components of anomalous dispersion[31b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma_1(|F_o|) + X(|F_o|)^2$ [X = 0.0005 (3), 0.003 (6)].

The structure of 3 was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. The molecule is located about a 2-fold rotation axis at $^1/_2$, y, $^1/_4$; no atoms lie on the axis, and thus, all site-occupancy factors are 1.0. Hydrogen atoms were included by using a riding model with d(C-H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and anisotropic thermal parameters led to convergence; see Table III.

The structure of 6 was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included by using a riding model with d(C-H) = 0.96 Å and U(iso) = 0.08 Å^2. Refinement of positional and anisotropic thermal parameters led to convergence (see Table III). The (241) reflection was omitted because of a large discrepancy between $|F_o|$ and $|F_c|$ values. Including this reflection in the refinement resulted in a significantly increased value for R_w of 0.098.

The molecule of 6 is polymeric with repeating InI_2Mes units along the c dimension of the unit cell. The repeat units are related by inversion centers ($^1/_2$, $^1/_2$, $-^1/_2$; $^1/_2$, $^1/_2$, 0; $^1/_2$, $^1/_2$, $^1/_2$, etc.; see Figure 2).

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Supplementary Material Available: Listings of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters (5 pages); tables of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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[31] International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1974: (a) pp 99–101; (b) pp 149–150.

Two Germaoxetanes from a Germene: Formation and Structure

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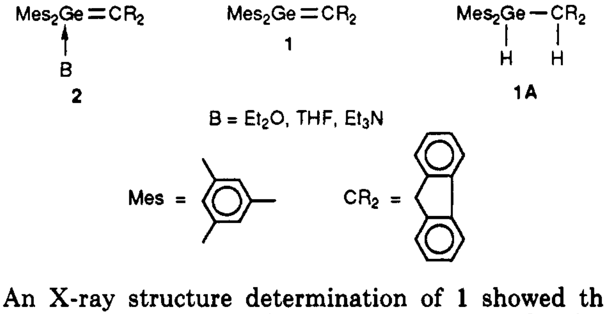
Dimesitylfluorenylidenegermane (1) reacts very readily with aldehydes and ketones, according to a [2 + 2] cycloaddition, leading to the corresponding germaoxetanes. These four-membered-ring heterocycles are quite stable, mainly due to the large steric hindrance of the substituents. In the case of acetone, reaction with the enolic form has been observed, followed by a germanotropic rearrangement. Germaoxetanes 3 (monoclinic, $P2_1/n$, a = 12.668 (5) Å, b = 16.794 (6) Å, c = 14.600 (5) Å, β = 90.25 (3)°, V = 3106 (2) Å^3, Z = 4, R = 0.0525) and 4 (monoclinic, $P2_1/c$, a = 22.807 (5) Å, b = 17.713 (6) Å, c = 18.425 (4) Å, β = 102.64 (2)°, V = 7263 (3) Å^3, Z = 8, R = 0.0697), obtained from benzaldehyde and benzophenone, have been characterized by X-ray diffraction methods and their data compared to those of the acyclic digermoxane 6 (triclinic, $P\bar{1}$, a = 13.002 (3), Å, b = 14.962 (2) Å, c = 16.094 (1) Å, α = 98.92 (1)°, β = 95.90 (2)°, γ = 114.52 (1)°, V = 2765 (1) Å^3, Z = 2, R = 0.0781) prepared by hydrolysis of germene 1.

Introduction

Germenes, $R'_2Ge{=}CR_2$, compounds with a germanium-carbon double bond, have long been speculated to be reactive intermediates; they were unambiguously first evidenced by Barton,[1] and then by other groups in trapping reactions.[2,3] Owing to the large steric hindrance around the double bond and large mesomeric effects, we have recently isolated the stable germene 2 as an adduct with Lewis bases (Et_2O, THF, Et_3N).[4,5] The "free" germene 1 was further obtained by thermal decomposition of 2.[6]



An X-ray structure determination of 1 showed the presence of a double bond between germanium and carbon ($Ge{=}C$ = 1.80 Å) with a 10.4% shortening relative to the single bond in the hydrogenated derivative 1A. The germene 1 is very reactive toward protic reagents,[4] hydrides,[4] dimethyl disulfide,[4] nitrones,[4] dienes,[4] and diazo derivatives.[7] In this paper we report the reactions of germene 1 with aldehydes and ketones and the first

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[1] Barton, T. J.; Kline, E. A.; Garvey, P. M. *J. Am. Chem. Soc.* 1973, *95*, 3078.

[2] (a) Barton, T. J.; Hoekman, S. K. *J. Am. Chem. Soc.* 1980, *102*, 1584. (b) Riviere, P.; Castel, A.; Satgé, J. *J. Am. Chem. Soc.* 1980, *102*, 5413. (c) Wiberg, N.; Kim, C. K. *Chem. Ber.* 1986, *119*, 2966, 2980.

[3] For reviews see: (a) Satgé, J. *Adv. Organomet. Chem.* 1982, *21*, 241. (b) Wiberg, N. *J. Organomet. Chem.* 1984, *273*, 141. (c) Barrau, J.; Escudie, J.; Satgé, J. *Chem. Rev.* 1990, *90*, 283.

[4] Couret, C.; Escudie, J.; Satgé, J.; Lazraq, M. *J. Am. Chem. Soc.* 1987, *109*, 4411.

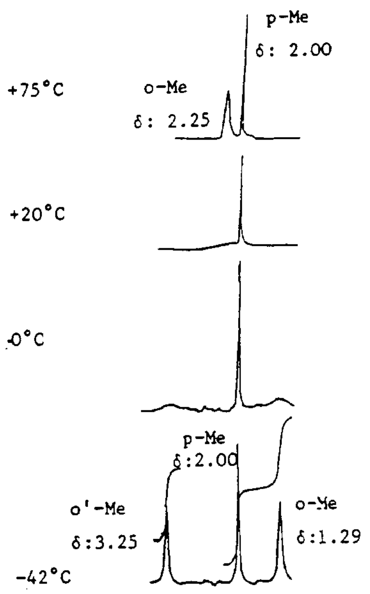
[5] In the same year as us, Berndt et al. described the synthesis of two other stable germenes: Meyer, H.; Baum, G.; Massa, W.; Berndt, A. *Angew. Chem.* 1987, *99*, 790; *Angew. Chem., Int. Ed. Engl.* 1987, *26*, 798. Berndt, A.; Meyer, H.; Baum, G.; Massa, W.; Berger, S. *Pure Appl. Chem.* 1987, *59*, 1011.

[6] Lazraq, M.; Escudie, J.; Couret, C.; Satgé, J.; Dräger, M.; Dammel, R. *Angew. Chem.* 1988, *100*, 885; *Angew. Chem., Int. Ed. Engl.* 1988, *27*, 828.

[7] Lazraq, M.; Couret, C.; Declercq, J. P.; Dubourg, A.; Escudie, J.; Riviere-Baudet, M. *Organometallics* 1990, *9*, 845.

0276-7333/91/2310-1771$02.50/0

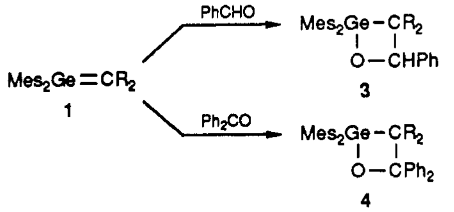
Chart I



structurally characterized 2-germaoxetanes, 3 and 4. Their X-ray data are compared to those of the acyclic digermoxane 6 obtained by slow hydrolysis of 1.

