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Synthesis and Spectroscopic Characterization of *S*-Ethyl, *S*-Isopropyl, *S*-*n*-Propyl, and *S*-*n*-Butyl Trithiocarbonate (Trixanthate) Derivatives of Trimethyl- and Triphenylgermane and Diphenyldigermane. Crystal Structure of $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$

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The *S*-alkyl trithiocarbonate (trixanthate) derivatives $Me_3Ge[S_2CSR]$, $Ph_3Ge[S_2CSR]$, and $Ph_2Ge[S_2CSR]_2$, where R = Et, *i*-Pr, *n*-Pr, and *n*-Bu, have been prepared in 73–85% yields by the reaction of the potassium salt of the appropriate trithiocarbonic (trixanthic) acid with iodotrimethylgermane, bromotriphenylgermane, or dichlorodiphenylgermane. The compounds were characterized by infrared, Raman, and ^1H and ^{13}C NMR spectroscopy. The crystal structure of $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ was determined, and it crystallizes in space group $P\bar{1}$ (No. 2) with the cell parameters $a = 10.752(9)$ Å, $b = 13.36(1)$ Å, $c = 9.64(2)$ Å, $\alpha = 105.8(1)°$, $\beta = 113.2(1)°$, $\gamma = 91.79(9)°$, $V = 1211(3)$ Å^3, and $Z = 2$; $R = 0.0638$, and $R_w = 0.0626$. The environment about germanium is essentially that of a distorted tetrahedron with monodentate linkages resulting in S–Ge–S and C–Ge–C angles of 87.3(2) and 118.1(3)°, respectively, and S–Ge–C angles ranging from 110.3(3) to 113.4(3)°. The Ge–S bond distances are 2.278(5) and 2.284(5) Å, and the Ge–C bond distances are 1.925(7) and 1.941(9) Å. The terminal (C=S) sulfur atoms are oriented toward the germanium center at distances of 3.224(5) and 3.304(5) Å. All of these trixanthate derivatives are unstable as a result of the ready elimination of carbon disulfide.

Introduction

Reports on *O*-alkyl dithiocarbonates (xanthates) as ligands, particularly on transition metals,[1,2] are considerably more extensive than those on the *S*-alkyl trithiocarbonate (trixanthate) analogues. Representative examples of work on trixanthates include earlier attempts to thoroughly characterize transition metal derivatives[3] and confirmation that trixanthates are usually bidentate[4–6] and that carbon disulfide elimination is characteristic of metal trixanthate complexes.[4,5] A logical extension of our studies on the xanthate derivatives of germanium[7–10] is to establish the existence of germanium trixanthate derivatives. Because of problems encountered on stability with other sulfur-containing germanium derivatives and the anticipated problem of compounds also undergoing CS_2 elimination, we selected organogermanium derivatives containing only one trixanthate group as the first series of compounds to be examined, namely $R'_3Ge[S_2CSR]$ in which R′ = Ph or Me and R = Et, *i*-Pr, *n*-Pr, or *n*-Bu. This was extended to include the corresponding $Ph_2Ge[S_2CSR]_2$ series.

Experimental Section

Starting Materials. Bromotriphenyl-, dichlorodiphenyl-, and iodotrimethylgermane were obtained from Alfa Products. Typically, potassium *S*-ethyl trithiocarbonate was prepared by placing KOH (4.5 g, 0.8 mmol) in a flask and adding to it a slight excess of EtSH (6.2 g, 1.0 mmol). The flask was surrounded by an ice bath, and CS_2 (approximately 7.5 mL) was added drop by drop, after which the reaction was allowed to proceed for 2 h. Ether was added with stirring in two portions of approximately 25 and 15 mL before KS_2CSEt was filtered off and dried under vacuum for 1–2 days to give an 85% yield of the trithiocarbonate salt. Its purity was then verified on the basis of its NMR and IR spectra. Potassium *S*-isopropyl, *S*-*n*-propyl, and *S*-*n*-butyl trithiocarbonates were prepared in a similar manner and their purities also verified on the basis of their NMR and IR spectra. Distilled carbon disulfide (dried over P_4O_{10}) was used in all of the reactions. These reactions and those used to prepare the germane derivatives were carried out on a vacuum line to exclude air and moisture.

Preparation of the $Ph_3Ge[S_2CSR]$ and $Me_3Ge[S_2CSR]$ Derivatives. $Ph_3Ge[S_2CSEt]$ (1). Typically, an excess of dried KS_2CSEt (0.22 g, 1.5 mmol) was placed in a flask with a side arm containing Ph_3GeBr (0.35 g, 0.91 mmol). The flask was degassed, and CS_2 (approximately 6 mL) was distilled into it at −196 °C. The liquid N_2 trap was removed, and when the flask had reached ambient temperature, Ph_3GeBr was tipped into the solution by tilting the side arm. The reaction was allowed to proceed for 4–5 h at 0 °C, at which time unreacted KS_2CSEt and the KBr that had formed were filtered off. The solvent was allowed to evaporate under vacuum to give $Ph_3Ge[S_2CSEt]$ as an oil (0.30 g, 0.69 mmol; yield 75%). The other triorganogermanium trixanthate derivatives were similarly formed in 73–85% yields by the addition of an excess of the appropriate KS_2CSR salt, where R = Et, *i*-Pr, *n*-Pr, or *n*-Bu, to Ph_3GeBr at 0 °C or Me_3GeI at −78 °C (in approximately 0.5–1.0-mmol amounts) followed by dissolution in CS_2. Thus were formed the following compounds: $Ph_3Ge[S_2CS(i\text{-}Pr)]$ (**2**), yield 85%; $Ph_3Ge[S_2CS(n\text{-}Pr)]$ (**3**), yield 77%; $Ph_3Ge[S_2CS(n\text{-}Bu)]$ (**4**), yield 78%; $Me_3Ge[S_2CSEt]$ (**9**), yield 80%; $Me_3Ge[S_2CS(i\text{-}Pr)]$ (**10**), yield 73%; $Me_3Ge[S_2CS(n\text{-}Pr)]$ (**11**), yield 75%; $Me_3Ge[S_2CS(n\text{-}Bu)]$ (**12**), yield 75%.

