selenium analogue GeH_3ECF_3 (E = S or Se) in which it might be anticipated that the strong electron-withdrawing character of the CF_3 group might effect spectroscopic properties and chemical stability.

Germylene dihalides, GeH_2X_2 (X = F, Cl, Br, or I), decompose much more readily than the corresponding germyl halides GeH_3X, and efforts to produce the disubstituted derivatives GeH_2Y_2 in which Y is a pseudohalogeno group bound through the nitrogen atom have met with failure.[8] By contrast we have been able to isolate the compounds $GeH_2(ECF_3)_2$ (E = S or Se); these are the first examples of well-characterized germylenedichalcogeno derivatives, although $(GeH_3Se)_2GeH_2$ has been tentatively identified[8] as a condensation product between SeH_2 and $Se(GeH_3)_2$.

Little is known about the substitution chemistry of digermane[2,9] and of the very restricted range of compounds Ge_2H_5Y (Y = F, Cl, Br or I,[10] Me or Et,[11] or $Mn(CO)_5$[12]); those in which Y is an electron-withdrawing center, the halides, exhibit the lowest thermal stability decomposing rapidly at ambient temperature.[10] We have found that at low temperature Ge_2H_5I can be converted in high yield to give the products $Ge_2H_5ECF_3$ (E = S or Se), novel examples of digermane derivatives incorporating germanium–chalcogen bonds which possess good thermal stability.

Experimental Section

Details of relevant manipulative techniques and the synthesis of germane and of halogenogermanes have been given previously.[2,7] Digermane[13] was iodinated at −63 °C as described[10] by Mackay and Roebuck. Samples of the trifluoromethylthio salts of silver(I) and mercury(II) were obtained according to literature preparations.[14,15] New compounds were fully characterized using spectroscopic methods (vide infra).

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IR spectra were measured using a Perkin-Elmer 283 instrument; Raman spectra from 488.0 nm (argon ion laser) were recorded with a J-Y Ramanor HG2 S spectrometer. NMR measurements including proton–proton decoupling experiments were performed using a Perkin-Elmer R32 instrument, and mass spectra were obtained with a Perkin-Elmer/Hitachi RMU 7E unit.

(a) Synthesis of Compounds. Bis(trifluoromethylseleno)mercury(II). This material was prepared using a modification of literature procedures.[16,17] Typically, a mixture of SeO_2 (5.00 g) and $O(OOCCF_3)_2$ (4.20 g) was heated at 260 °C for 17 h in a Carius tube. Fractionation of volatile products yielded $Se(CF_3)_2$ (2.10 g) at −127 °C and $Se_2(CF_3)_2$ (0.12 g) at −78 °C, characterized by IR and mass spectra.[17] In a Carius tube $Se(CF_3)_2$ (3.08 g) obtained in this way and Cl_2 (2.20 g) were allowed to react in sunlight for 72 h. Removal of volatiles left quantitatively white, solid $Se(CF_3)Cl_3$, which on shaking for 1 h with excess Hg metal in an evacuated ampule was converted to $Se_2(CF_3)_2$. (During this reaction both liquid and gaseous phases became red-brown owing to the formation of $Se(CF_3)Cl$, identified by IR, and then colorless.) Finally a sample of $Se_2(CF_3)_2$ (ca. 2.0 g) was sealed with excess Hg (ca. 1.5 cm^3) in an evacuated quartz Carius tube and shaken under a medium-pressure UV lamp for 4 days. Subsequent extraction with dry diethyl ether gave colorless $Hg(SeCF_3)_2$ (90%) purified by sublimation in vacuo at 25 °C; mp 51 °C.