Results and Discussion

(a) Benzaldehyde and Benzophenone. Benzaldehyde and benzophenone react very readily with germene 1 to afford nearly quantitatively the corresponding germaoxetanes 3 and 4 according to a [2 + 2] cycloaddition. 3 and 4 have been characterized by various physicochemical methods, including X-ray diffraction. Wiberg[2c] has observed both [2 + 2] and [2 + 4] cycloadditions between benzophenone and the transient germene $Me_2Ge{=}C(SiMe_3)_2$. The four-membered-ring germaoxetane, which easily decomposes to the starting material by thermal cycloreversion, can be considered as a store for this germene.



^{1}H NMR and Mass Spectrometry. While the ^{1}H NMR spectrum of 3 appears normal, the spectrum of 4 at room temperature displays only a singlet for the methyl groups of the mesityls; this singlet is attributable to the two magnetically equivalent *p*-Me groups (because of the folding of the four-membered ring, there are two enantiomers for 4; however, 4 is not far from C_s symmetry in the solid state (Figure 2) and will average to ideal C_s symmetry in solution by equilibrating the two chiral enantiomers contained in the centrosymmetric unit cell), whereas the *o*-Me groups appear as very broad signals. Such a phenomenon is, of course, due to the very slow rotation of the mesityl groups along the $Ge-C_{ipso}$(Mes) axis at this temperature. As expected, a singlet for the four magnetically equivalent *o*-Me groups is observed at higher temperature and two singlets are seen at low temperature when the rotation is completely hindered (see Chart I). A dynamic NMR study performed between −42 and +75 °C allowed us to determine the coalescence temperature as ~20 °C. Therefore, the free energy of activation for the rotation of the mesityl groups, calculated by the Eyring equation, is ~13.8 kcal/mol.

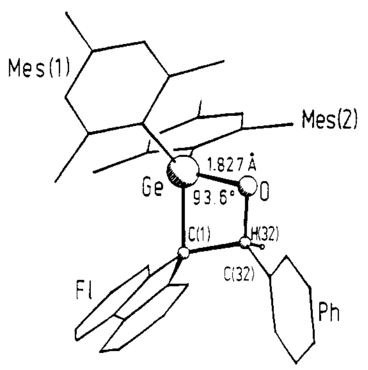
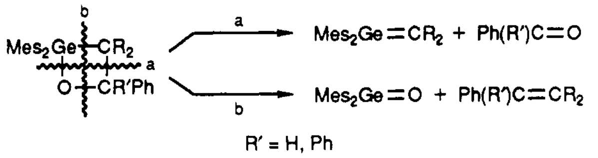


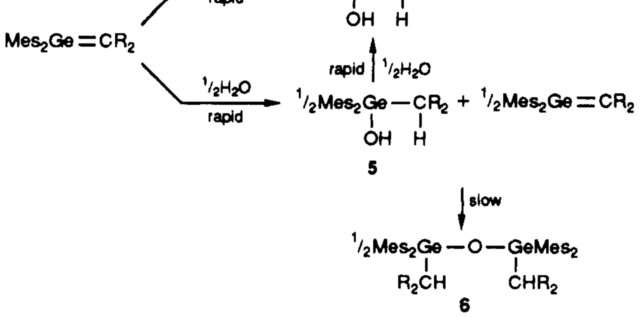
Figure 1. Drawing of 3. Labels of atoms and groups are as given in Table III.

In mass spectrometry, besides the molecular ion peak, we have observed two types of [4] → [2 + 2] decomposition (a and b) of the four-membered ring:



The ratios of routes a and b are comparable, even if route b is slightly favored. We can note that we always observed in the case of route b a signal corresponding to $Mes_2Ge{=}O$ + H. It seems that this germanone abstracts an hydrogen immediately after its formation to become stabilized in the form $(Mes_2GeOH)^+$. The same phenomenon has been observed for the germanethione $Mes_2Ge{=}S$.[8] However, it also seems possible that the germaoxetane can be protonated in the spectrometer ion source, giving Mes_2GeOH^+ and alkene directly, whereas if it is not protonated, it gives germene and ketone.

Description of the Molecular Structures of 3, 4, and 6. The structures of 3 (Figure 1) and 4 (two crystallographically independent molecules, Figure 2) have been determined by X-ray analysis. For a useful model of typical structural data (Table I) and of the steric strain of 3 and 4 we have synthesized the acyclic compound 6, which has also been structurally determined by X-ray diffraction (Figure 3). Digermoxane 6 could be prepared by direct hydrolysis of 1 with $^1/_2$ equiv of water: the formation of 6 can be explained by the preliminary formation of 5, which behaves as the protic reagent ROH and reacts slowly (about one night at room temperature), probably because of the great steric hindrance, with starting 1.



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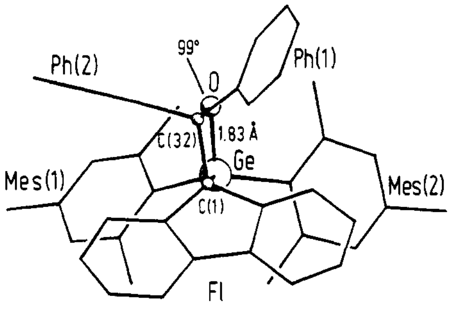
[8] Lavayssiere, H.; Dousse, G. Private communication.

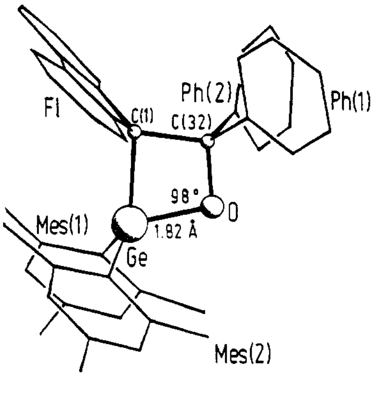
Table I. Geometries of the Compounds 3, 4 (Two Crystallographically Independent Molecules) and 6 (Two Ge Atoms), Compared with the Results[6] for 1 (Ge=C Double Bond; Two Crystallographically Independent Molecules) and 1A (Hydrogenated 1 with GeH—CH Bond) (Esd's in Parentheses)