Preparation of the $Ph_2Ge[S_2CSR]_2$ Derivatives. $Ph_2Ge[S_2CSEt]_2$ (5). Typically, a large excess of KS_2CSEt (0.90 g, 5.1 mmol) was added to degassed Ph_2GeCl_2 (0.25 g, 0.84 mmol) dissolved in $CHCl_3$ (approximately 10 mL) in the manner described above but with the temperature held at 0 °C. The reaction was allowed to proceed for 4 h at 0 °C before the potassium chloride and unreacted xanthate salt were filtered off and the solvent was allowed to evaporate to give $Ph_2Ge[S_2CSEt]_2$ as an oil (0.32 g, 0.65 mmol; yield 77%). If a large excess of xanthate salt is not used, then a mixture of products results containing $Ph_2GeCl[S_2CSEt]$. The use of CS_2 as solvent with a reaction temperature of −78 °C gave essentially the same results. The following compounds were similarly formed: $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**), yield 78% (mp 101–103 °C); $Ph_2Ge[S_2CS(n\text{-}Pr)]_2$ (**7**), yield 79%; $Ph_2Ge[S_2CS(n\text{-}Bu)]_2$ (**8**), yield 77%. Despite extensive efforts to bring about crystallization, only **6** could be crystallized; all of

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Table 1. Crystallographic Data for $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**)

chem formula	$C_{20}H_{24}S_6Ge$	fw	529.36
a, Å	10.752 (9)	space group	$P\bar{1}$ (No. 2)
b, Å	13.36 (1)	T, °C	–30
c, Å	9.64 (2)	λ, Å	0.710 69
α, deg	105.8 (1)	ρ_{obsd}, g cm^{-3}	1.44
β, deg	113.2 (1)	ρ_{calc}, g cm^{-3}	1.45
γ, deg	91.79 (9)	μ, cm^{-1}	17.50
V, Å^3	1211 (3)	$R(F_o)^a$	0.0638
Z	2	$R_w(F_o)^a$	0.0626

[a] $R = \sum\|F_o| - |F_c|/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

Table 2. Final Fractional Coordinates and B(eq) Values for Non-Hydrogen Atoms of $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**) with Standard Deviations in Parentheses

atom	x	y	z	B(eq),[a] Å^2
Ge	0.0721(1)	–0.2471(1)	–0.2461(1)	2.15(4)
S(1)	0.1572(3)	–0.3847(2)	–0.3581(4)	3.1(1)
S(2)	0.3911(3)	–0.2593(3)	–0.0564(4)	3.6(1)
S(3)	0.4212(3)	–0.4437(3)	–0.2960(4)	3.6(1)
S(4)	–0.1296(3)	–0.3076(2)	–0.4672(4)	2.7(1)
S(5)	–0.1853(3)	–0.1136(3)	–0.2715(4)	3.2(1)
S(6)	–0.3963(3)	–0.2539(2)	–0.5837(4)	3.0(1)
C(1)	0.329(1)	–0.3538(9)	–0.223(1)	2.9(4)
C(2)	0.599(1)	–0.395(1)	–0.160(2)	3.8(5)
C(3)	0.682(1)	–0.424(1)	–0.257(2)	5.9(7)
C(4)	0.642(1)	–0.435(1)	–0.017(2)	6.3(7)
C(5)	–0.233(1)	–0.2170(9)	–0.429(1)	2.6(4)
C(6)	–0.497(1)	–0.1564(9)	–0.523(1)	3.4(5)
C(7)	–0.556(2)	–0.189(1)	–0.419(2)	6.7(8)
C(8)	–0.604(1)	–0.145(1)	–0.675(2)	4.5(5)
C(9)	0.0612(8)	–0.2625(6)	–0.0565(7)	2.3(2)
C(10)	0.0841(8)	–0.3568(5)	–0.0216(8)	2.9(2)
C(11)	0.0753(8)	–0.3695(5)	0.113(1)	3.6(3)
C(12)	0.0436(8)	–0.2879(6)	0.2134(8)	4.1(3)
C(13)	0.0207(8)	–0.1936(5)	0.1785(8)	3.8(3)
C(14)	0.0295(8)	–0.1809(4)	0.0436(9)	2.5(2)
C(15)	0.1516(7)	–0.1125(4)	–0.2349(9)	2.0(2)
C(16)	0.2387(8)	–0.0419(6)	–0.0881(7)	3.4(3)
C(17)	0.3009(7)	0.0539(5)	–0.0801(7)	4.0(3)
C(18)	0.2759(8)	0.0793(5)	–0.219(1)	3.6(3)
C(19)	0.1888(8)	0.0087(6)	–0.3657(7)	3.6(3)
C(20)	0.1266(7)	–0.0871(5)	–0.3737(7)	3.1(2)

[a] $B(\mathrm{eq}) = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table 3. Important Interatomic Distances (Å) and Angles (deg) for $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**)

Ge–S(1)	2.278(5)	Ge–S(4)	2.284(5)
Ge–C(9)	1.941(9)	Ge–C(15)	1.925(7)
S(1)–C(1)	1.75(1)	S(4)–C(5)	1.74(1)
S(2)–C(1)	1.62(1)	S(5)–C(5)	1.64(1)
S(3)–C(1)	1.75(1)	S(6)–C(5)	1.74(1)
S(3)–C(2)	1.82(1)	S(6)–C(6)	1.84(1)
C(2)–C(3)	1.51(2)	C(6)–C(7)	1.52(3)
C(2)–C(4)	1.52(2)	C(6)–C(8)	1.52(2)
Ge- -S(2)	3.224(5)	Ge- -S(5)	3.304(5)
Ge- -S(3)	4.752(6)	Ge- -S(6)	4.783(8)
S(1)–Ge–S(4)	87.3(2)	C(9)–Ge–C(15)	118.1(3)
S(1)–Ge–C(9)	110.6(3)	S(4)–Ge–C(15)	110.3(3)
S(4)–Ge–C(15)	113.4(3)	S(4)–Ge–C(9)	113.2(3)
Ge–S(1)–C(1)	100.3(3)	Ge–S(4)–C(5)	102.6(3)
S(1)–C(1)–S(2)	125.0(8)	S(4)–C(5)–S(5)	125.3(8)
S(1)–C(1)–S(3)	108.8(6)	S(4)–C(5)–S(6)	109.2(6)
S(2)–C(1)–S(3)	126.1(7)	S(5)–C(5)–S(6)	125.5(8)
C(1)–S(3)–C(2)	104.7(6)	C(5)–S(6)–C(6)	104.5(5)
S(3)–C(2)–C(3)	106.2(8)	S(6)–C(6)–C(8)	106.1(9)
S(3)–C(2)–C(4)	112(1)	S(6)–C(6)–C(7)	111(1)
C(3)–C(2)–C(4)	114(1)	C(7)–C(6)–C(8)	114(1)
S(1)–Ge- -S(2)	63.1(2)	S(4)–Ge- -S(5)	61.7(2)

the other compounds remained as oils. Attempts to distill any of the oils under vacuum resulted in the rapid expulsion of CS_2.

Carbon Disulfide Elimination. The ^1H and ^{13}C NMR spectra of sealed samples of solutions of compounds **1–4** held at room temperature showed a steady decrease in the intensity of the signals attributable to the $Ph_3Ge[S_2CSR]$ species. The rate of decline was first order, with typical values of rate constants being of the order of 1×10^{-1} h^{-1}. Thus, after 1–2 days, the original signals disappeared to be replaced by peaks attributable to the corresponding Ph_3GeSR compounds. Organogermanium sulfides have been known for some time,[11] and the independent preparation of authentic samples provided confirmation of their formation. Their synthesis was based on an earlier report involving the interaction, in the presence of pyridine, of appropriate organo(halo)germanes with mercaptans, the latter being available because of their use for the preparation of the trixanthate salts. In the ^{13}C NMR spectra, a peak at 192.7 ppm, attributable to CS_2, steadily increased in intensity with time as the peak originally observed at approximately 222 ppm, attributable to the S_2CS carbon, decreased in intensity to disappear after 1–2 days.