(Trifluoromethylthio)germane. A mixture of acid-washed, dried sand (ca. 30 cm^3) and $Hg(SCF_3)_2$ (820 mg, 2.04 mmol) was placed in a U-column and attached to a vacuum manifold.[6] Iodogermane (175 mg, 0.86 mmol) was streamed through the column leaving a yellow then bright orange coloration. The colorless, liquid product (105 mg, 0.60 mmol), separated by trap-to-trap fractionation, passed through the −73 °C trap and was collected at the −95 °C trap. Reaction between GeH_3Br and $AgSCF_3$ afforded the same compound.

(Trifluoromethylseleno)germane. Reaction as described above between GeH_3I (410 mg, 2.02 mmol) and $Hg(SeCF_3)_2$ (672 mg, 1.35 mmol) gave unchanged iodogermane at −78 °C and colorless product at −95 °C (346 mg, 1.56 mmol), purified by repeated condensation at −83 °C. An inseparable mixture of the same compound and GeH_3Br was obtained when the latter was passed through a column containing a twofold molar excess of the mercury salt.

Bis(trifluoromethylthio)germane. On allowing GeH_2Br_2 (137 mg, 0.58 mmol) to react with $Hg(SCF_3)_2$ (560 mg, 1.39 mmol) we collected the colorless product (110 mg, 0.40 mmol) and purified it by repeated condensation at −78 °C.

Bis(trifluoromethylseleno)germane. Reaction between GeH_2I_2 (207 mg, 0.63 mmol) and $Hg(SeCF_3)_2$ (700 mg, 1.41 mmol) yielded the colorless liquid product (217 mg, 0.59 mmol) which condensed at −78 °C; vapor pressure at 25 °C was ca. 0.7 mmHg. A similar reaction using GeH_2Br_2 afforded a mixture of the same product and bromo(trifluoromethylseleno)germane which could not be completely separated.

(Trifluoromethylthio)digermane. At −78 °C a solution of $Hg(SCF_3)_2$ (178 mg, 0.44 mmol) in dry diethyl ether (1.5 cm^3) was added against a countercurrent of nitrogen gas to Ge_2H_5I, prepared from digermane (144 mg, 0.96 mmol). The reaction vessel was reevacuated and the mixture maintained at −63 °C with occasional shaking for 3 h. Fractionation then afforded the colorless product (252 mg, 0.85 mmol) condensed in a trap held at −63 °C.

(Trifluoromethylseleno)digermane. Addition of $Hg(SeCF_3)_2$ (250 mg, 0.50 mmol) in dry diethyl ether (2.0 cm^3) to Ge_2H_5I (from Ge_2H_6, 160 mg, 1.07 mmol) in an identical manner to that described above yielded colorless liquid product recovered virtually quantitatively at −78 °C.

(b) Thermal Stability of Products. All the new derivatives were stable at ambient temperature in the liquid phase in vacuo over at least 24 h, although slight yellowing of the selenium-containing compounds was sometimes encountered. After 14 days in a glass capillary at 25 °C, GeH_3SCF_3 (29 mg, 0.16 mmol) was unchanged and showed no noticeable signs of decomposition on heating to 110 °C for 12 h. After 72 h at 110 °C, a metallic mirror had been deposited and volatile products (IR) were GeH_4 and SCF_2; after 3 h at 110 °C, GeH_3SeCF_3 (36.0 mg, 0.16 mmol) had deposited a black mirror, the only volatile product being CHF_3 (IR).

Results and Discussion

Reactions of halogenosilanes with argentous salts constitute an important route to a range of silane derivatives.[18] This situation is paralleled in the chemistry of germane, in which context the utility of lead(II) as well as silver(I) and mercury(II) salts has been established.[7] Accordingly, we have found that iodogermane reacts smoothly with bis(trifluoromethylthio)mercury(II) and its selenium analogue to give the chalcogenogermanes GeH_3ECF_3 (E = S or Se) in high yield; with diiodogermane the corresponding disubstituted species $GeH_2(ECF_3)_2$ were obtained. The new germane derivatives are colorless, volatile liquids with low melting points and exhibit high thermal stability in clean evacuated glass systems. Experiments using bromogermanes afforded the same compounds less reliably for E = S and gave mixtures of products for E = Se, developing an analogy to the "silver salt conversion" series for substituted silanes[18] with SCF_3 lying to the right of Br (and I) and $SeCF_3$ very close to Br. Preliminary experiments involving GeH_3X (X = Br or I) with potassium or cesium trifluoromethoxides[19] yielded only fluorinated germanes.