	3[a]	4[a]		6		1		1A
		molecule 1	molecule 2	Ge(1)	Ge(2)	molecule 1	molecule 2	
Bond Lengths (Å)								
Ge–O	1.827 (3)	1.83 (1)	1.82 (1)	1.80 (1)	1.78 (1)			
Ge–C(1)	2.031 (4)	2.07 (2)	2.04 (2)	2.02 (1)	2.03 (1)	1.806 (4)	1.801 (4)	2.010 (4)
C(1)–C(32)	1.572 (6)	1.62 (3)	1.60 (3)					
C(32)–O	1.441 (5)	1.46 (3)	1.43 (3)					
Ge–Mes(1)	1.957 (5)	1.96 (2)	1.96 (2)	2.00 (1)	1.98 (1)	1.944 (4)	1.937 (4)	1.964 (3)
Ge-Mes(2)	1.965 (5)	2.04 (2)	1.98 (3)	1.98 (1)	1.99 (1)	1.931 (4)	1.933 (4)	1.965 (3)
Bond Angles within the Four-Membered Rings (deg)								
Ge–O–C(32)	93.7 (2)	99 (1)	98 (1)	*b*	*b*			
O–C(32)–C(1)	103.6 (3)	101 (2)	103 (2)					
C(32)–C(1)–Ge	82.4 (2)	85 (1)	84 (1)					
C(1)–Ge–O	75.6 (2)	75 (1)	75 (1)					
Torsion Angles within the Four-Membered Rings (deg)								
Ge–O–C(32)–C(1)	−19.6 (3)	−10 (1)	−7 (2)					
O–C(32)–C(1)–Ge	+17.7 (3)	+9 (1)	+6 (1)					
C(32)–C(1)–Ge–O	−13.9 (2)	−7 (1)	−5 (1)					
C(1)–Ge–O–C(32)	+15.1 (3)	+8 (1)	+5 (1)					
Folding of the Four-Membered Rings (deg)								
C(1)GeO–C(1)C(32)O	23.7 (4)	12 (2)	8 (2)					
GeC(1)C(32)–GeOC(32)	22.8 (4)	12 (2)	8 (2)					
Twist between the Aromatic Groups (deg)								
Fl–Mes(1)	40.1 (5)	33 (2)	38 (2)	64 (1)	84 (1)	65.9 (3)	64.4 (3)	85.9 (2)
Fl–Mes(2)	40.9 (4)	48 (2)	27 (2)	86 (1)	61 (1)	65.4 (3)	68.8 (3)	41.4 (3)
Mes(1)–Mes(2)	67.3 (6)	70 (3)	56 (3)	73 (1)	69 (1)	84.0 (5)	88.1 (5)	82.6 (4)

[a] Additional distances (Å): 3, C(32)–Ph = 1.503 (7); 4, C(32)–Ph(1) = 1.53 (3), 1.54 (3), C(32)–Ph(2) = 1.54 (3), 1.55 (4). [b] Ge–O–Ge angle 151.0 (4)°.



molecule(1)



molecule(2)

Figure 2. Drawings of the two crystallographically independent molecules of 4 in different views, with hydrogen atoms omitted. Labels of atoms and groups are as given in Table IV (group Ph(22) distorted because of partial disorder).

As previously described,[4] hydrolysis of 1 with an excess of water leads to the immediate and exclusive formation of 5.

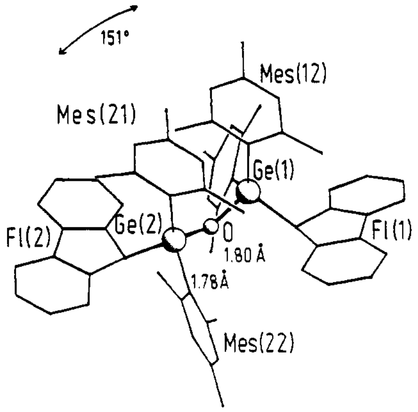


Figure 3. Drawing of 6. Labels of atoms and groups are as given in Table V (label Mes(11) omitted).

The three independent four-membered rings are folded to relieve steric strain; this is more clear-cut in 3 (23°) than in 4 (8 and 12°). In all three cases the folding around the rings remains nearly constant. The fold angles are comparable to that observed in silaoxetanes (20.1°)[9] and in 1,3-digermaoxetanes (8.4 and 8.8°)[10] but higher than in the homocycle $(Ph_2Ge)_4$ (3.9°).[11] Much bigger fold angles are observed in 1,3-digermazanes (34 and 38°)[7] and in cyclobutanes (35°).[12]

The bond angles in the four-membered rings are comparable in 3 and 4, with the exception of the Ge–O–C angle

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(9) (a) Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246. (b) Brook, A. G.; Vorspohl, K.; Ford, R. R.; Hesse, M.; Chatterton, W. J. *Organometallics* **1987**, *6*, 2128.

(10) Masamune, S.; Batcheller, S. A.; Park, J.; Davis, W. M.; Yamashita, O.; Ohta, Y.; Kabe, Y. *J. Am. Chem. Soc.* **1989**, *111*, 1888.

(11) Ross, L.; and Dräger, M. *J. Organomet. Chem.* **1980**, *199*, 195.

(12) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 129.

Table II. Crystallographic Data for 3 ($Mes_2GeFl(OCHPh)$), 4 ($Mes_2GeFl(OCPh_2)\bullet{}^1/_4$(*n*-pentane)), and 6 ($Mes_2FlGe{-}O{-}GeFlMes_2\bullet{}^1/_2$(diphenylacetylene))[25] and Structure Determination Details

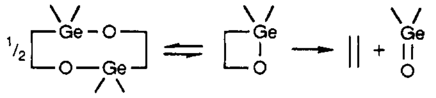
	3	4	6
	Crystal Data (Mo $K\alpha_1$, λ = 0.709 26 Å)		
formula; M_r	$C_{38}H_{36}GeO$; 581.30	$C_{44}H_{40}GeO\cdot{}^1/_4C_5H_{12}$; 675.44	$C_{62}H_{62}Ge_2O\cdot{}^1/_2C_{14}H_{10}$; 1057.48
cryst habit	thick plate	triangular thin plate	fragment, cut from a bigger fragment (0.25 × 0.0.16 × 0.23 mm)
face indices (dist from a common origin inside the cryst, mm)	1, −1,0, −1,1,0 (0.50); 1,0,−1, −1,0,1 (0.125); 0,1,−1,0,−1,1 (0.50); 010, 0,−1,0 (0.39); 01,0,0, 0,0,−1 (0.35)	100, −1,0,0 (0.015); 010, 0,−1,0 (0.13); 001, 0,0,−1 (0.11); 011, 0,−1,−1 (0.08)	no definable faces
cryst color	light yellow	light yellow	yellow
cryst syst, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
unit cell dimens	a = 12.668 (5) Å, b = 16.794 (6) Å, c = 14.600 (5) Å, β = 90.25 (3)°	a = 22.807 (5) Å, b = 17.713 (6) Å, c = 18.425 (4) Å, β = 102.64 (2)°	a = 13.002 (3) Å, b = 14.962 (2) Å, c = 16.094 (1) Å, α = 98.92 (1)°, β = 95.90 (2)°, γ = 114.52 (1)°
least-squares fit	25 rflns; θ = 18–21°	66 rflns; θ = 9–14°	124 rflns; θ = 15–18°
packing: V, Å^3; Z; $F(000)$	3106 (2); 4; 1216	7263 (3); 8; 2836	2765 (1); 2; 1106
D_{calcd}, D_{exptl}, g cm^{-3}	1.243, 1.238	1.235, 1.245	1.270, 1.243
	Intensity Data Collection (Mo $K\bar{\alpha}$, λ = 0.710 69 Å, Graphite Monochromator)		
temp, °C; θ range, deg; $(\sin \theta_{max})/\lambda$, Å^{-1}	22; 1.5–30.0; 0.704	22; 1.5–25; 0.59	21; 1.5–27; 0.64
range of *hkl*	+17,+23,±20	+27,+21,±21	+16,±19,±20
no. of ref rflns	3, every 5000 s	3, every 6000 s	2, every 4000 s
loss of intens, % (time, days); cor	12.5 (8); dir fit	26 (13); linear	32 (12); dir fit
no. of rflns: measd, indep (int R)	9414, 9044 (0.0143)	12 993, 12 654 (0.0260)	12 588, 12 040 (0.0390)
no. of rflns used (limit)	3965 ($I > 2\sigma(I)$)	2146 ($I > 2\sigma(I)$)	4049 ($I > 2\sigma(I)$)
μ, cm^{-1}; abs cor	9.71; by face indices	8.36; by face indices	10.86; no
range of transmissn	0.7889–0.5135	0.9751–0.8839	
	Refinement		
choice of thermal params	Ge, O, C anisotr; H(32) isotr; arom H common isotr; aliph H isotr fixed	Ge anisotr; O, C, isotr; H same as rel C	Ge, O, anisotr; C isotr; H same as rel C
no. of variables; rfln/variable ratio, last shift	369; 10.7, $<0.02\sigma$	421; 5.1, $<0.05\sigma$	341; 11.9, $<0.05\sigma$
final R, R_w	0.0525, 0.0695	0.0697, 0.0711	0.0781, 0.0846
weighting scheme	$w = 1/(\sigma^2(F) + 0.003F^2)$	$w = 1/(\sigma^2(F) + 0.00114F^2)$	$w = 1/(\sigma^2(F) + 0.00111F^2)$
final diff Fourier max, e Å^{-3}	0.45, near Ge	0.45, near disordered Ph(22)	0.66, near Ge(2)