Similar results were obtained for compounds **9–12** under identical conditions with the exception that weeks rather than days were required before peaks attributable to the $Me_3Ge[S_2CSR]$ species were totally lost. Peaks assignable to the R groups in other species are as follows (ppm). Ph_3GeSR: 2.45, 1.15 (Et); 2.90, 1.21 (*i*-Pr); 2.40, 1.50, 0.84 (*n*-Pr); 2.45, 1.53, 1.30, 0.84 (*n*-Bu). Me_3GeSR: 2.52, 1.27 (Et); 3.02, 1.30 (*i*-Pr); 2.44, 1.56, 0.94 (*n*-Pr); 2.48, 1.55, 1.36, 0.88 (*n*-Bu).

Similar studies on compounds **5–8** resulted in more complex NMR spectra being observed for the freshly-prepared $Ph_3Ge[S_2CSR]_2$ species and as compared to the final spectra, which contained only peaks attributable to CS_2 and $Ph_2Ge[Sr]_2$, those arising from the R groups of the latter being seen at 2.61, 1.32 (Et); 2.89, 1.18 (*i*-Pr); 2.55, 1.57, 0.91 (*n*-Pr); and 2.57, 1.52, 1.35, 0.81 ppm (*n*-Bu). The additional peaks were entirely consistent with the formation of the intermediate $Ph_2Ge[S_2CSR][SR]$ compounds. The relevant ^1H and ^{13}C NMR data are presented in Tables 6 and 7.

Physical Measurements. The ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 FT NMR spectrometer in $CDCl_3$ solutions. The infrared spectra were recorded on an Nicolet 5DX FT spectrometer as KBr pellets or as oils smeared between KBr windows in the 4000–400-cm^{-1} region. The far-infrared spectra were recorded on a Bomen DA3 infrared spectrometer between polyethylene plates as oils or as Nujol mulls. The Raman spectra were recorded on a JEOL-XY Raman spectrometer using the 5145-Å exciting line of an argon ion laser with samples sealed in capillary tubes. The melting point was determined on a Fisher-Johns apparatus.

X-ray Crystallographic Analysis. A yellow block crystal of $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**) was sealed in a thin-walled glass capillary that was then mounted on a Rigaku AFC6S diffractometer, with graphite-monochromated Mo Kα radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 22 carefully centered reflections in the range $25.01 < 2\theta < 29.75°$ corresponded to a triclinic cell whose dimensions are given in Table 1. On the basis of packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (No. 2).

The data were collected at -30 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 50.0°. The ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.34° with a takeoff angle of 6.0°. Scans of $(1.73 + 0.30 \tan\theta)°$ were made at a speed of 16.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of two rescans), and the counts were accumulated to ensure good counting statistics. Stationary-background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 250.0 mm.

Of the 4522 reflections which were collected, 4271 were unique ($R_{int} = 0.115$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Mo Kα radiation is 17.5 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied, which resulted in transmission factors ranging from 0.68 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[12] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in their idealized positions with C–H set at 0.95 Å and with isotropic thermal

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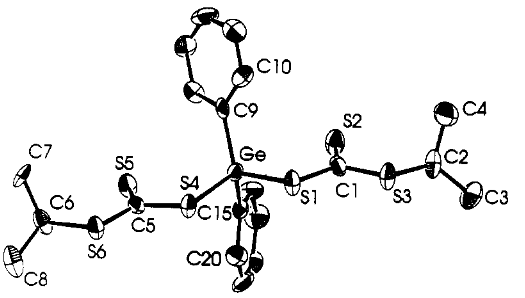

Figure 1. ORTEP diagram of the molecule $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**). Atoms are drawn with 30% probability ellipsoids and hydrogen atoms are omitted for clarity.

parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement[13] was based on 1925 observed reflections ($I > 3.00\sigma(I)$) and 160 variable parameters and converged (largest parameter shift was 0.001 times its esd) with weighted and unweighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.0638$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.0626$.

The standard deviation of an observation of unit weight[14] was 1.50. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.76 and −0.51 e/Å^3, respectively.

Neutral-atom scattering factors were taken from Cromer and Waber.[15] Anomalous-dispersion effects were included in F_c;[16] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[17] All calculations were performed using the TEXSAN[18] crystallographic software package of the Molecular Structure Corp.

The final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Table 2, important distances and bond angles are listed in Table 3, and an ORTEP diagram of **6** is given in Figure 1. Additional crystallographic data are available as supplementary material.

Results and Discussion

The syntheses of several (*S*-alkyl trithiocarbonato)trimethylgermanium (*S*-alkyl trithiocarbonato)triphenylgermanium, and bis(*S*-alkyl trithiocarbonato)diphenylgermanium complexes were readily achieved in 73–85% yields by the reaction of the potassium salt of the appropriate trithiocarbonic acid with bromotriphenylgermane, dichlorodiphenylgermane, or iodotrimethylgermane, in CS_2 as solvent, in accord with the equations

$$Ph_3GeBr + KS_2CSR \rightarrow Ph_3Ge[S_2CSR] + KBr$$

$$Ph_2GeCl_2 + 2KS_2CSR \rightarrow Ph_2Ge[S_2CSR]_2 + 2KCl \quad (R = Et, i\text{-}Pr, n\text{-}Pr, n\text{-}Bu)$$

$$Me_3GeI + KS_2CSR \rightarrow Me_3Ge[S_2CSR] + KI$$

The salt was in excess to ensure complete reaction. In general, all of the compounds **1–12** are susceptible to moisture and air on any extensive exposure, as was found for the corresponding dithiocarbonates. They also readily undergo CS_2 elimination, which is a well-recognized process in transition metal chemistry,[4,5] in accord with the equations

$$Ph_3Ge[S_2CSR] \rightarrow Ph_3Ge[SR] + CS_2$$

$$Me_3Ge[S_2CSR] \rightarrow Me_3Ge[SR] + CS_2 \quad (R = Et, i\text{-}Pr, n\text{-}Pr, n\text{-}Bu)$$

$$Ph_2Ge[S_2CSR]_2 \rightarrow Ph_2Ge[S_2CSR][SR] + CS_2$$

$$Ph_2Ge[S_2CSR][SR] \rightarrow Ph_2Ge[SR]_2 + CS_2$$

The eliminatation can be followed by recording the ^1H and ^{13}C NMR spectra over time when peaks attributable to the decomposition products appear and increase in intensity, along with that attributable to CS_2 in the ^{13}C NMR spectra, as the peaks of the $Ph_3Ge[S_2CSR]$, $Me_3Ge[S_2CSR]$, or $Ph_2Ge[S_2CSR]_2$ species decrease in intensity and eventually disappear. In general, the $Ph_3Ge[S_2CSR]$ compounds are totally decomposed in 1–2 days at room temperature while the $Me_3Ge[S_2CSR]$ species take 1–2 weeks. The total decomposition of the $Ph_2Ge[S_2CSR]_2$ series takes several days, the decomposition is sufficiently slow to allow for the ready identification of the intermediate $Ph_2Ge[S_2CSR][SR]$ series, and of course the extent of decomposition decreases when the samples are kept at reduced temperatures. The presence of CS_2, or indeed the lack of its presence, can also be detected readily in the vibrational spectra, so that it is possible to be sure that both the NMR and vibrational spectra of freshly prepared samples are indeed those of authentic samples of these novel series of (*S*-alkyl trithiocarbonato)organogermanium complexes.