As was encountered in earlier related reactions,[10] on streaming digermanyl iodide through a column containing $Hg(SCF_3)_2$ extensive decomposition occurred, and only traces of a substitution product were obtained. However, in situ addition to Ge_2H_5I at −63 °C of a solution in ether of $Hg(ECF_3)_2$ (E = S or Se) afforded the digermanes $Ge_2H_5ECF_3$ in excellent yield, compounds which extend the range of such simple monosubstituted products beyond the alkyls[11] and halides[10] and show very much higher thermal stability than the latter.

Thermal decomposition of GeH_3SCF_3 took place only after prolonged heating at 110 °C, giving GeH_4 and SCF_2; GeH_3SeCF_3 degraded differently, to CHF_3 and (presumably) metallic Ge and Se. A brief survey of the chemistry of these compounds showed the anticipated results: for example, $GeH_2(SeCF_3)_2$ with HCl at ambient temperature gave the cleavage products GeH_2Cl_2 and $HSeCF_3$ while reaction between GeH_3SCF_3 and $SnCl_4$ at 32 °C observed using ^{19}F NMR generated a single resonance consistent with either cleavage (to CF_3SCl) or substitution (to $GeCl_3SCF_3$). Reaction occurred with PPh_3, but no sensible products could be isolated.

The new compounds could be characterized definitively by mass spectrometry, qualitative analysis of the data being facilitated by the polyisotopic nature of germanium (and also selenium). Combination of the latter with successive hydrogen loss complicates examination of the fragmentation,[7,11] but some general observations are unequivocal.[31] Dominant ions are GeH_x^+ and GeH_xE^+ for the monogermanes with analogous $Ge_2H_x^+$ and $Ge_2H_xE^+$ families in addition for the digermanes; in the latter ca. 25% ion current was carried by fragments in which the Ge–Ge bond nominally remained intact. For GeH_3ECF_3, the molecular ion family is much more abundant for E = Se (16.5%) than for E = S (4.5%) and the same is true of the digermanes (E = Se, 5.2%; E = S, <0.5%) while for $GeH_2(ECF_3)_2$ molecular ion abundances were 4.3% (S) and 0.4% (Se). Of the non-germanium-containing fragments, the most intense arose from ECF_2^+ and ECF^+. Transfer of F to Ge gave rise to GeH_xF^+ as a prominent rearrangement ion in all the spectra with indications of H transfer to S or Se.

NMR Spectra: ^{1}H and ^{19}F. Data for the monogermane derivatives are set out in Table I and data for the digermanes and some related compounds in Table II. It has previously been shown that the behavior of the digermanyl group approximates to that of an a_3x_2 system,[10,11,20] and since there is a large separation between ^1H and ^{19}F resonance frequencies, all the experimental spectra should be first order. "Satellite" resonances due to the magnetically active ^{77}Se isotope ($I = {}^1/_2$, 7.58% abundance) were found in ^1H and ^{19}F spectra of appropriate compounds.

Table I. NMR Data (^1H and ^{19}F) for Germane Derivatives

	chemical shifts[a]		coupling constants, Hz		
compound	$\tau(GeH_3)$	$\phi(CF_3)$	$^4J(^{19}F-H)$	$^2J(^{77}Se-H)$	$^2J(^{77}Se-^{19}F)$
H_3GeSCF_3	5.51	33.0	1.85		
$H_2Ge(SCF_3)_2$	4.11	28.0	2.10		
$H_3GeSeCF_3$	5.50	25.5	1.60	15.6	25.5
$H_2Ge(SeCF_3)_2$	4.04	24.3	1.94	18.0	*d*
$H_2Ge(SeCF_3)Br$[b]		24.1[c]			

[a] Neat liquid samples; τ (±0.03) vs. external $CDCl_3/Me_4Si$ (^1H) or ppm upfield from $CFCl_3$ (^{19}F). [b] Product not isolated (see Experimental Section); identified by ^{19}F NMR. [c] Triplet, $J = 2.10$ Hz. [d] Not observed.

