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Organometalloidal derivatives of the transition metals

XXVII *. Chemical and structural investigations on (ferrocenylacyl)germanes

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Abstract

(Ferrocenylacyl)germanes, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{COGeR}_3$ ($\text{R}_3 = \text{Me}_3$ (I), Ph_3 (II)) have been synthesized and their physical and structural properties investigated, both spectroscopically and via single crystal X-ray analysis. Basicity measurements, via H-bonding to phenol, indicate that I and II are less basic than their silicon analogs, a feature corroborated by infrared and structural analysis. Thus, the $\nu(\text{C}=\text{O})$ frequencies for I and II at 1594 and 1596 cm^{-1} are approximately 18 cm^{-1} higher than the corresponding acylsilanes, and the C=O bond lengths of 1.223 Å are shorter than the silicon analogs, 1.231 Å.

Introduction

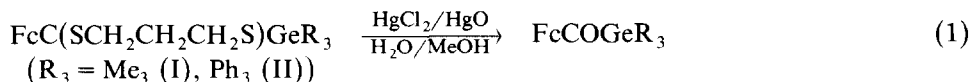
Whereas acylsilanes have been thoroughly investigated by the comprehensive studies of Brook and co-workers and have been shown to exhibit many unusual chemical, spectral, and photochemical properties [2–9], considerably less interest has been reported in acylgermanes [3,4,6,10,13,14]. This is due to their relative lack of chemistry, since in general they do not exhibit the range of rearrangements observed for the acylsilanes. We have recently reported on some chemical and structural aspects of (ferrocenylacyl)silanes, FcCOSiR_3 [12], a class of compound first reported by Reuter and Damrauer [11] in 1974. There are no literature reports on the related (ferrocenylacyl)germanes, and we now wish to report on two examples of this group, FcCOGeMe_3 (I) and FcCOGePh_3 (II).

Results and discussion

(Ferrocenylacyl)germanes were readily synthesized by hydrolysis of 2-ferrocenyl-2-germyl-1,3-dithianes in a polar medium (eq. 1). The complexes are air stable, red

* For part XXVI see ref. 1.

crystalline materials.



We did not attempt synthesis via the alternative routes involving reaction of germyllithium reagents with ferrocene-containing acyl halides or esters [10a,14].

The (ferrocenylacyl)germanes did not undergo reduction to corresponding alcohols with sodium borohydride in ethereal solvents. Partial reduction of the germanium-acyl carbon took place to yield ferrocenecarboxaldehyde.

The spectral properties of (ferrocenylacyl)germanes (Table 2) are similar to those of the silicon analogs, and exhibit low carbonyl stretching frequencies (CH_2Cl_2) at 1594 (I), 1596 cm^{-1} (II), values which are 16 cm^{-1} (I) and 21 cm^{-1} (II) higher than their silicon analogs [11,12]. These values are significantly lower than related non-ferrocenyl containing acylgermanes for example RCOGeR'_3 ($\text{R} = \text{Me}, \text{Ph}$) [4,10], illustrating the feature first observed by Reuter and Damrauer of the significant effect of the ferrocenyl group.

The higher C=O stretching frequencies of the acylgermanes suggest that they possess more C=O double bond character than the corresponding acylsilanes, and thus should be poorer bases. This prediction is borne out by H-bonding studies to phenol in CCl_4 . The shift between the OH stretching frequency of H-bonded phenol and the free phenol in the presence of (ferrocenylacyl)germanes, and other related ferrocenylacyl compounds, are presented in Table 3. Direct comparison of the data for FcCOER_3 ($\text{E} = \text{Si}, \text{Ge}$) shows the germanium compounds produce a smaller shift, and have lower formation constants for the H-bonded complex. This reduction in basicity, Δcm^{-1} , is greater in the ferrocenylacyl systems than in the related benzoyl systems, but clearly, as noted before, the Fc group is having a very large base enhancing effect due to the steric bulk of the ferrocenyl group.

(Ferrocenylacyl)silanes exhibit ^{13}C carbonyl-carbon chemical shifts in the range 231–237 ppm, similar to those of acylsilanes, 230–240 ppm [8b], and complexes I and II exhibit similar data, 234.4 and 227.4 ppm respectively. The Ge atom is slightly less deshielding than the Si atom, since (ferrocenyl)acyl compounds generally possess such resonances in the range 200 ppm.

Structural analysis of ferrocenylacylgermanes

There is only a single example of the structural characterization of an acylgermane in the literature [13], hence such an analysis of I and II was performed. The various pertinent bond lengths and bond angles are presented in Table 5, and the structures are illustrated in Fig. 1.