NMR Spectra. The ^1H and $^{13}C\{H\}$ NMR spectral data for compounds **1–12** are presented in Tables 4 and 5. All of the compounds are stored at −15 °C in sealed containers. The ^1H NMR spectra, recorded immediately after dissolving compounds **5–12** in $CDCl_3$, confirm that the diphenyl and trimethyl derivatives are over 98% pure relative to any hydrogen-containing impurities. All of the peaks have the fine structure and relative intensities expected for first-order spectra, except of course for the central CH_2 groups in the *n*-propyl and *n*-butyl groups of the trixanthate. Additional peaks are observed after a matter of hours which are readily assignable to the compounds that result from CS_2 elimination. Thus, as peaks assignable to Me_3GeSR grow, so those assignable to $Me_3Ge[S_2CSR]$ diminish and eventually disappear after approximately 1–2 weeks. For compounds **5**, **7**, and **8**, evidence for CS_2 formation is apparent in the ^{13}C NMR spectra within approximately 20 min by the emergence of a peak at 192.7 ppm attributable to CS_2. At the same time, peaks assignable to $Ph_2Ge[S_2CSR]_2$ decrease in intensity and peaks attributable to $Ph_2Ge[S_2CSR][SR]$ appear (see Tables 6 and 7) soon followed by the appearance of those attributable to $Ph_2Ge[SR]_2$. After approximately 5 days, the peaks attributable to **5**, **7**, and **8**, as well as those attributable to the $Ph_2Ge[S_2CSR][SR]$ species, have essentially disappeared and the spectra show only the presence of CS_2 and $Ph_2Ge[SR]_2$. By contrast, the spectrum of a solid sample of $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**) which was left at room temperature for several months indicated that some of the intermediate decomposition product, $Ph_2Ge[S_2CS(i\text{-}Pr)][S(i\text{-}Pr)]$, was still present along with $Ph_2Ge[S(i\text{-}Pr)]_2$ in excess. For the triphenyl derivatives **1–4**, the additional peaks arising from CS_2 elimination are apparent even when the ^1H and ^{13}C NMR spectra are recorded immediately after dissolution of freshly-prepared samples. The assignment of peaks to Ph_3GeSR

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(13) Least-squares, function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2(F_o^2)$, $\sigma^2(F_0^2) = [S^2(C + R^2B) + (pF_o^2)^2]/(Lp)^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, Lp = Lorentz-polarization factor, and p = p factor.

(14) Standard deviation of an observation of unit weight: $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

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Table 4. ^1H NMR Chemical Shifts for Compounds **1–12**[a–c]

compound	$Ge–(C_6H_5)/(CH_3)$	$S–CH_2/CH$	$SC–CH_3'/CH_2'$	$SC_2–CH_2''$
$Ph_3Ge[S_2CSCEt]$ (**1**)	7.70–7.66, 7.44 7.37 (15H)	3.12 (2H, q, 7.5)	1.23 (3H, t, 7.5)	
$Ph_3Ge[S_2CS(i\text{-}Pr)]$ (**2**)	7.69–7.66, 7.42–7.37 (15H)	3.79 (1H, sept, 6.9)	1.30 (6H, d, 6.9)	
$Ph_3Ge[S_2CS(n\text{-}Pr)]$ (**3**)	7.68–7.62, 7.44–7.37 (15H)	3.10 (2H, t, 7.4)	1.63 (2H, m, 7.4, 7.3)	0.92 (3H, t, 7.3)
$Ph_3Ge[S_2CS(n\text{-}Bu)]$(**4**)	7.67–7.61, 7.45–7.36 (15H)	3.10 (2H, t, 7.4)	1.58 (2H, m, 7.4, 6.9)	1.39 (2H, m, 6.9, 7.3)
$Ph_2Ge[S_2CSEt]_2$ (**5**)	7.84–7.81, 7.42–7.39 (10H)	3.06 (4H, q, 7.4)	1.20 (6H, t, 7.4)	
$Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**)	7.84–7.81, 7.42–7.39 (10H)	3.68 (2H, sept, 6.9)	1.26 (12H, d, 6.9)	
$Ph_2Ge[S_2CS(n\text{-}Pr)]_2$ (**7**)	7.84–7.81, 7.41–7.39 (10H)	3.04 (4H, t, 7.4)	1.58 (4H, m, 7.4, 7.3)	0.90 (6H, t, 7.3)
$Ph_2Ge[S_2CS(n\text{-}Bu)]_2$ (**8**)	7.85–7.81, 7.42–7.38 (10H)	3.08 (4H, t, 7.3)	1.54 (2H, m, 7.3, 7.3)	1.31 (2H, m, 7.3, 7.3)
$Me_3Ge[S_2CSEt]$ (**9**)	0.72 (9H, s)	3.19 (2H, q, 7.5)	1.29 (3H, t, 7.5)	
$Me_3Ge[S_2CS(i\text{-}Pr)]$ (**10**)	0.73 (9H, s)	3.90 (1H, sept, 6.9)	1.36 (6H, d, 6.9)	
$Me_3Ge[S_2CS(n\text{-}Pr)]$ (**11**)	0.71 (9H, s)	3.19 (2H, t, 7.2)	1.68 (2H, m, 7.2, 7.2)	0.98 (3H, t, 7.2)
$Me_3Ge[S_2CS(n\text{-}Bu)]$ (**12**)	0.72 (9H, s)	3.19 (2H, t, 7.1)	1.63 (2H, m, 7.1, 7.1)	1.38 (2H, m, 7.1, 7.1)

[a] The spectra were recorded in $CDCl_3$ and are reported in ppm from Me_4Si, using $CHCl_3$ as a second standard. [b] Number of protons, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet, sept = septet), and coupling constants in Hz are given in parentheses. [c] Peaks also assigned to $SC_3–CH_3'''$ at 0.93 (3H, t, 7.3) for **4**, 0.86 (3H, t, 7.3) for **8**, and 0.90 (3H, t, 7.1) for **12**.