Table II. NMR Data (^1H and ^{19}F) for (Trifluoromethylthio)digermane, (Trifluoromethylseleno)digermane, and Related Compounds

	chemical shifts[a]			coupling constants, Hz				
compound	$\tau(GeH_3)$	$\tau(GeH_2)$	$\phi(CF_3)$	$^3J(H-H)$	$^4J(^{19}F-H)$	$^5J(^{19}F-H)$	$^2J(^{77}Se-H)$	$^2J(^{77}Se-^{19}F)$
$Ge_2H_5SCF_3$	6.34	5.09	29.4	3.85	1.85	1.50		
$Ge_2H_5SeCF_3$	6.20	5.26	28.2	3.85	1.60	1.30	17.3	27.3
$Ge_2H_5CH_3$[b]	6.79	6.42		3.9				
Ge_2H_5I[c]	5.96	6.57		4.3				
Ge_2H_5Br[c]	6.21	5.31		4.1				
Ge_2H_5Cl[c]	6.37	4.61		4.1				

[a] Cf. Table I for experimental details. [b] Reference 11. [c] Reference 10.

Simple quartet/quartet or septet/triplet structures were clearly resolved in $^1H/^{19}F$ spectra of GeH_3ECF_3 and $GeH_2(ECF_3)_2$ (E = S or Se), respectively. For the former compounds the chemical shifts are close to those reported for silyl analogues,[21] while a substantial downfield shift in the GeH resonance accompanies disubstitution, as has been found for halogenogermanes.[22] The well-established electron-withdrawing character of the CF_3 group does not appear to be reflected by enhanced inductive deshielding since chemical shifts for GeH_3SCH_3 (τ 5.52)[2,3] and GeH_3SeCH_3 (τ 5.81)[2,4] are close to those reported in Table I. If the present data are taken as an estimate of effective electronegativity, the SCF_3 and $SeCF_3$ groups are exerting a similar influence to that of Br, in line with electronegativities of the chalcogen atoms themselves. However, such correlations between chemical shift and electronegativity are not very consistent, and a noticeable increase in $^2J(^{77}Se-H)$ from 12.5 Hz in[24] GeH_3SeCH_3 to 15.6 Hz (Table I) may be of more significance.[21] The ^{19}F parameters are close to those available for corresponding silanes.[21]

For the digermanes, the appearance of the ^1H NMR spectra is typified by that of the selenium compound, reproduced in Figure 1. The complex multiplets observed were analyzed by double irradiation at either the GeH_2 or the GeH_3 resonance frequency, resulting in collapse of the undecoupled signal to a simple quartet through coupling to the CF_3 group. In both compounds the GeH_3 protons resonate well to high field of those of the GeH_2 group; $\Delta_{ax} = \delta(GeH_3) - \delta(GeH_2) = 1.25$ and 0.94 ppm, respectively, for the sulfur and selenium derivatives, which if interpreted in terms of electronegativity effects[20] locates these substituents between Cl ($\Delta_{ax} = 1.76$ ppm) and Br (0.90 ppm), paralleling the empirical relation provided by the data for the monogermanes. Calculation of the so-called[25] "catenation shifts", Δ^X_{MM} = [($\delta(MH_3)$ in MH_3X) − ($\delta(MH_2)$ in MH_3MH_2X)], gives "germanium–germanium bond shifts"[21] Δ^X_{GeGe} of 0.42 ppm for for X = SCF_3 and 0.24 ppm for $SeCF_3$. The first of these values well exceeds those given for the digermanyl halides, and the second lies close to that for X = Cl,[21] so that from the foregoing discussion it is clear that Δ^X_{MM} may not be closely related to the effective electronegativity of X. Through-space distances from fluorine to hydrogen in either germyl or germylene groups will not be markedly different, and this may account for the similarity of the $^4J_{HF}$ and $^5J_{HF}$ couplings.