(94° in **3**, 99° in **4**). This latter bond angle contains most of the steric strain of the rings: normal Ge–O–Ge angles range from 130 to 180°,[13] as exemplified by the structure of **6** (151°). The small angle of 75° at the germanium atom is not unusual: e.g. 79.6° in 1,3-digermazane,[7] 74.1° in 3,4-digerma-1,2-dioxetane,[10] and 75.0° in 2-germaphosphetene.[14] In $(Ph_2Ge)_4$ the angles at Ge are near 90°.[11]

The bond lengths in the three four-membered rings are somewhat longer than the standard corresponding bonds. This elongation concerns particularly the Ge–O bond (1.83 Å, standard range 1.73–1.79 Å[13]) and is not a result of the bulky substituents at germanium: **6** displays normal Ge–O distances. In contrast, the long Ge–fluorenyl bond is induced by this bulky fluorenyl group. With the exception of the Ge=C double bond in **1** (1.80 Å),[6] all compounds in Table I show Ge—C bonds longer than 2 Å between Ge and fluorenyl. Normal Ge—C distances range from 1.90 to 1.98 Å;[15] the germanium–mesityl distances of Table I are placed in the upper third of this range. An exception is again the compound **1**, with shorter Ge(sp^2)–mesityl bonds.[6] The bond lengths and bond angles within the phenyl, the mesityl, and the fluorenyl groups span the normal limits[6] and deserve no special comment.

The overall shape of the five compounds of Table I is dominated by the twist between the bulky aromatic groups fluorenyl, Mes(1), and Mes(2). In this respect, all three cyclic molecules are remarkably similar, with a break in going to the acyclic species. Between the acyclic molecules there is again not much difference. The crystal structures of **4** and **6** contain the solvent of crystallization, *n*-pentane and diphenylacetylene,[25] respectively. Both solvent molecules are statistically ordered around a center of symmetry of the respective unit cell and serve only as "gap fillers". The cores of the molecules **4** and **6** are far off these centers; interaction with the solvent molecules does not exist.

3 and **4** have good thermal stability (they are recovered unchanged after heating at 100 °C for 10 h), in contrast to other heterocycles of this type, which generally dimerize[16] or decompose by a [4] → [2 + 2] process with formation of germanone and alkene:[3a]



For example, germaoxetanes obtained from the transient germenes $Ph_2Ge{=}C(H)COOEt$,[2b] $Et_2Ge{=}C(H)Ph$,[17] and $Me_2Ge{=}CH_2$[18] and aldehydes such as benzaldehyde and formaldehyde undergo this type of [4] → [2 + 2] decomposition.

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[13] For a summary, see: Ross, L.; Dräger, M. *Z. Naturforsch.* **1984**, *39B*, 868.

[14] Andrianarison, M.; Couret, C.; Declercq, J. P.; Dubourg, A.; Escudie, J.; Satgé, J. *J. Chem. Soc., Chem. Commun.* **1987**, 921.

[15] For a summary, see: Dräger, M.; Ross, L.; Simon, D. *Rev. Silicon, Germanium, Tin Lead Compd.* **1983**, *7*, 299.

[16] Barrau, J.; Massol, M.; Mesnard, D.; Satgé, J. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 321.

[17] Marchand, A.; Gerval, P.; Duboudin, F.; Joanny, M.; Mazerolles, P. *J. Organomet. Chem.* **1984**, *267*, 93.

[18] Barrau, J.; Rima, G.; El Amine, M.; Satgé, J. *Synth. React. Inorg. Met.-Org. Chem.* **1988**, *18*, 317.

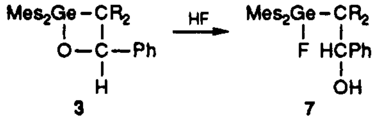
Table III. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for 3 ($Mes_2GeFl(OCHPh)$) (Esd's in Parentheses)

group	atom	*x/a*	*y/b*	*z/c*	*U*(eq),[a] Å^2
	Ge(1)	0.11715 (4)	0.21040 (3)	0.10534 (3)	0.0445 (2)
Fl	C(1)	0.1705 (3)	0.2117 (2)	−0.0255 (2)	0.044 (2)
	C(2)	0.0942 (3)	0.1887 (2)	−0.1009 (2)	0.043 (2)
	C(3)	−0.0042 (3)	0.2184 (3)	−0.1225 (3)	0.055 (2)
	C(4)	−0.0613 (4)	0.1821 (3)	−0.1920 (3)	0.067 (3)
	C(5)	−0.0196 (4)	0.1178 (3)	−0.2394 (3)	0.071 (3)
	C(6)	0.0796 (4)	0.0893 (3)	−0.2204 (3)	0.061 (3)
	C(7)	0.1376 (3)	0.1254 (2)	−0.1513 (2)	0.047 (2)
	C(8)	0.2441 (3)	0.1093 (2)	−0.1174 (3)	0.049 (2)
	C(9)	0.3182 (4)	0.0534 (3)	−0.1454 (3)	0.063 (3)
	C(10)	0.4144 (4)	0.0526 (3)	−0.1025 (4)	0.072 (3)
	C(11)	0.4386 (4)	0.1050 (3)	−0.0323 (4)	0.069 (3)
	C(12)	0.3645 (3)	0.1597 (3)	−0.0022 (3)	0.058 (3)
	C(13)	0.2657 (3)	0.1613 (2)	−0.0447 (3)	0.045 (2)
Mes(1)	C(14)	0.1813 (3)	0.1500 (2)	0.2058 (3)	0.048 (2)
	C(15)	0.1892 (3)	0.1900 (2)	0.2909 (3)	0.051 (2)
	C(16)	0.1400 (4)	0.2707 (2)	0.3059 (3)	0.064 (3)
	C(17)	0.2393 (4)	0.1525 (3)	0.3644 (3)	0.062 (3)
	C(18)	0.2805 (4)	0.0770 (3)	0.3576 (3)	0.069 (3)
	C(19)	0.3338 (5)	0.0376 (4)	0.4392 (4)	0.101 (5)
	C(20)	0.2704 (4)	0.0376 (3)	0.2738 (3)	0.065 (3)
	C(21)	0.2233 (3)	0.0722 (2)	0.1980 (3)	0.053 (2)
	C(22)	0.2172 (4)	0.0225 (2)	0.1119 (3)	0.064 (3)
Mes(2)	C(23)	−0.0365 (3)	0.2253 (2)	0.1105 (2)	0.046 (2)
	C(24)	−0.0982 (3)	0.1576 (2)	0.0884 (2)	0.047 (2)
	C(25)	−0.0478 (4)	0.0794 (2)	0.0652 (3)	0.059 (3)
	C(26)	−0.2078 (3)	0.1621 (3)	0.0895 (3)	0.056 (3)
	C(27)	−0.2581 (4)	0.2326 (3)	0.1125 (3)	0.063 (3)
	C(28)	−0.3774 (4)	0.2368 (4)	0.1161 (5)	0.097 (4)
	C(29)	−0.1978 (4)	0.2988 (3)	0.1329 (3)	0.063 (3)
	C(30)	−0.0881 (3)	0.2968 (2)	0.1311 (3)	0.051 (2)
	C(31)	−0.0318 (4)	0.3746 (2)	0.1530 (3)	0.066 (3)
	O(1)	0.1854 (2)	0.3057 (1)	0.0947 (2)	0.054 (1)
	C(32)	0.1880 (4)	0.3024 (2)	−0.0038 (3)	0.046 (2)
	H(32)	0.1292 (31)	0.3283 (23)	−0.0253 (26)	0.034 (10)[b]
Ph	C(33)	0.2863 (3)	0.3398 (2)	−0.0420 (3)	0.047 (2)
	C(34)	0.2983 (4)	0.3480 (3)	−0.1347 (3)	0.069 (3)
	C(35)	0.3884 (5)	0.3806 (3)	−0.1700 (3)	0.082 (4)
	C(36)	0.4678 (5)	0.4076 (3)	−0.1139 (4)	0.080 (4)
	C(37)	0.4557 (4)	0.4007 (3)	−0.0216 (4)	0.080 (4)
	C(38)	0.3653 (4)	0.3659 (3)	0.0144 (3)	0.065 (3)