Table 5. ^{13}C NMR Chemical Shifts for Compounds **1–12**[a]

	$Ge\text{-}C_6H_5/CH_3$								
compound	$C(1)$	$C(2,6)$	$C(4)$	$C(3,5)$	SCH_n	$SCCH_n$	SC_2CH_2	SC_3CH_3	CS_2
$Ph_3Ge[S_2CSEt]$ (**1**)	134.60	134.93	130.11	128.62	34.16	12.61			222.07
$Ph_3Ge[S_2CS(i\text{-}Pr)]$ (**2**)	134.70	134.93	130.08	128.61	44.74	21.84			221.58
$Ph_3Ge[S_2CS(n\text{-}Pr)]$ (**3**)	134.63	134.90	130.21	128.39	41.86	21.18	13.62		222.27
$Ph_3Ge[S_2CS(n\text{-}Bu)]$ (**4**)	134.69	134.98	130.07	128.59	39.75	29.63	22.19	13.71	222.24
$Ph_2Ge[S_2CSEt]_2$ (**5**)	134.40	134.14	130.59	128.65	34.29	12.55			222.34
$Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**)	134.61	134.22	130.52	128.68	44.99	21.73			221.36
$Ph_2Ge[S_2CS(n\text{-}Pr)]_2$ (**7**)	134.40	134.26	130.56	128.62	41.98	21.11	13.55		222.56
$Ph_2Ge[S_2CS(n\text{-}Bu)]_2$ (**8**)	134.37	134.28	130.56	128.62	39.90	29.56	22.16	13.67	222.50
$Me_3Ge[S_2CSEt]$ (**9**)	2.80				33.74	12.80			226.31
$Me_3Ge[S_2CS(i\text{-}Pr)$ (**10**)	2.80				44.27	21.73			225.96
$Me_3Ge[S_2CS(n\text{-}Pr)]$ (**11**)	2.81				41.46	21.38	13.68		226.48
$Me_3Ge[S_2CS(n\text{-}Bu)]$ (**12**)	2.80				39.34	29.87	22.27	13.78	226.41

[a] The spectra were recorded in $CDCl_3$ and are reported in ppm from Me_4Si.

Table 6. ^1H NMR Chemical Shifts for the Decomposition Intermediates $Ph_2Ge[S_2CSR][SR]$ (R = Et, *i*-Pr, *n*-Pr, *n*-Bu) Along with Those of $Ph_2Ge[S_2CSEt]_2$ and $Ph_2Ge[SEt]_2$ for Comparison[a–c]

		$[S_2CSR]$				$[SR]$			
compound	$(C_6H_5)_2Ge$	S_2CSCH	S_2CSCCH	S_2CSC_2CH	S_2CSC_3CH	SCH	$SCCH$	SC_2CH	SC_3CH
$Ph_2Ge[S_2CSEt]_2$ (**5**)	7.84–7.81 7.42–7.34	3.06 (q) [7.4]	1.20 (t) [7.4]						
$Ph_2Ge[SEt]_2$	7.66–7.64 7.41–7.38					2.62 (q) [7.4]	1.25 (t) [7.4]		
$Ph_2Ge[S_2CSR][SR]$ (R = Et)	7.73–7.71 7.43–7.38	3.13 (q) [7.4]	1.24 (t) [7.4]			2.47 (q) [7.4]	1.15 (t) [7.4]		
$Ph_2Ge[S_2CSR][SR]$ (R = *i*-Pr)	7.74–7.66 7.45–7.38	3.65 (sp) [6.9]	1.30 (d) [6.9]			2.90 (sp) [6.8]	1.18 (d) [6.8]		
$Ph_2Ge[S_2CSR][SR]$ (R = *n*-Pr)	7.72–7.69 7.42–7.38	3.10 (t) [7.3]	1.63 (m)	0.98 (t) [7.3]		2.41 (t) [7.3]	1.50 (m)	0.82 (t) [7.3]	
$Ph_2Ge[S_2CSR][SR]$ (R = *n*-Bu)	7.73–7.70 7.44–7.38	3.12 (t) [7.4]	1.57 (m)	1.38 (m)	0.89 (t) [7.4]	2.44 (t) [7.4]	1.49 (m)	1.28 (m)	0.75 (t) [7.3]

[a] The spectra were recorded in $CDCl_3$ and are reported in ppm from Me_4Si, using $CHCl_3$ as a second standard. [b] Multiplicities (d = doublet, t = triplet, m = multiplet, sp = septet) are given in parentheses. [c] Coupling constants in Hz are given in square brackets.

Table 7. ^{13}C NMR Chemical Shifts of the Decomposition Intermediates $Ph_2Ge[S_2CSR][SR]$ (R = Et, *i*-Pr, *n*-Pr, *n*-Bu) Along with Those of $Ph_2Ge[S_2CSEt]_2$ and $Ph_2Ge[SEt]_2$ for Comparison[a]

	$(C_6H_5)_2Ge$				$[S_2CSR]$					$[SR]$			
compound	C_1	$C_{2,6}$	C_4	$C_{3,5}$	S_2CS	S_2CSC	S_2CSCC	S_2CSC_2C	S_2CSC_3C	SC	SCC	SC_2C	SC_3C
$Ph_2Ge[S_2CSEt]_2$ (**5**)	134.40	134.28	130.59	128.65	222.34	34.29	12.55						
$Ph_2Ge[SEt]_2$	135.99	133.86	130.27	128.68						22.54	18.13		
$Ph_2Ge[S_2CSR][SR]$ (R = Et)	134.83	134.63	130.60	128.60	222.24	34.09	12.70			23.28	18.35		
$Ph_2Ge[S_2CSR][SR]$ (R = *i*-Pr)	134.95	134.18	130.49	128.66	221.75	44.78	21.64			34.92	27.47		
$Ph_2Ge[S_2CSR][SR]$ (R = *n*-Pr)	134.69	134.12	130.65	128.67	222.43	41.79	21.14	13.58		30.83	26.18	13.30	
$Ph_2Ge[S_2CSR][SR]$ (R = *n*-Bu)	134.73	134.15	130.52	128.68	222.40	39.72	29.65	22.19	13.67	34.90	28.53	21.73	13.55

[a] The spectra were recorded in $CDCl_3$ and are reported in ppm from Me_4Si.

species was confirmed by the preparation of authentic samples. Thus all of the assignments in Tables 4 and 5 are definitive.

The signals due to the phenyl groups in compounds **1**–**4** and **5**–**8** are very similar in appearance and chemical shift to those of the analogous dithiocarbonate series reported earlier,[8] so the chemical shifts depend on the presence of the Ge–S link(s) rather than the nature of the thiocarbonate attached to sulfur.[8,9,19–21] The chemical shifts of the hydrogen atoms on the carbon atom attached to sulfur (*i.e.*, SCH_2/SCH) are similar for a given trixanthate regardless of the number of phenyl groups attached to germanium, as was observed for the corresponding OCH_2/OCH groups in the analogous dithiocarbonates, and are shifted

Table 8. Selected Features and Their Assignments in the Vibrational Spectra of Compounds **1**–**4**[a,b]