The C=O bond lengths of the two acylgermanes are equivalent at 1.223(10) Å, a value shorter than the related acylsilanes, confirming the higher C=O stretching frequencies, and decreased base strength of the acylgermanes. These bond lengths are comparable to the value of 1.20(22) Å for MeCOGePh_3 [13], an old structure with a relatively poor refinement, but significantly longer than that of 1.203(7) Å, recently reported for FcCOPh [15].

The angle Ge–C–O in I and II is 117.8 and 114.5°, respectively. These values exhibit a considerable squeezing of this angle compared to that reported for

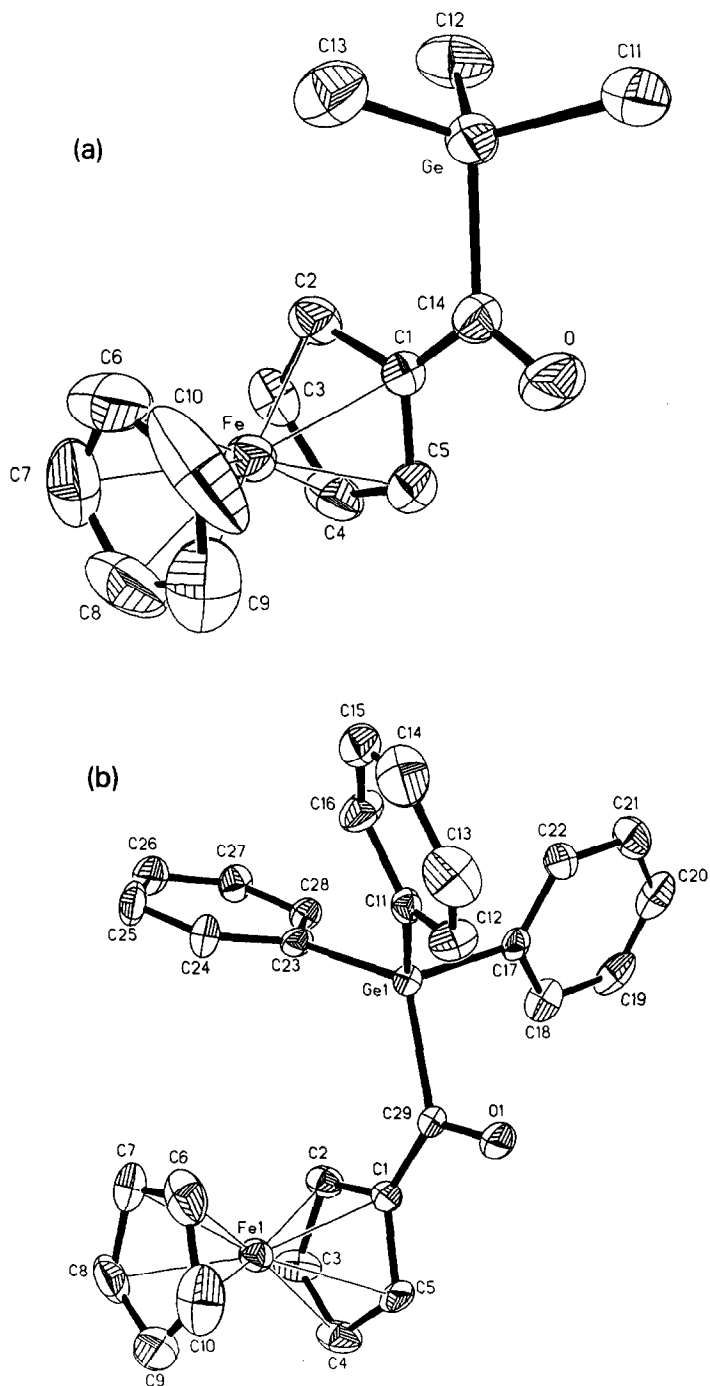


Fig. 1. (a) Structure of complex I; (b) structure of complex II.

MeCOGePh_3 , 119.4 [13]. In conjunction with the much larger Fc-C-Ge angle in I and II, compared to the angle Me-C-Ge in MeCOGePh_3 , such squeezing reinforces earlier conclusions that the steric requirement of the Fc group plays a dominant rôle in both the structure and base characteristics of the general system FcCOER_3 ($\text{E} = \text{Si, Ge}$).