[a] *U*(eq) is one-third of the trace of the orthogonal **U**(*ij*) tensor. [b] Isotropic *U*.

In the case of the germene $Me_2Ge{=}C(SiMe_3)_2$, Wiberg et al. observed with benzophenone both [2 + 2] and [2 + 4] cycloadditions, with the [2 + 2] process as the major one.[2c] Benzaldehyde and benzophenone react also with other doubly bonded organometallic species such as silenes or disilenes to give [2 + 2] and [2 + 4] (silenes)[19] or exclusively [2 + 2] (disilenes)[20] cycloadditions.

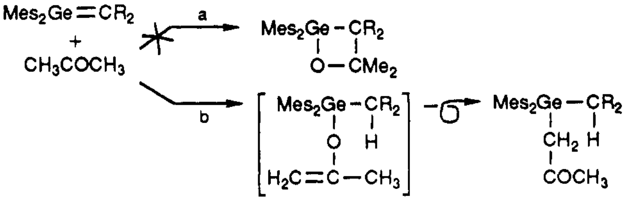
Heterocycles 3 and 4 also are very stable toward oxidation and hydrolysis. They can be easily purified by column chromatography on silica. The Ge–O bond is not cleaved by water, acetic acid, or solutions of hydrofluoric acid at room temperature, in contrast to what is generally observed. We have only obtained the opening of the Ge–O bond with an excess of hydrofluoric acid in refluxing THF:



3 7

This chemical inertness of the Ge–O bond in these heterocycles is probably due to the large steric hindrance caused by mesityl groups on germanium, which is clearly demonstrated by the X-ray structure determinations and by ^1H NMR spectroscopy (see above).

(b) Acetone. Between acetone and germene 1, two types of reactions are possible: a [2 + 2] cycloaddition, as in the case of benzaldehyde or benzophenone (route a), or the reaction of acetone in its enolic form (route b). We have only observed this last reaction, leading to the transient intermediate 8, which immediately undergoes germanotropic rearrangement[21] to afford 9.



8 9

This reaction is not surprising, as 1 is very reactive toward protic reagents. Note that, with other doubly bonded main-group derivatives, acetone reacts either as a protic reagent or in [2 + 2] cycloadditions and sometimes gives both reactions, depending on the group 14 metal used and on its substituents. For example, on digermenes and disilenes substituted by four mesityl groups, only [2 + 2]

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[21] (a) Lutsenko, I. F.; Foss, V. L.; Semenenko, N. M. *Zh. Obshch. Khim.* **1969**, *39*, 1174. (b) Semenenko, N. M.; Foss, V. L.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1971**, *41*, 2458.

Table IV. Fractional Atomic Coordinates and Thermal Parameters for the Two Crystallographically Independent Molecules and the Statistically Ordered Solvent of 4 (Mes$_2$GeFl(OCPh$_2$)$\cdot$$^1/_4$(*n*-pentane)) (Esd's in Parentheses)