$Ph_3Ge[S_2CSEt]$ (**1**)		$Ph_3Ge[S_2CS(i\text{-}Pr)]$ (**2**)		$Ph_3Ge[S_2CS(n\text{-}Pr)]$ (**3**)		$Ph_3Ge[S_2CS(n\text{-}Bu)]$ (**4**)		
IR[c]	Raman[d]	IR[c]	Raman[d]	IR[c]	Raman[d]	IR[c]	Raman[d]	assgnt
1575 w	1583 (23)	1579 vs	1584 (28)	1580 w	1584 (25)	1579 vw	1584 (25)	*l*-phenyl
1426 m	n.o.[e]	1432 ms	n.o.	1430 m	n.o.	1430 ms	n.o.	*n*-phenyl
1180 w	1185 (10)	1185 vw	1185 (8)	1187 w	1185 (5)	1186 w	1185 (7)	*a*-phenyl
1156 w, sh	1156 (13)	1156 mw	1158 (10)	1158 m	1158 (6)	1158 vw	1157 (9)	*e*-phenyl
1083 s	1084 (11)	1083 s	1083 (7)	1088 s	1088 (16)	1088 s	1088 (15)	*q*-phenyl[f]
1076 sh	1076 (32)	1069 s	1072 (20)	1060 sh	1063 (18)	1065 s, sh	1063 (13)	$\nu(S_2CSC)_a$[g]
1055 sh	1058 (4)	1044 s	1043 (29)	1049 m	1050 (15)	1058 s	1056 (20)	$\nu(S_2CSC)_b$[g]
1024 ms	1027 (15)	1027 ms	1027 (20)	1026 ms	1026 (30)	1027 sh	1027 (20)	*b*-phenyl
998 w, sh	999 (100)	1003 sh	999 (100)	999 w	999 (100)	998 w	999 (100)	*p*-phenyl
802 s	n.o.	808 s	n.o.	810 s	n.o	811 s	n.o.	$\nu(S_2CSC)_c$[g]
735 s	n.o.	735 s	n.o.	735 s	n.o.	735 s	n.o.	*f*-phenyl
694 s	n.o.	697 s	n.o.	698 s	n.o.	698 s	n.o.	*v*-phenyl
665 vw, sh	665 (17)	665 sh	665 (14)	665 sh	668 (20)	665 sh	665 (18)	*r*-phenyl[f]
508 w	508 (25)	528 w	526 (21)	528 w	510 (17)	508 w	509 (10)	$\nu(S_2CSC)_d$[g]
459 s	n.o.	463 s	n.o.	460 s	n.o.	463 s	n.o.	*y*-phenyl[f]
407 m	411 (9)	403 ms	405 (12)	403 ms	408 (5)	401 ms	402 (5)	ν(Ge-S)
335 s	n.o.	337 s	n.o.	335 s	n.o.	336 s	n.o.	*t*-phenyl[f]
316 s	316 (10)	318 s	n.o.	318 s	n.o.	317 s	n.o.	$\delta(S_2CSC)$
280 s	280 (12)	280 s	279 (5)	279 ms	n.o.	279 m	n.o.	*u*-phenyl[f]
228 w, br	228 (33)	229 w, br	229 (17)	229 w, br	229 (20)	227 w, br	223 (13)	*x*-phenyl[f]
192 m	196 (13)	191 m	196 (13)	194 m	197 (8)	194 w, br	193 (10)	$\rho(S_2CSC)$

[a] Parentheses denote relative intensities in the Raman effect. [b] s = strong, m = medium, w = weak, sh = shoulder, br = broad, and v = very. [c] Run neat between KBr plates down to 400 cm^{-1} and between polyethylene below 400 cm^{-1}. [d] Run neat in sealed glass capillaries. [e] Not observed. [f] X-sensitive modes. [g] In the trixanthate salts these appear at approximately 1030 s, 1021 (29); 998 s, 998 (27); 847 vs, 847 (26); and n.o., 516 (100).

toward Me_4Si relative to the corresponding *O*-linked dithiocarbonates. The shift is between 1.10 and 1.16 ppm for the ethyl and *n*-butyl derivatives but larger, between 1.62 and 1.68 ppm, for the two propyl derivatives.[8] The chemical shifts for the hydrogen atoms further from sulfur or oxygen show decreasing differences but in the opposite sense, so that for $Ph_3Ge[S_2CSCH_2CH_3]$ the CH_3 chemical shift is 1.23 ppm compared to 0.77 ppm for $Ph_3Ge[S_2COCH_2CH_3]$, a shift of 0.56 ppm away from Me_4Si. With the longer chain *n*-butyl species, the chemical shifts of the terminal CH_3 groups hardly differ; for $Ph_3Ge[S_2CSCH_2CH_2CH_2CH_3]$ the CH_3 chemical shift is 0.93 ppm, which is similar to the value of 0.89 ppm for $Ph_3Ge[S_2COCH_2CH_2CH_2CH_3]$.

For the $Me_3Ge[S_2CSR]$ species **9**–**12**, the CH_3 chemical shifts of methyl groups attached to germanium are essentially the same (0.71–0.73 ppm) regardless of the trixanthate group, and the values are close to that reported for $Me_3Ge[S_2CNMe_2]$, 0.67 ppm. This is consistent with the electronegativity of the trithiocarbonate group being qualitatively similar to or slightly greater than that of the dithiocarbamate group.[19,20] The chemical shifts of the protons in each of the trithiocarbonate groups are similar to those for the corresponding triphenyl series **1**–**4**, with the values of the coupling constants being slightly higher for the trithiocarbonate series than for the corresponding dithiocarbonates. The similarity of all the spectra is indicative of the trixanthate groups being in identical environments in compounds **1**–**12**.

In the ^{13}C NMR spectra, the chemical shifts of the ethyl, *i*-propyl, *n*-propyl, and *n*-butyl groups of the ligands are similar regardless of whether methyl or phenyl groups are attached to germanium or the number of such groups. Comparison with the corresponding S_2COR derivatives[8,9] indicates that substitution of an oxygen atom for sulfur has little influence on the chemical shifts beyond the carbon atom directly bonded to the chalcogens. However, there is a large difference, consistently approximately 35 ppm toward Me_4Si, in the values of the chemical shifts of the carbon atom when it is directly attached to sulfur instead of oxygen. Thus, the chemical shift of the CH_2 carbon in $Ph_2Ge[S_2CSCH_2CH_3]_2$ is 34.29 ppm compared to 69.94 ppm for $Ph_2Ge[S_2COCH_2CH_3]_2$.[8] There is a corresponding shift of approximately 14 ppm away from Me_4Si for the central C atom of the S_2CSR group, so that the S_2CS chemical shift is between 221.36 and 226.41 ppm for compounds **1**–**12** compared to 207.04 and 212.12 ppm for S_2CO in a variety of analogous dithiocarbonates. The $(CH_3)_3Ge$ chemical shift of approximately 2.80 ppm for all of the trimethyl derivatives is consistent with the concept that trixanthate and dithiocarbamate groups have similar group electronegativities,[19,20] and the similarities in the values of the ^{13}C NMR chemical shifts again indicate similar trixanthate environments for **1**–**12**.

The ^1H and ^{13}C NMR spectra for the $Ph_2Ge[S_2CSR][SR]$ species are given in Tables 6 and 7. The values of the chemical shifts are close to those of the initial $Ph_2Ge[S_2CSR]_2$ compound and the final decomposition product, $Ph_2Ge[SR]_2$, but differ sufficiently to allow ready identification. This is demonstrated by the inclusion of the data for both $Ph_2Ge[S_2CSEt]_2$ and $Ph_2Ge[SEt]_2$ in the body of the tables.