The phenyl groups in II, as those in Ph_3SiCOFc , do not exhibit the propeller orientation observed in Ph_3GeCOMe . In I the two cyclopentadienyl rings are slightly staggered, 4.5° , whereas for II they are totally eclipsed.

Experimental

All reactions were performed under a nitrogen atmosphere. Solvents used were dry and oxygen free; Me_3GeCl , and Ph_3GeCl were obtained from Gelest Inc. Bensalem, PA. Ferrocenecarboxaldehyde, 1,3-propanedithiol, and *n*-BuLi (1.6 *M* in hexane) were purchased from Aldrich Chemical Co., Milwaukee, WI. Silica gel (grade 950, 60–200 mesh) was purchased from MCB Reagents, Gibbstown, NJ.

Infrared spectra were recorded on a Perkin-Elmer 580B spectrophotometer; UV spectra on a Perkin-Elmer Lambda 4C UV-Vis spectrophotometer, and NMR spectra on an IBM NR/200 FTNMR spectrometer. Analyses were performed by Galbraith Laboratories Inc, Knoxville, TN.

2-Ferrocenyl-1,3-dithiane was prepared from ferrocenecarboxaldehyde by the reported methods [11,12]. Typical reactions are described below and all the analytical and spectral data are provided in the Tables 1 and 2.

Synthesis of 2-ferrocenyl-2-triphenylgermyl-1,3-dithiane

Into a 100 mL Schlenk flask equipped with a magnetic stirring bar and septum was placed 1.64 g (5.41 mmol) of 2-ferrocenyl-1,3-dithiane dissolved in 25 mL of freshly distilled THF. The solution was maintained at -25°C as 3.35 mL (5.70 mmol) of a 1.6 *M* *n*-butyllithium solution was added slowly via a syringe. The color of the reaction mixture immediately changed to dark red and the solution was stirred at -25°C for 15 min. To this solution 15 mL of a THF solution of triphenylchlorogermane (2.0 g, 5.85 mmol) was added dropwise. An orange compound started precipitating after 5 min.

The reaction mixture was stirred at -25°C for 1 h and further stirred for 2 h at room temperature. At this time the solid compound was filtered through a sintered glass crucible and washed with cold THF. Recrystallization from hexane yielded 2.35 g, (84%), m.p. $166\text{--}167^\circ\text{C}$.

Table 1
Physical and analytical data

Compound	Analysis (calc. (found) (%))		Yield (%)	M.p. ($^\circ\text{C}$)
	C	H		
FcCOGeMe_3 (I)	50.8 (50.3)	5.44 (5.42)	55	77–78
FcCOGePh_3 (II)	67.3 (67.0)	4.64 (4.74)	62	89
$\text{FcC}(\text{S}_2\text{C}_3\text{H}_6)\text{GeMe}_3$ (III)	48.5 (48.7)	5.71 (5.75)	94	121–122
$\text{FcC}(\text{S}_2\text{C}_3\text{H}_6)\text{GePh}_3$ (IV)	63.3 (63.7)	4.95 (5.03)	84	166–167

Table 2

Spectral data for new compounds ^{a,b}

<i>FeCOGeMe₃ (I)</i>	
IR, $\nu(\text{CO}) \text{ cm}^{-1}$ (CH_2Cl_2)	1594
UV	336(183), 369(sh), 462(55)
¹ H	0.46(9H, s, GeMe_3); 4.18(5H, s, C_5H_5); 4.50(2H, t, C_5H_4); 4.74(2H, t, C_5H_4)
¹³ C	0.82(GeMe_3); 69.2, 69.8, 72.5, 85.2(C_5H_5); 234.4(C=O)
<i>FcCOGePh₃ (II)</i>	
IR, $\nu(\text{CO}) \text{ cm}^{-1}$ (CH_2Cl_2)	1596
UV	349(147), 385(sh), 472(65)
¹ H	3.94(5H, s, C_5H_5); 4.43(2H, t, C_5H_4); 4.65(2H, t, C_5H_4); 7.39, 7.41, 7.67(Ph)
¹³ C	70.1, 72.8, 86.6(C_5H_5); 128.8, 129.8, 135.8, 136.2(Ph); 227.4(C=O)
<i>Fc(dithiane)GeMe₃ (III)</i>	
¹ H	0.09(9H, s, Me_3Ge), 2.06(2H, m, CH_2); 2.77(2H, m, $\text{CH}_2\text{-S}$); 3.12(2H, m, CH_2S), 4.08 – 4.23(9H, m, s, Fe)
<i>Fc(dithiane)GePh₃ (IV)</i>	
¹ H	2.07(2H, m, CH_2); 2.59(2H, m, CH_2S); 3.38(2H, m, SCH_2); 3.99–4.15(9H, m, s, Fe); 7.30–7.62(15H, m, Ph)

^a Ppm relative to TMS, s = singlet, d = doublet, t = triplet. ^b NMR spectra run in CDCl_3 . ^c UV spectra recorded in 80/20 hexane/ CH_2Cl_2 solvent, λ (extinction coefficient).