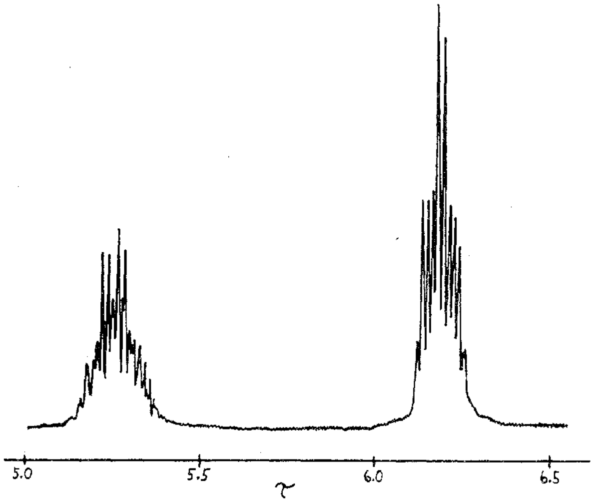

Figure 1. Proton NMR spectrum, 90 MHz, of (trifluoromethylseleno)digermane.

Vibrational Spectra. Data are listed in Tables III (germane derivatives) and IV (digermanes). Only the disubstituted germanes (C_{2v}) possess more symmetry elements than E and σ_v (C_s) so that assignments are restricted to approximate description of the vibrations. Also as a result of this situation, depolarization ratios for Raman shifts were not very informative except in relation to stretching vibrations of the skeletal framework. However, in the IR of GeH_3ECF_3(E = S or Se), in-plane (symmetric) components did give rise to conspicuously type-A contours (Table III) as expected from the form of these modes. In the following discussion vibrations of the GeH_3 group, the CF_3 group, and of the skeletal framework are examined consecutively.

Features associated with GeH stretching are conspicuous near 2100 cm^{-1} in all the spectra, the symmetric components where distinguishable being found at lowest energy. The intense type-A IR absorptions near 800 cm^{-1} for GeH_3ECF_3 (E = S or Se) arising from the symmetric GeH_3 deformation are replaced by similarly strong bands at 730 and 706 cm^{-1} in $GeH_2(ECF_3)_2$ which are the out-of-plane GeH_2 bends (b_2 under C_{2v}). For the digermanes two such absorptions occur; that at 787 cm^{-1}, insensitive to the nature of E, can be assigned to the symmetric deformation of the GeH_3 group while the other (691 cm^{-1}, E = S; 672 cm^{-1}, E = Se) is the GeH_2 wagging vibration. For a range of substituted silanes and germanes, relationships have been discerned between the

Table III. Vibrational Spectra (cm^{-1}) of Germane Derivatives[a]