Isotropic Atoms

	molecule 1					molecule 2				
group	atom	*x/a*	*y/b*	*z/c*	*U*, Å^2	atom	*x/a*	*y/b*	*z/c*	*U*, Å^2
	Ge(1)	0.2197 (1)	0.0750 (1)	0.4663 (1)		Ge(2)	0.7018 (1)	0.3875 (1)	0.4256 (1)	
Fl	C(11)	0.2111 (9)	0.0631 (12)	0.5752 (11)	0.042 (6)	C(21)	0.7157 (9)	0.3924 (12)	0.5389 (10)	0.034 (6)
	C(12)	0.2728 (9)	0.0316 (11)	0.6192 (10)	0.033 (6)	C(22)	0.6755 (11)	0.3484 (12)	0.5780 (12)	0.050 (7)
	C(13)	0.3288 (9)	0.0545 (11)	0.6210 (10)	0.039 (6)	C(23)	0.6138 (13)	0.3487 (15)	0.5705 (14)	0.084 (9)
	C(14)	0.3759 (13)	0.0101 (14)	0.6642 (13)	0.079 (8)	C(24)	0.5902 (15)	0.2952 (16)	0.6196 (15)	0.101 (10)
	C(15)	0.3606 (12)	−0.0515 (15)	0.6988 (13)	0.077 (8)	C(25)	0.6287 (15)	0.2534 (19)	0.6641 (17)	0.113 (11)
	C(16)	0.3063 (10)	−0.0780 (14)	0.7008 (11)	0.060 (7)	C(26)	0.6866 (15)	0.2503 (19)	0.6743 (16)	0.108 (10)
	C(17)	0.2594 (11)	−0.0336 (12)	0.6586 (11)	0.047 (6)	C(27)	0.7125 (12)	0.2997 (14)	0.6286 (13)	0.063 (8)
	C(18)	0.1963 (11)	−0.0431 (13)	0.6477 (12)	0.058 (7)	C(28)	0.7706 (12)	0.3077 (13)	0.6262 (13)	0.060 (7)
	C(19)	0.1623 (11)	−0.0971 (14)	0.6770 (13)	0.070 (8)	C(29)	0.8257 (11)	0.2670 (14)	0.6640 (13)	0.066 (8)
	C(110)	0.1040 (12)	−0.0927 (15)	0.6573 (13)	0.082 (9)	C(210)	0.8763 (12)	0.2886 (13)	0.6476 (13)	0.069 (8)
	C(111)	0.0715 (12)	−0.0430 (13)	0.6104 (13)	0.070 (8)	C(211)	0.8849 (12)	0.3439 (13)	0.5997 (12)	0.066 (8)
	C(112)	0.1014 (11)	0.0131 (13)	0.5765 (13)	0.064 (8)	C(212)	0.8341 (10)	0.3824 (13)	0.5605 (11)	0.049 (6)
	C(113)	0.1644 (10)	0.0095 (11)	0.5979 (10)	0.035 (6)	C(213)	0.7779 (10)	0.3642 (11)	0.5746 (11)	0.038 (6)
Mes(1)	C(114)	0.1512 (9)	0.0521 (10)	0.3844 (10)	0.033 (6)	C(214)	0.6241 (10)	0.3529 (12)	0.3676 (11)	0.046 (6)
	C(115)	0.1358 (9)	0.1028 (11)	0.3260 (10)	0.039 (6)	C(215)	0.6003 (12)	0.2795 (13)	0.3753 (13)	0.067 (8)
	C(116)	0.1778 (11)	0.1702 (12)	0.3223 (12)	0.072 (8)	C(216)	0.6337 (12)	0.2265 (14)	0.4320 (13)	0.103 (10)
	C(117)	0.0838 (9)	0.0938 (11)	0.2713 (11)	0.049 (6)	C(217)	0.5448 (12)	0.2600 (16)	0.3284 (12)	0.079 (8)
	C(118)	0.0473 (10)	0.0342 (12)	0.2740 (11)	0.048 (7)	C(218)	0.5150 (12)	0.3082 (15)	0.2800 (14)	0.078 (9)
	C(119)	−0.0100 (11)	0.0260 (14)	0.2146 (12)	0.086 (9)	C(219)	0.4568 (14)	0.2776 (19)	0.2278 (16)	0.149 (13)
	C(120)	0.0617 (10)	−0.0190 (12)	0.3284 (11)	0.055 (7)	C(220)	0.5352 (12)	0.3765 (16)	0.2687 (14)	0.081 (9)
	C(121)	0.1144 (10)	−0.0130 (12)	0.3826 (11)	0.048 (6)	C(221)	0.5885 (11)	0.4013 (13)	0.3157 (13)	0.068 (8)
	C(122)	0.1288 (9)	−0.0780 (12)	0.4355 (11)	0.063 (7)	C(222)	0.6056 (12)	0.4795 (14)	0.2944 (14)	0.094 (9)
Mes(2)	C(123)	0.3029 (9)	0.0643 (12)	0.4433 (10)	0.038 (6)	C(223)	0.7710 (11)	0.3616 (13)	0.3813 (13)	0.063 (8)
	C(124)	0.3181 (12)	−0.0092 (15)	0.4332 (13)	0.067 (8)	C(224)	0.8073 (11)	0.2950 (13)	0.4042 (12)	0.056 (7)
	C(125)	0.2799 (11)	−0.0774 (14)	0.4363 (13)	0.097 (9)	C(225)	0.7851 (11)	0.2336 (13)	0.4472 (12)	0.080 (9)
	C(126)	0.3763 (12)	−0.0278 (16)	0.4181 (12)	0.078 (8)	C(226)	0.8608 (10)	0.2893 (12)	0.3817 (11)	0.049 (7)
	C(127)	0.4103 (13)	0.0300 (17)	0.4172 (14)	0.075 (8)	C(227)	0.8836 (12)	0.3387 (15)	0.3394 (14)	0.074 (8)
	C(128)	0.4763 (13)	0.0249 (16)	0.4028 (16)	0.125 (11)	C(228)	0.9432 (11)	0.3283 (14)	0.3176 (13)	0.085 (9)
	C(129)	0.3976 (12)	0.1027 (15)	0.4263 (12)	0.076 (8)	C(229)	0.8455 (11)	0.4011 (14)	0.3149 (13)	0.076 (8)
	C(130)	0.3408 (11)	0.1269 (14)	0.4409 (12)	0.059 (7)	C(230)	0.7940 (11)	0.4137 (14)	0.3359 (12)	0.069 (8)
	C(131)	0.3284 (11)	0.2054 (12)	0.4578 (12)	0.078 (9)	C(231)	0.7601 (14)	0.4851 (16)	0.3070 (16)	0.129 (12)
	O(1)	0.2136 (6)	0.1712 (7)	0.4998 (7)	0.045 (4)	O(2)	0.7040 (6)	0.4881 (7)	0.4471 (7)	0.045 (4)
	C(132)	0.1992 (10)	0.1532 (12)	0.5711 (12)	0.048 (7)	C(232)	0.7079 (10)	0.4815 (12)	0.5254 (12)	0.044 (6)
Ph(1)	C(133)	0.2433 (10)	0.1962 (11)	0.6311 (12)	0.041 (6)	C(233)	0.7601 (9)	0.5304 (11)	0.5671 (11)	0.038 (6)
	C(134)	0.2563 (9)	0.1735 (12)	0.7042 (11)	0.046 (6)	C(234)	0.7870 (10)	0.5187 (13)	0.6437 (12)	0.055 (7)
	C(135)	0.2903 (11)	0.2150 (13)	0.7607 (14)	0.073 (8)	C(235)	0.8318 (11)	0.5607 (13)	0.6808 (13)	0.066 (7)
	C(136)	0.3111 (10)	0.2864 (12)	0.7397 (13)	0.057 (7)	C(236)	0.8559 (11)	0.6191 (15)	0.6464 (13)	0.078 (8)
	C(137)	0.2981 (11)	0.3124 (14)	0.6699 (13)	0.072 (8)	C(237)	0.8314 (11)	0.6318 (14)	0.5714 (13)	0.076 (8)
	C(138)	0.2638 (9)	0.2664 (12)	0.6151 (12)	0.049 (6)	C(238)	0.7840 (11)	0.5871 (13)	0.5317 (14)	0.072 (7)
Ph(2)	C(139)	0.1339 (9)	0.1766 (10)	0.5702 (11)	0.035 (6)	C(239)	0.6506 (11)	0.5152 (12)	0.5452 (13)	0.048 (7)
	C(140)	0.1156 (11)	0.1819 (12)	0.6361 (13)	0.054 (7)	C(240)	0.6416 (12)	0.5242 (13)	0.6139 (14)	0.065 (8)
	C(141)	0.0522 (11)	0.2008 (13)	0.6317 (15)	0.077 (8)	C(241)	0.5917 (13)	0.5588 (15)	0.6303 (17)	0.098 (10)
	C(142)	0.0177 (13)	0.2112 (13)	0.5631 (15)	0.087 (9)	C(242)	0.5494 (16)	0.5866 (17)	0.5757 (17)	0.123 (11)
	C(143)	0.0345 (13)	0.2055 (14)	0.4974 (16)	0.088 (9)	C(243)	0.5600 (24)	0.5829 (28)	0.5028 (27)	0.237 (21)
	C(144)	0.0951 (11)	0.1878 (12)	0.5016 (13)	0.061 (7)	C(244)	0.6083 (17)	0.5448 (19)	0.4885 (22)	0.155 (15)

Anisotropic Ge Atoms

atom	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
Ge(1)	0.047 (2)	0.041 (1)	0.036 (1)	0.002 (1)	0.011 (1)	0.000 (1)
Ge(2)	0.063 (2)	0.038 (1)	0.038 (1)	0.003 (1)	0.011 (1)	0.001 (1)

Statistically Ordered *n*-Pentane

atom	*x/a*	*y/b*	*z/c*	*U*, Å^2	sof
C(31)	0.0359 (50)	−0.0464 (58)	0.0138 (46)	0.019 (28)	0.25
C(32)	−0.0417 (46)	−0.0188 (58)	0.0007 (53)	0.016 (27)	0.25
C(33)	−0.0140 (60)	0.0141 (87)	−0.0218 (60)	0.034 (36)	0.25
C(34)	0.0649 (45)	−0.0066 (56)	0.0386 (45)	0.010 (22)	0.25
C(35)	0.0874 (64)	0.0494 (90)	0.0521 (75)	0.078 (43)	0.25
C(36)	0.1094 (44)	0.0948 (54)	0.0789 (49)	0.048 (32)	0.25
C(37)	0.0528 (58)	0.0817 (71)	0.0152 (65)	0.047 (34)	0.25
C(38)	0.0059 (82)	0.0896 (71)	0.0059 (76)	0.092 (43)	0.25
C(39)	0.0276 (67)	0.0347 (98)	0.0343 (79)	0.064 (46)	0.25
C(310)	0.0527 (56)	0.0883 (58)	0.0560 (61)	0.045 (32)	0.25

cycloadditions occurred.[20,22] With silenes only the reaction of acetone with the enolic form has been described by Wiberg,[23] and with disilenes substituted by two *tert*-butyl groups, both reactions are observed.[24]

Facile and high-yield [2 + 2] cycloadditions have been observed between 1 and aldehydes and ketones. Thus, the

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(24) Schäfer, A.; Weidenbruch, M.; Pohl, S. *J. Organomet. Chem.* **1985**, *282*, 305.