Hydrolysis of 2-ferrocenyl-2-triphenylgermyl-1,3-dithiane

A 250 mL 2-necked flask equipped with a magnetic stirring bar and a reflux condenser was charged with 2.0 g (3.3 mmol) of 2-ferrocenyl-2-triphenylgermyl-1,3-dithiane, 1.97 g (7.25 mmol) of HgCl_2 and 1.07 g (4.94 mmol) of HgO . Aqueous methanol (49 mL methanol + 1 mL water) was then added and the mixture was stirred vigorously and heated at reflux for 2 h. The color of the solution changed to dark red. The red solution was filtered through a sintered glass crucible and the residue was washed with 15 mL of methanol. The filtrate was poured into three times its volume of water and the organic layer was extracted 3 times with 75 mL of methylene chloride. This solution was washed once with concentrated ammonium acetate solution, twice with water, and dried over sodium sulfate. The solvent was removed on a rotary evaporator to give the crude product as a red solid. Recrystallization of this crude material from an 80/20 hexane/methylene chloride mixture yielded FcCOGePh_3 , 1.05 g (62%), m.p. 89 °C. Full spectral and analytical data are recorded in Tables 1 and 2.

Reaction of (ferrocenylacetyl)triphenylgermane with sodium borohydride

To a slurry of 0.014 g (0.37 mmol) sodium borohydride in 5 mL of THF at 0 °C was added 0.2 g (0.38 mmol) of (ferrocenylacetyl)triphenylgermane in 30 mL of THF. The reaction mixture was stirred for 3 h at room temperature. Infrared monitoring of the reaction did not show any change in the carbonyl stretching frequency. The reaction was quenched in cold water and the aqueous layer was extracted twice with hexane and dried over sodium sulfate. After the organic layer was filtered and

Table 3

 K_F for phenol/acylgermane and related complexes, $\Delta\nu$ for phenol $\nu(\text{OH})$

Compound	K_F	$\Delta\nu$ (cm^{-1})
PhCOSiMe ₃	4.5	180 [9]
PhCOGeMe ₃		175 [9b]
FcCOCH ₃	30.7	269
FcCOSiMe ₃	32.0	261
FcCOSiPh ₃	17.2	248
FcCOGeMe ₃	21.6	235
FcCOGePh ₃	11.2	234

Table 4

Crystal data, data collection, least-squares parameters

	I	II
Empirical formula	C ₁₄ H ₁₈ OGeFe	C ₂₉ H ₂₄ OGeFe
M (a.m.u.)	330.7	516.9
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$
a (Å)	6.244(2)	14.765(4)
b (Å)	16.295(4)	17.892(5)
c (Å)	13.780(5)	17.963(4)
α (°)	90	90
β (°)	95.00(3)	94.96(2)
γ (°)	90	90
V (Å ³)	1396.7(8)	4727(2)
Z	4	8
D_{calc} (Mg m ⁻³)	1.573	1.453
μ (Mo- K_α) (mm ⁻¹)	3.145	1.886
$F(000)$	672	2112
Approx. crystal size (mm)	0.1 × 0.14 × 0.2	0.2 × 0.1 × 0.3
Crystal color	Red	Red
λ (Mo- K_α) (Å)		0.71073
2θ limits (°)		3.5–45
Scan technique		ω
Scan speed (° min ⁻¹)		3.0 to 15.0
Index ranges	$0 \leq h \leq 6$ $0 \leq k \leq 17$ $-14 \leq l \leq 14$	$0 \leq h \leq 15$ $-8 \leq k \leq 19$ $-19 \leq l \leq 19$
Reflections collected	2230	6854
Independent reflections	1819	6177
R_{int}	0.015	0.010
Observed data	1819	2886
[$F > X.0\sigma(F)$]	$X.0 = 3.0$	$X.0 = 6.0$
Structure solution		Heavy-atom method
Weighting scheme		$w = [\sigma^2(F) = \text{abs}(g)F^2]^{-1}$
Weighting g	0.0010	0.0003
R_{obs}	0.0487	0.0399
R_w	0.0529	0.0403
R_{tot}	0.0698	0.1092
Goodness-of-fit	1.08	1.19
Largest and mean Δ/σ	0.015, 0.000	0.380, -0.001
Data-to-parameter ratio	9.2/1	5.0/1
Largest difference peak (e Å ⁻³)	0.52	0.50
Largest difference hole (e Å ⁻³)	-0.62	-0.47