Infrared and Raman Spectra. Distinctive features in the infrared and Raman spectra and their assignments are given in Tables 8–10 for compounds **1**–**4**, **5**–**8**, and **9**–**12** respectively. Three intense peaks between 1250 and 1020 cm^{-1} in the infrared spectra of the corresponding dithiocarbonates,[8-10] which were unambiguously assigned to S_2COC stretching vibrations, dominated the spectra relative to peaks assignable to phenyl or alkyl groups.[8,9] These peaks were very weak or were not observed in the Raman effect, but a strong peak between 650 and 690 cm^{-1} was assigned to the fourth S_2COS stretch. The smaller changes in dipole moments and larger polarizabilities to be expected for S_2CSC vibrations result in three strong, but less dominant, peaks between 1088 and 802 cm^{-1} in the infrared spectra of compounds **1**–**12**, with corresponding significant features in the Raman effect. These are readily assigned to the first three S_2CSC stretching vibrations. The fourth S_2CSC stretch is observed between 508 and 534 cm^{-1}, close to the position reported for the symmetric stretch in the CS_3^{2-} ion.[22] The assignments in Tables 8 and 9 are facilitated by distinct features associated with phenyl groups attached to germanium, which consist of three pairs of peaks of decreasing intensity at approximately 740 and 695, 460 and 335, and 1435 and 1095 cm^{-1} in the infrared spectra and the very intense peak

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Table 9. Selected Features and Their Assignments in the Vibrational Spectra of Compounds **5**–**8**[a,b]

$Ph_2Ge[S_2CSEt]_2$ (**5**)		$Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**)		$Ph_2Ge[S_2CS(n\text{-}Pr)]_2$ (**7**)		$Ph_2Ge[S_2CS(n\text{-}Bu)]_2$ (**8**)		
IR[c]	Raman[d]	IR[e]	Raman[d]	IR[c]	Raman[d]	IR[c]	Raman[d]	assgnt
1578 vw	1584 (32)	1574 vw	1582 (21)	1582 w	1583 (11)	1582 vw	1583 (20)	*l*-phenyl
1431 s	n.o.[f]	1431 mw	n.o.	1433 m	n.o.	1433 ms	n.o.	*n*-phenyl
1185 w	1185 (5)	1182 vw	1182 (4)	1183 w	1186 (2)	1183 vw	1186 (3)	*a*-phenyl
1150 vw	1159 (8)	1152 w	1157 (9)	1158 vw	1154 (4)	1154 vw	1154 (5)	*e*-phenyl
[1088][g]	1088 (6)	1084 ms	1080 (3)	1087 s	1082 (7)	1086 s	1084 (15)	*q*-phenyl[h]
1075 vs	1073 (19)	1066 s	1071 (70)	1060 s	1055 (6)	1060 vs, br	1062 (15)	$\nu(S_2CSC)_a$[i]
1031 s	1043 (5)	1043 s	1043 (68)	1044 s	1048 (6)	1052 vs	1048 (25)	$\nu(S_2CSC)_b$[i]
[1026]	1026 (26)	1024 ms	1026 (20)	1026 s	1025 (17)	1026 m	1025 (19)	*b*-phenyl
1001 sh	999 (100)	999 sh	1000 (100)	998 sh	998 (100)	998 w	998 (100)	*p*-phenyl
813 s	n.o.	816 vs	n.o.	814 vs	n.o.	823 s, br	n.o.	$\nu(S_2CSC)_c$[i]
735 s	n.o.	735 s	n.o.	733 s	n.o.	735 s	n.o.	*f*-phenyl
692 s	n.o.	693 s	n.o.	691 s	n.o.	692 s	n.o.	*ν*-phenyl
670 sh	672 (12)	672 w	670 (5)	674 m	670 (15)	675 sh	670 (10)	*r*-phenyl[h]
515 vw	512 (17)	533 vw	534 (64)	510 w	509 (10)	510 sh	513 (14)	$\nu(S_2CSC)_d$[i]
456 ms	n.o.	456 ms	n.o.	458 s	n.o.	459 s	n.o.	*y*-phenyl[h]
412 ms	415 (10)	410 mw	410 (41)	404 ms	410 (4)	419 ms	419 (8)	$\nu(Ge\text{-}S)_{asym}$
389 ms	380 (8)	385 s	380 (5)	362 ms	362 (7)	367 ms	367 (7)	$\nu(Ge\text{-}S)_{sym}$
336 sh	n.o.	336 sh	n.o.	336 sh	n.o.	336 ms	n.o.	*t*-phenyl[h]
326 s	n.o.	329 s	n.o.	326 s	n.o.	326 s	n.o.	$\delta(S_2CSC)$
286 m	280 (6)	283 m	285 (10)	284 ms	284 (7)	279 ms	288 (3)	*u*-phenyl[h]
250 m	237 (10)	239 s	239 (20)	250 ms	248 (5)	233 ms	237 (13)	*x*-phenyl[h]
195 m	188 (15)	188 ms	185 (37)	197 m	196 (9)	200 ms	200 (13)	$\rho(S_2CSC)$

[a] Parentheses denote relative intensities in the Raman effect. [b] s = strong, m = medium, w = weak, sh = shoulder, br = broad, and v = very. [c] Run neat between KBr plates down to 400 cm^{-1} and between polyethylene below 400 cm^{-1}. [d] Run neat in glass capillaries. [e] Run as CsI pellets. [f] Not observed. [g] Square brackets indicate expected peak is masked by a stronger, overlapping feature. [h] X-sensitive modes. [i] In the trixanthate salts these appear at approximately 1030 s, 1021 (29); 998 s, 998 (27); 847 vs, 847 (26); and n.o., 516 (100).

Table 10. Selected Features and Their Assignments in the Vibrational Spectra of Compounds **9**–**12**[a,b]

$Me_3Ge[S_2CSEt]$ (**9**)		$Me_3Ge[S_2CS(i\text{-}Pr)]$ (**10**)		$Me_3Ge[S_2CS(n\text{-}Pr)]$ (**11**)		$Me_3Ge[S_2CS(n\text{-}Bu)]$ (**12**)		
IR[c]	Raman[d]	IR[c]	Raman[d]	IR[c]	Raman[d]	IR[c]	Raman[d]	assgnt
1070 s	1072 (100)	1088 s	1088 (69)	1054 s	1054 (64)	1078 s, sh	1083 (30)	$\nu(S_2CSC)_a$[e]
1029 s	1026 (62)	1039 s	1040 (100)	1039 s	1044 (69)	1055 s	1049 (100)	$\nu(S_2CSC)_b$[e]
840 s, sh	n.o.[f]	840 s, sh	n.o.	838 s	n.o.	840 s, sh	n.o.	$\rho(CH_3\text{–}Ge)$
810 vs	810 (2)	810 vs	815 (6)	803 vs	805 (7)	805 vs	805 (6)	$\nu(S_2CSC)_c$[e]
612 ms	608 (42)	612 ms	609 (31)	612 s	608 (44)	612 s	608 (35)	$\nu(Ge\text{-}C)_{asym}$
567 m	568 (70)	568 m	567 (65)	568 m	568 (100)	568 m	567 (98)	$\nu(Ge\text{-}C)_{sym}$
509 vw	509 (54)	525 vw	527 (59)	510 w	509 (57)	510 w	509 (54)	$\nu(S_2CSC)_d$[e]
398 m	397 (35)	399 ms	395 (42)	395 m	394 (21)	396 ms	397 (34)	$\nu(Ge\text{-}S)$
318 w	318 (10)	330 m	330 (10)	322 w	320 (7)	330 vw	n.o.	$\delta(S_2CSC)$
195 m, br	195 (50)	192 m	187 (50)	195 s	195 (60)	195 ms	191 (50)	$\rho(S_2CSC)$