GeH_3SCF_3		GeH_3SeCF_3		$GeH_2(SCF_3)_2$		$GeH_2(SeCF_3)_2$		
IR	Raman	IR	Raman	IR	Raman	IR	Raman	approx description
2134 Q s	2128 w, sh	2129 s, sh	2135 m, sh	2141 m	2145 w, br	2127 m, sh	2133 w, br	ν_{asym}(GeH)
2121 R		2120 R		2121 s	2121 s	2102 m	2107 s	ν_{sym}(GeH)
2117 Q vs	2109 s	2114 Q vs	2110 vs					
2112 P		2110 P						
1222 w, br								
1196 w, br				1199 w, sh				
						1169 s, sh		
1164 vs			1156 vvs	1171 vs		1164 vvs		ν_{asym}(CF)
1140 vs			1147 Q vvs	1146 R vs		1121 R vs		
				1138 P		1114 P		
1122 R		1111 R						
1116 Q vvs	1102 vw, br	1108 Q vvs	1105 w	1110 vvs	1105 vw	1105 vs	1105 vw	ν_{sym}(CF)
1112 P		1104 P						
1090 vw, br						1066 m	1077 vw	
		1067 m				1040 w		
				906 w, br				
		882 w, sh						
876 m	867 w, br	873 m, sh	875 m, br					δ_{asym}(GeH_3)
874		863 m						
838 m		835 m		832 m	827 m, br	834 m	834 m, br	δ(GeH_2) (twist)
836								
821 R		809 R						
818 Q vs	806 w, br	804 Q vs	803 w, br					δ_{sym}(GeH_3)
814 P		801 P						
762 R		746 R						
757 Q m	755 s	740 Q m	747 s	753 m, sh	758 s	743 m, sh	748 s	δ_{sym}(CF_3)
752 P		735 P				730 m		
				730 vs	728 w, br	706 s	708 w	δ(GeH_2)(wag)
597 vw, br	598 vw, br	560 w, br	565 w, br	580 w, br			660 w, br	δ_{asym}(CF_3) + ρ(GeH_3) or ρ(GeH_2)
592							540 vw, br	
465 w, br	461 w, br							
					460 m, br			ν_{asym}(GeS_2)
	414 s				417 s			
			333 s				330 s	ρ(CF_3)
			314 s				311 m	
							293 m	ν_{asym}($GeSe_2$)
	279 s		252 vs		274 vs		250 s, sh	ν(GeE) or ν_{sym}(GeE_2)[b]
							241 vvs	
	117 m							

[a] IR, gas phase; Raman, neat liquid. [b] E = S or Se.

Table IV. Vibrational Spectra (cm^{-1}) of (Trifluoromethylthio)digermane and (Trifluoromethylseleno)digermane[a]

$GeH_3GeH_2SCF_3$		$GeH_3GeH_2SeCF_3$		
IR	Raman	IR	Raman	approx description
2104 s, sh	2096 s	2102 s, sh	2085 m	ν(GeH)
2082 vs	2074 s	2081 vs	2078 vs	
1164 vs				ν(CF)
1146 R } vs		1154 vs		
1136 P		1107 vs		
1116 vs		1070 m	1090 vw	
925 vw, br		930 w, br		$\delta(GeH_2)$(scissors)
		876 m		$\delta_{asym}(GeH_3)$
868 m, br	859 s	859 m	854 m, br	
787 s		787 vs		$\delta_{sym}(GeH_3)$
756 740 } w	761 m	740 m	739 m	$\delta_{sym}(CF_3)$
691 vs		672 vs		$\delta(GeH_2)$(wag)
			617 w, br	$\rho(GeH_3) + \rho(GeH_2)$
	517 w			
491 w				
466 w	459 w	470 w, br		
	417 w		330 m	$\rho(CF_3)$
			312 w	
	269 vs		274 s	ν(GeGe) and ν(GeS) or ν(GeSe)[b]
	256 s, sh		232 vvs	
			100 m	skel def
			77 m	

[a] IR, gas phase; Raman, neat liquid. [b] See text for discussion of these bands.

Table V. Relative Energy (cm^{-1}) of GeH Deformation Vibrations

	F	Cl	Br	SCF_3	I	$SeCF_3$	
GeH_3X	859	848	832	818	806	804	$\delta(GeH_3)$
GeH_2X_2	814	779	754	730	708	706	$\delta(GeH_2)$ (wag)
GeH_3GeH_2X	754	721	704	691	681	672	$\delta(GeH_2)$ (wag)

energy of these bending vibrations and the substituent volume and electronegativity.[26,27] Comparison (Table V) of the current data with those presented elsewhere leads consistently to the conclusion that in this respect the $SeCF_3$ group exerts an influence similar to that of I while SCF_3 is intermediate between I and Br and suggests a relationship with substituent mass or size. As for related compounds,[28] C–F stretching modes give rise to extremely strong IR absorption (1100–1200 cm^{-1}) and disappearingly weak Raman shifts. A feature consistently near 750 cm^{-1} showing as a type-A IR contour in GeH_3ECF_3 (E = S or Se) is confidently assigned to the symmetric CF_3 deformation. Related bending modes are less distinctive.