Table V. Fractional Atomic Coordinates and Thermal Parameters of 6 ($Mes_2FlGe–O–GeFlMes_2 \bullet {}^1/_2$(diphenylacetylene)) (Esd's in Parentheses)[25]

Anisotropic Atoms

atom	*x/a*	*y/b*	*z/c*	*U*(11)	*U*(22)	*U*(33)	*U*(23)	*U*(13)	*U*(12)
Ge(1)	0.0692 (1)	0.21702 (9)	0.31844 (7)	0.0455 (9)	0.0443 (8)	0.0457 (8)	0.0150 (6)	0.0167 (7)	0.0218 (7)
Ge(2)	0.2304 (1)	0.11520 (9)	0.21687 (7)	0.0465 (9)	0.0471 (8)	0.0419 (8)	0.0139 (60)	0.0159 (7)	0.0233 (7)
O(1)	0.1264 (6)	0.1579 (5)	0.2424 (3)	0.053 (5)	0.063 (4)	0.040 (4)	0.016 (3)	0.021 (3)	0.037 (4)

Isotropic Atoms

	C atoms at Ge(1)					C atoms at Ge(2)				
group	atom	*x/a*	*y/b*	*z/c*	*U*, Å²	atom	*x/a*	*y/b*	*z/c*	*U*, Å²
Fl	C(11)	0.0452 (9)	0.3177 (7)	0.2582 (6)	0.045 (2)	C(21)	0.1332 (9)	−0.0289 (7)	0.1513 (6)	0.051 (3)
	C(12)	0.1450 (9)	0.4042 (8)	0.2401 (6)	0.049 (3)	C(22)	0.0516 (10)	−0.1040 (8)	0.1933 (6)	0.051 (3)
	C(13)	0.2337 (10)	0.4046 (8)	0.1981 (6)	0.055 (3)	C(23)	−0.0327 (10)	−0.0993 (9)	0.2367 (7)	0.065 (3)
	C(14)	0.3136 (11)	0.4961 (8)	0.1876 (7)	0.066 (3)	C(24)	−0.0969 (12)	−0.1802 (9)	0.2708 (8)	0.079 (4)
	C(15)	0.3067 (11)	0.5861 (9)	0.2163 (7)	0.067 (3)	C(25)	−0.0812 (12)	−0.2674 (11)	0.2593 (8)	0.086 (4)
	C(16)	0.2201 (10)	0.5859 (9)	0.2562 (7)	0.061 (3)	C(26)	0.0010 (12)	−0.2741 (10)	0.2146 (8)	0.079 (4)
	C(17)	0.1381 (10)	0.4955 (8)	0.2684 (7)	0.054 (3)	C(27)	0.0696 (10)	−0.1923 (8)	0.1817 (7)	0.060 (3)
	C(18)	0.0357 (11)	0.4717 (9)	0.3052 (7)	0.063 (3)	C(28)	0.1585 (11)	−0.1782 (9)	0.1333 (7)	0.065 (3)
	C(19)	−0.0062 (13)	0.5373 (12)	0.3415 (8)	0.093 (4)	C(29)	0.2072 (12)	−0.2437 (11)	0.1074 (8)	0.090 (4)
	C(110)	−0.1098 (14)	0.4957 (12)	0.3660 (9)	0.100 (5)	C(210)	0.2911 (14)	−0.2098 (12)	0.0606 (9)	0.107 (5)
	C(111)	−0.1736 (16)	0.3919 (12)	0.3558 (10)	0.115 (5)	C(211)	0.3293 (14)	−0.1191 (11)	0.0387 (9)	0.100 (5)
	C(112)	−0.1307 (12)	0.3248 (11)	0.3203 (8)	0.084 (4)	C(212)	0.2807 (12)	−0.0533 (10)	0.0630 (8)	0.078 (4)
	C(113)	−0.0226 (11)	0.3689 (9)	0.2984 (7)	0.062 (3)	C(213)	0.1979 (10)	−0.0825 (8)	0.1134 (7)	0.054 (3)
Mes(1)	C(114)	−0.0929 (9)	0.1201 (7)	0.3177 (6)	0.046 (2)	C(214)	0.3439 (9)	0.1491 (8)	0.3222 (6)	0.048 (3)
	C(115)	−0.1377 (11)	0.1201 (8)	0.3943 (7)	0.058 (3)	C(215)	0.3647 (9)	0.0793 (7)	0.3609 (6)	0.046 (2)
	C(116)	−0.0742 (11)	0.1883 (9)	0.4783 (7)	0.077 (4)	C(216)	0.2925 (11)	−0.0337 (8)	0.3290 (7)	0.069 (3)
	C(117)	−0.2534 (11)	0.0531 (9)	0.3909 (8)	0.074 (3)	C(217)	0.4548 (10)	0.1133 (8)	0.4306 (7)	0.057 (3)
	C(118)	−0.3221 (12)	−0.0081 (10)	0.3171 (9)	0.079 (4)	C(218)	0.5232 (10)	0.2130 (8)	0.4612 (7)	0.058 (3)
	C(119)	−0.4471 (14)	−0.0789 (12)	0.3150 (10)	0.124 (6)	C(219)	0.6250 (11)	0.2476 (9)	0.5354 (8)	0.081 (4)
	C(120)	−0.2804 (12)	−0.0050 (10)	0.2417 (8)	0.078 (4)	C(220)	0.5014 (10)	0.2826 (9)	0.4256 (7)	0.058 (3)
	C(121)	−0.1665 (11)	0.0599 (8)	0.2412 (7)	0.061 (3)	C(221)	0.4144 (10)	0.2532 (8)	0.3568 (6)	0.048 (3)
	C(122)	−0.1330 (12)	0.0590 (9)	0.1549 (7)	0.077 (4)	C(222)	0.4036 (10)	0.3365 (8)	0.3213 (7)	0.062 (3)
Mes(2)	C(123)	0.1726 (9)	0.2577 (7)	0.4306 (6)	0.043 (2)	C(223)	0.3022 (9)	0.1791 (7)	0.1249 (6)	0.046 (2)
	C(124)	0.1803 (10)	0.1797 (8)	0.4660 (7)	0.053 (3)	C(224)	0.4176 (11)	0.2050 (9)	0.1212 (7)	0.064 (3)
	C(125)	0.1105 (10)	0.0695 (7)	0.4259 (7)	0.057 (3)	C(225)	0.4968 (12)	0.1827 (10)	0.1808 (9)	0.093 (4)
	C(126)	0.2565 (10)	0.2055 (9)	0.5421 (7)	0.063 (3)	C(226)	0.4645 (14)	0.2493 (10)	0.0557 (8)	0.088 (4)
	C(127)	0.3208 (11)	0.3027 (9)	0.5845 (7)	0.064 (3)	C(227)	0.3972 (14)	0.2655 (11)	−0.0058 (9)	0.093 (4)
	C(128)	0.4010 (13)	0.3302 (11)	0.6687 (9)	0.100 (5)	C(228)	0.4549 (16)	0.3143 (13)	−0.0778 (11)	0.139 (6)
	C(129)	0.3111 (11)	0.3787 (9)	0.5529 (7)	0.064 (3)	C(229)	0.2843 (13)	0.2363 (9)	−0.0071 (8)	0.082 (4)
	C(130)	0.2379 (10)	0.3581 (8)	0.4746 (7)	0.052 (3)	C(230)	0.2349 (10)	0.1923 (8)	0.0588 (7)	0.053 (3)
	C(131)	0.2295 (11)	0.4454 (9)	0.4437 (8)	0.075 (4)	C(231)	0.1098 (10)	0.1638 (9)	0.0499 (7)	0.070 (3)