[a] Parentheses denote relative intensities in the Raman effect. [b] s = strong, m = medium, w = weak, sh = shoulder, br = broad, and v = very. [c] Run neat between KBr plates down to 400 cm^{-1} and between polyethylene below 400 cm^{-1}. [d] Run neat in sealed capillaries. [e] In the trixanthate salts these appear at approximately 1030 s, 1021 (29); 998 s, 998 (27); 847 vs, 847 (26); and n.o., 516 (100). [f] Not observed.

close to 1000 cm^{-1} in the Raman spectra.[8] The strong methyl rocking mode associated with methylgermanes at approximately 840 cm^{-1} is a distinctive feature in the infrared spectra of compounds **9**–**12** in Table 10. The asymmetric and symmetric Ge–C stretches are assigned at approximately 610 and 568 cm^{-1}, respectively, for all four trimethyl derivatives. These values are close to those for Me_3GeBr[23] and could indicate that the C–Ge–C angles in **9**–**12** are similar to those of 112.4 (1)° in Me_3GeBr.[24] The Ge–S stretching vibration close to 400 cm^{-1} is as expected for a monodentate-linked thiocarbonate.[8–10]

Molecular Structure of $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (6). Diphenylbis(*S*-isopropyl trithiocarbonato)germanium (**6**) crystallizes in the space group $P\bar{1}$. The ORTEP diagram (Figure 1) illustrates, along with Table 3, that the immediate environment about germanium is that of a distorted tetrahedron. The Ge–C bond lengths of 1.925(7) and 1.941(9) Å are typical for Ph_2GeL_2 species, where L is a sulfur-bonding moiety. Comparable Ge–C bond lengths are 1.927(6) and 1.939(7) Å in $Ph_2Ge[S_2CO(i\text{-}Pr)]_2$[8] and 1.928(3) Å in $Ph_2[S_2CNEt_2]_2$.[19] The values of the C–Ge–C and S–Ge–S angles of 118.1(3) and 87.3(2)°, respectively, indicate more distortion from the all-tetrahedral angle than was found for the analogous dithiocarbonate, $Ph_2Ge[S_2CO(i\text{-}Pr)]_2$, where the corresponding angles are 115.6(3) and 103.2(1)°, respectively.[8] However, the distortion is slightly less than that observed in diphenylbis(*N*,*N*-diethyldithiocarbamato)germanium, $Ph_2Ge[S_2CNEt_2]_2$, where the C–Ge–C and S–Ge–S angles are 121.8(1) and 84.4(1)°, respectively.[19] These larger distortions are associated with the fact that a terminal sulfur (C═*S*) atom is oriented toward the germanium at Ge--S distances of 3.183(1) Å for $Ph_2Ge[S_2CNEt_2]_2$ and 3.224(5) and 3.304(5) Å for $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ (**6**). By contrast, in $Ph_2Ge[S_2CO(i\text{-}Pr)]_2$, where the terminal sulfur atom is oriented away from the germanium center, the shortest distance between Ge and a terminal S atom is 4.753(4) Å.[8] Whether distances of 3.1–3.3 Å, which are considerably less than the sum of the van der Waals radii of 3.75 Å,[25] are sufficiently short to be considered as partial bonds may be questionable, but there appears to be a relationship between these Ge--S nonbonding or anisobonding distances and the distortion from all tetrahedral angles. Also the C═S bonds in **6**, averaging 1.63(1) Å, are slightly longer than those in $Ph_2Ge[S_2CO(i\text{-}Pr)]_2$, 1.61(1) Å, which could be another indication of the presence of secondary interactions leading to the orientation of the terminal

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C═S rather than the CSR moiety toward the germanium center. The average bite angle of 62.4(7)° in **6** is essentially the same as that in $Ph_2Ge[S_2CNEt_2]_2$, and anisobidentate linkages appear to give a better overall description of the bonding of dithiocarbamates to germanium.

The $S-CH(CH_3)_2$ bonds in the two trixanthate groups are slightly longer, 1.82(1) and 1.84(1) Å, than the sum of the covalent radii of S and C. The average $C-S-CH(CH_3)_2$ angle, 104.6(2)°, is only slightly larger than the Ge–S–C angles, 100.3(4) and 102.6(3)°, which is also consistent with the $S-CH(CH_3)_2$ bond having no π-character. The nominally single C–S bonds of the thio-carbon atom are shorter than the sum of their covalent radii, and the average bond lengths are the same, an average of 1.745(10) Å for both C–SGe and $C-SCH(CH_3)_2$, which suggests that any delocalization of π-electron density into these bonds is identical whether sulfur is bonded to the germanium center or to the isopropyl group. The terminal C═S bonds, averaging 1.62(2) Å, are considerably shorter than the other C–S bonds, and in each of the trixanthate groups, the two angles around the planar thio-carbon atom that involve the terminal bond, S═C—SGe and $S{=}C{-}SCH(CH_3)_2$, are very similar, averaging 125.5(3)°, compared with an average of 109.0(2)° for the $GeS-C-SCH(CH_3)_2$ angles.

The Ge–S bond lengths of 2.278(5) and 2.284(5) Å in $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$ are longer than those of 2.252(3) Å in the analogous dithiocarbonate, $Ph_2Ge[S_2CO(i\text{-}Pr)]_2$, in which there are no secondary interactions involving the terminal sulfur atoms,[8] but similar to those in $Ph_2Ge[S_2CNEt_2]_2$ and other dithiocarbamates where there is secondary bonding. In view of the similarities noted in the spectra of the trixanthates discussed above, it is reasonable to assume that all of the members of this new class of *S*-alkyl trithiocarbonate (xanthate) derivatives of organogermanes have the anisobidentate bonding demonstrated in the molecular structure of $Ph_2Ge[S_2CS(i\text{-}Pr)]_2$.

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Supplementary Material Available: Tables SI–SIII, listing experimental details, anisotropic thermal parameters of non-hydrogen atoms, and final fractional coordinates and thermal parameters for hydrogen atoms (3 pages). Ordering information is given on any current masthead page. Structure factor tables may be obtained directly from the authors.