The skeletal Ge–E or Ge–Ge bond-stretching vibrations were identified in the Raman effect and were clearly distinguishable from CF_3 rocking modes, which appear in the same region, by comparison of the spectra. Symmetric components gave rise to shifts which were conspicuously polarized. The ν(GeS) mode at 279 cm^{-1} in GeH_3SCF_3 divides, for $GeH_2(SCF_3)_2$, into components at 274 (sym) and 460 cm^{-1} (asym), and a similar smaller splitting occurs for the selenides from 252 to 241 (sym) and 293 cm^{-1} (asym). The lowering of ν(GeSe) from 290 cm^{-1} in GeH_3SeMe[24] may arise through increased mass of the alkyl group or may reflect weakening of the bond by removal of electron density to the CF_3 center. The Raman spectrum of $Ge_2H_5SeCF_3$ (Figure 2) contains two shifts in the 200–300 cm^{-1} range of which that at lower energy (232 cm^{-1}) is much the more intense and is strongly polarized. This is assigned to a vibration which is probably best described as ν_{sym}(GeGeSe) in view of the nearly identical atomic masses for germanium and selenium and since their electronegativities are not very different. The weaker band at higher energy (274 cm^{-1}) is then the corresponding ν_{asym}(GeGeSe). Assignments for the skeletal vibrations of polygermanes and silylgermanes[29] support this interpretation. In the sulfur analogue where Ge–Ge and Ge–S bonds possess less in common, the strong shift at 269 cm^{-1} and a weaker low-energy shoulder account for both stretching modes.

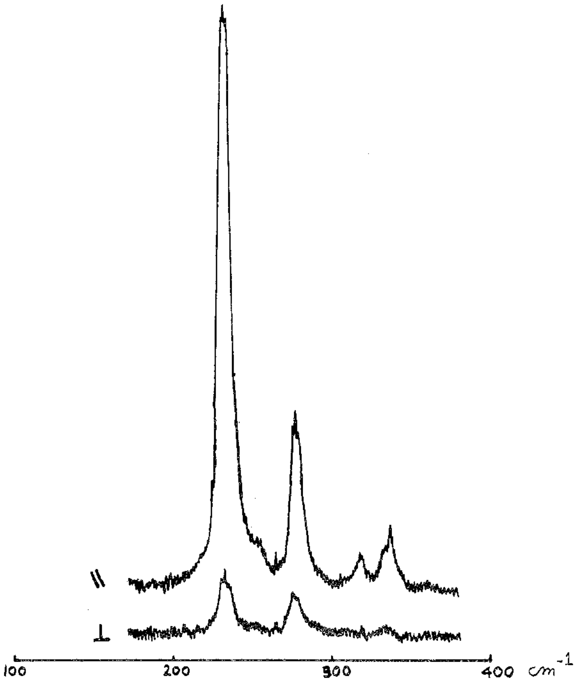

Figure 2. Raman spectrum of (trifluoromethylseleno)digermane, showing scattering with incident polarization parallel and perpendicular.