Table 5

Selected bond lengths (Å) and angles (°)^a

	Me ₃ GeCOFc (I)	Ph ₃ GeCOFc ^b (II)
Ge–C(CO)	1.998(7)	2.016(9)
C–O	1.225(9)	1.221(11)
Fc–C(CO)	1.479(10)	1.458(13)
Ge–C(CO)–Fc	122.6(5)	124.4(6)
O–C(CO)–Ge	117.8(5)	114.5(7)
O–C(CO)–Fc	119.6(7)	120.9(8)

^a The full set of bond angles, bond lengths, anisotropic thermal parameters, and lists of observed and calculated structure factors are available from the authors. ^b The data from the two molecules in the asymmetric unit are essentially identical.

solvent removed, the red viscous material was extracted with hexane and placed on a 2 × 20 cm silica gel column. Elution with 50/50 hexane/methylene chloride produced a red band, which was collected. Removal of the solvent yielded 0.07 g (34%) of the starting material. Continued elution with CH₂Cl₂ yielded 0.035 g (43%) of FcCHO.

Structure determination and refinement

All data were collected at room temperature on a Nicolet R3m/V four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ 0.71073 Å). Unit cell parameters and estimated standard deviations were obtained by least-squares fit to 25 reflections chosen randomly in the 2θ range of 15–30°. Crystal data and experimental settings are given in Table 4. The intensities were corrected for Lorentz and polarization effects but not for absorption. The structures were solved

Table 6a

Atomic coordinates (×10⁴) and equivalent isotropic displacement coefficients (Å² × 10³) for complex I

Atom	x	y	z	U _{eq} ^a
Ge	749(1)	533(1)	3155(1)	46(1)
Fe	2284(2)	2873(1)	4801(1)	43(1)
O	–2355(9)	1603(3)	3761(4)	74(2)
C(14)	–484(12)	1399(4)	3969(5)	45(3)
C(1)	750(11)	1775(4)	4820(5)	41(2)
C(2)	2986(12)	1676(4)	5085(5)	48(3)
C(3)	3559(13)	2152(5)	5929(5)	54(3)
C(4)	1635(15)	2534(5)	6191(6)	61(3)
C(5)	–64(13)	2327(5)	5507(5)	54(3)
C(6)	4007(34)	3229(8)	3710(14)	126(7)
C(7)	4510(19)	3709(9)	4496(10)	92(5)
C(8)	2848(30)	4083(6)	4766(8)	99(6)
C(9)	1137(20)	3902(9)	4140(15)	126(8)
C(10)	1791(39)	3368(10)	3494(9)	144(9)
C(11)	–1739(14)	–35(6)	2549(7)	88(4)
C(12)	2535(15)	–234(5)	3921(6)	73(4)
C(13)	2396(14)	1048(5)	2208(6)	70(3)

^a Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U_{ij}* tensor.