Conclusion

The new compounds described here exhibit remarkable stability: this is well illustrated by comparison of $GeH_2(SeCF_3)_2$ with $GeH_2(SMe)_2$ which is explosively unstable and has been incompletely characterized[24] and of $Ge_2H_5ECF_3$ with Ge_2H_5X (X = Cl, Br, or I).[10] Lowering of electron availability at the E atom via the influence of the CF_3 group to provide a diminished susceptibility to electrophilic attack may partly account for the observed stabilization.[30]

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Registry No. H_3GeSCF_3, 68457-15-8; $H_2Ge(SCF_3)_2$, 68457-16-9; $H_3GeSeCF_3$, 68457-17-0; $H_2Ge(SeCF_3)_2$, 68457-18-1; $H_2Ge(SeCF_3)Br$, 68457-19-2; $Ge_2H_5SCF_3$, 68457-20-5; $Ge_2H_5SeCF_3$, 68457-21-6; $Hg(SeCF_3)_2$, 60129-77-3; $Hg(SCF_3)_2$, 21259-75-6; GeH_3I, 13573-02-9; GeH_3Br, 13569-43-2; $AgSCF_3$, 811-68-7; GeH_2Br_2, 13769-36-3; GeH_2I_2, 14694-31-6; Ge_2H_5I, 19021-93-3.

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Reactions of Primary Alkylantimony Compounds. Formation of the Macromolecular Species $(RSb)_x$ and $(RSbI_{0.4})_x$

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Reactions of the primary alkylstibines CH_3SbH_2, $C_2H_5SbH_2$, and n-$C_4H_9SbH_2$ with organosilicon chlorides or HCl produce a pale green macromolecular species with a metallic sheen analyzing as $(RSb)_x$ while the same stibines with iodine-containing reagents, I_2, ICl, CI_4, and $(CH_3)_2AsI$, produce a purple-black species, $(RSbI_{0.4})_x$. With CH_3AsCl_2, the stibines yield only the all-arsenic macromolecule $(CH_3As)_x$ and $RSbCl_2$. No evidence for the formation of cyclooligomers of antimony is found.

Introduction

Low-dimensional organometallic macromolecules warrant study as potential sources of new materials with unusual electrical properties.[1] Earlier studies of a homoatomic ladder-structure catenate of arsenic, $(CH_3As)_x$,[2,3] exposed a rich variety of thermal and photoconductivity properties[4,5] that encouraged us to extend this study to antimony.

Few reports exist of compounds which analyze satisfactorily as multiples of the unit RSb; those that do are restricted to cyclooligomers with sterically demanding phenyl[6] or *tert*-butyl[7] R groups. Previous reports of high-molecular-weight organoantimony catenates invariably describe products containing excess antimony.[8,9] In two earlier papers we briefly reported procedures which provide the $(CH_3Sb)_x$ polymer, specifically the reactions of CH_3SbH_2 with dibenzylmercury[10] and with sulfur monochloride.[11] The present study concerns the reactions of primary alkylstibines with elemental halogen, halocarbons, and organometallic halides.

Since our primary interest was a study of the ability of the RSb unit to form macromolecular compositions, it was important that the primary alkylarsenic reagents be as free as possible from potentially chain-terminating dialkyl derivatives and chain-branching antimony trihalide. The results of our study of both existing and novel procedures to obtain high-purity organoantimony monomers is described in a recent review.[12]

Results

Reactions of Alkylstibines. Primary alkylstibines react rapidly with iodine, iodine monochloride, or carbon tetraiodide in benzene to form a microcrystalline purple-black solid and alkyldiiodostibine. A ^1H NMR spectrum of the reaction mixture within 1 min of combination shows a complete absence of alkylstibine. The ^1H NMR spectrum is consistent with $RSbI_2$ formation: R = Me, singlet at δ 1.84; R = Et, δ 1.95 (quartet) 1.65 (triplet) ($^3J_{HH'} = 7$ Hz). After opening of the reaction tube and removal of the purple-black solid by filtration, evaporation of solvent affords a bright yellow crystalline solid identified as $RSbI_2$. The purple-black solid showed consistent C, H, and I percentages near the empirical composition $RSbI_{0.4}$ (or $R_5Sb_5I_2$). We are seeking crystals large

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