Table 6b

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$) for complex II

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Ge(1)	3766(1)	1325(1)	-2979(1)	38(1)
Fe(1)	4872(1)	2328(1)	-4934(1)	46(1)
O(1)	4297(4)	417(3)	-4103(3)	59(3)
C(29)	4456(6)	1045(5)	-3859(5)	41(4)
C(2)	5458(6)	2217(6)	-3878(5)	52(4)
C(3)	6096(7)	2493(6)	-4346(7)	63(5)
C(4)	6192(6)	1975(7)	-4915(6)	65(5)
C(5)	5609(6)	1358(6)	-4815(5)	55(4)
C(1)	5142(5)	1514(5)	-4163(5)	38(4)
C(6)	3531(9)	2422(10)	-5219(11)	93(8)
C(7)	3875(10)	3102(9)	-4962(8)	89(6)
C(8)	4521(9)	3308(7)	-5435(9)	86(6)
C(9)	4589(11)	2756(10)	-5961(7)	89(7)
C(10)	3958(12)	2220(9)	-5839(10)	108(8)
C(12)	2247(7)	419(6)	-3687(5)	62(4)
C(13)	1347(10)	196(7)	-3797(7)	89(6)
C(14)	713(9)	516(8)	-3400(8)	92(7)
C(15)	973(8)	1047(7)	-2881(7)	81(6)
C(16)	1857(7)	1290(6)	-2772(6)	64(4)
C(11)	2509(6)	975(5)	-3179(5)	42(4)
C(18)	5310(7)	718(6)	-2063(6)	64(5)
C(19)	5735(8)	303(7)	-1464(7)	76(5)
C(20)	5209(10)	-48(7)	-998(6)	81(6)
C(21)	4290(10)	-15(6)	-1083(6)	83(6)
C(22)	3873(7)	384(6)	-1668(5)	61(4)
C(17)	4370(7)	751(5)	-2166(5)	42(4)
C(24)	3123(7)	2873(5)	-3044(6)	55(4)
C(25)	3049(7)	3593(6)	-2773(6)	69(5)
C(26)	3513(7)	3820(6)	-2115(6)	67(5)
C(27)	4095(7)	3323(6)	-1744(6)	57(4)
C(28)	4198(7)	2613(5)	-2001(6)	47(4)
C(23)	3724(7)	2365(6)	-2654(6)	46(4)
Ge(2)	1391(1)	1281(1)	2015(1)	40(1)
Fe(2)	2316(1)	2310(1)	62(1)	47(1)
O(1A)	2106(4)	380(4)	964(4)	64(3)
C(29A)	2169(6)	1028(6)	1181(5)	42(4)
C(2A)	3172(6)	1422(6)	167(5)	50(4)
C(3A)	3660(6)	2066(7)	5(6)	60(5)
C(4A)	3572(7)	2610(7)	555(7)	67(5)
C(5A)	3016(7)	2305(7)	1094(6)	58(4)
C(1A)	2764(6)	1565(5)	855(5)	42(4)
C(6A)	1346(8)	2071(7)	-782(7)	71(5)
C(7A)	1857(8)	2713(9)	-956(7)	79(6)
C(8A)	1748(9)	3244(7)	-424(9)	91(6)
C(9A)	1218(10)	2961(9)	109(8)	94(7)
C(10A)	940(7)	2241(9)	-124(7)	75(6)
C(12A)	1552(7)	686(6)	3528(6)	72(5)
C(13A)	1972(10)	409(8)	4168(7)	103(7)
C(14A)	2869(11)	200(7)	4190(7)	91(6)
C(15A)	3311(8)	262(6)	3563(7)	74(5)
C(16A)	2896(7)	563(5)	2917(6)	56(4)
C(11A)	1992(7)	778(5)	2885(5)	44(4)

Table 6b (continued)

Atom	x	y	z	U_{eq}^a
C(18A)	1900(8)	2624(6)	2862(6)	57(5)
C(19A)	1800(9)	3341(7)	3128(6)	74(5)
C(20A)	1034(11)	3736(7)	2876(8)	93(7)
C(21A)	402(10)	3459(7)	2367(8)	87(7)
C(22A)	511(8)	2748(6)	2073(6)	62(5)
C(17A)	1251(7)	2320(6)	2343(6)	43(4)
C(24A)	-550(7)	1051(5)	2119(5)	57(4)
C(25A)	-1421(7)	787(7)	1879(7)	72(5)
C(26A)	-1542(9)	367(7)	1252(7)	88(6)
C(27A)	-847(9)	206(7)	856(6)	93(6)
C(28A)	17(7)	455(6)	1079(6)	67(5)
C(23A)	190(6)	886(5)	1708(5)	42(4)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

and refined using the SHELXTL-PLUS package of crystallographic programs on a MicroVAX-II computer. The hydrogen atoms were placed at calculated positions (C-H 0.96 Å, U_H 0.08 Å²) during refinement. Full-matrix least-squares refinement, minimizing $\sum w(F_0 - F_c)^2$, was carried out with anisotropic thermal parameters for non-hydrogen atoms. Selected bond lengths and angles are presented in Table 5, and atomic coordinates are given in Table 6A and 6B.

Structure II contains two molecules per asymmetric unit which differ only slightly in conformation, particularly concerning the planarity of Ge₂, O_{1a}, C_{29a} and C_{1a} with Ge₂ 0.15 Å below and O_{1a} 0.11 Å above the least-squares plane for Ge₂, O_{1a}, C_{29a}, C_{1a}, C_{2a}, C_{3a}, C_{4a} and C_{5a}; this, in addition to some differences in the orientation of the phenyl rings might be the reason for having two molecules in the asymmetric unit.

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