Statistically Ordered Diphenylacetylene

atom	*x/a*	*y/b*	*z/c*	*U*, Å²	sof
C(311)	0.8542 (38)	0.4284 (24)	0.1052 (23)	0.076 (9)	0.5
C(321)	0.7864 (34)	0.4804 (26)	0.1031 (23)	0.088 (9)	0.5
C(331)	0.8030 (44)	0.5434 (33)	0.0438 (27)	0.092 (11)	0.5
C(341)	0.8994 (53)	0.5411 (49)	0.0029 (35)	0.117 (17)	0.5
C(351)	0.9847 (44)	0.4656 (31)	0.0315 (28)	0.099 (11)	0.5
C(361)	0.9269 (48)	0.4165 (32)	0.0879 (28)	0.116 (14)	0.5
C(312)	0.8027 (40)	0.4196 (30)	0.1308 (26)	0.112 (15)	0.5
C(322)	0.7121 (54)	0.4621 (43)	0.1332 (37)	0.198 (23)	0.5
C(332)	0.7359 (54)	0.5224 (41)	0.0710 (37)	0.176 (22)	0.5
C(342)	0.8565 (52)	0.5706 (34)	0.0158 (32)	0.116 (17)	0.5
C(352)	0.9436 (43)	0.5167 (29)	0.0086 (24)	0.080 (11)	0.5
C(362)	0.9147 (42)	0.4538 (29)	0.0613 (26)	0.088 (11)	0.5
C(371)	0.9500 (70)	0.5861 (49)	−0.0290 (44)	0.073 (17)	0.25
C(372)	1.0039 (59)	0.5934 (40)	−0.0587 (35)	0.049 (13)	0.25
C(373)	0.8559 (88)	0.5048 (68)	0.0525 (59)	0.108 (25)	0.25
C(374)	0.9731 (75)	0.3310 (69)	0.0625 (51)	0.145 (30)	0.25

replacement in alkenes of a carbon by a heavier element of group 14 confers to this new "organometallic alkene" a much greater reactivity, which should be very promising in organic and organometallic synthesis.

Experimental Section

Solutions of germene 1 are highly air- and moisture-sensitive. Therefore, the synthesis and the handling of 1 require high-vacuum-line techniques and carefully deoxygenated solvents, which must be freshly distilled over sodium–benzophenone.

^1H NMR spectra were recorded on a Varian EM 360 A spectrometer at 60 MHz and a Bruker WH 90 instrument at 90 MHz. ^{13}C NMR spectra were recorded on a Bruker AM 300 WB spectrometer at 75.4 MHz (TMS internal standard) and ^{19}F NMR spectra on a Perkin-Elmer instrument at 84.6 MHz (CF_3COOH external standard). Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer. Mass spectra were measured on a Varian MAT 311 A spectrometer (EI). Experimental molecular peak patterns were assigned after comparison with theoretical peak patterns calculated on a Tektronics 4051 instrument. Melting points were determined on a Reichert apparatus. Elemental analyses were done by the "Service de Microanalyse de l'Ecole de Chimie", Toulouse, France.

Reaction of 1 with Benzophenone. A solution of benzophenone (0.76 g, 4.20 mmol) in Et_2O (10 mL) was added to a solution of germene 1 (2.0 g, 4.20 mmol) in 10 mL of Et_2O at −20 °C. After 5 h at room temperature, the initially orange reaction mixture turned yellow. After elimination of solvents in vacuo, recrystallization from pentane gave 2.10 g (76%) of light yellow crystals of 4 mp 165–166 °C. ^{1}H NMR (toluene-d_8, −42 °C): δ 1.29 (s, 6 H, *o*-Me), 2.00 (s, 6 H, *p*-Me), 3.25 (s, 6 H, *o*-Me), 6.50–7.70 (m, 22 H, Ph, Mes, CR_2). At +75 °C, only one singlet is observed for the *o*-Me groups at 2.25 ppm. IR (Nujol): ν-(Ge–O–C) 1005 cm^{-1}. MS (EI, 70 eV, ^{74}Ge): *m/z* 658 (M, 2), 539 (M − Mes, 4), 476 ($Mes_2Ge{=}CR_2$, 25), 330 ($Ph_2C{=}CR_2$, 100), 329 ($Mes_2Ge{=}O$ + H, 75), 253 ($PhC{=}CR_2$, 25), 182 ($Ph_2C{=}O$, 4). Anal. Calcd for $C_{44}H_{40}GeO$: C, 80.39; H, 6.13. Found: C, 80.23; H, 6.36.

Reaction of 1 with Benzaldehyde. A solution of benzaldehyde (0.27 g, 2.52 mmol) in Et_2O (5 mL) was slowly added to a solution of germene 1 (1.20 g, 2.52 mmol) in Et_2O (10 mL) and the mixture cooled at −20 °C. The reaction mixture was warmed to room temperature and stirred for 3 h; the color changed gradually from orange to yellow. After removal of solvents under reduced pressure, the crude 3 was recrystallized in pentane to afford 1.32 g (79%) of light yellow crystals of 3, mp 67–68 °C. ^{1}H NMR (C_6D_6): δ 2.17 (s, 6 H *o*-Me), 2.30 (s, 3 H, *p*-Me), 2.56 (s, 6 H, *o*-Me), 2.70 (s, 3 H, *p*-Me), 6.70 (s, 2 H, arom Mes) 6.76 (s, 2 H, arom Mes), 6.80–8.00 (m, 14 H, OCH, Ph, and CR_2). IR (Nujol): ν(Ge–O–C) 1005 cm^{-1}. MS (IE, 70 eV, ^{74}Ge): *m/z* 582 (M, 5), 476 ($Mes_2Ge{=}CR_2$, 90), 329 ($Mes_2Ge{=}O$ + H, 100), 254 ($PhCH{=}CR_2$, 85), 106 (PhCHO, 8). Anal. Calcd for $C_{38}H_{36}GeO$: C. 78.50; H, 6.24. Found: C, 78.43; H, 6.27.

Reaction of 3 with Hydrofluoric Acid. To a solution of 3 (1.18 g, 2.03 mmol) in pentane (25 mL) was added 1 equivalent of hydrofluoric acid (40% in water). After 1 h of stirring at room temperature, the organic solution was dried over Na_2SO_4; then the crude 7 recrystallized in pentane as white crystals in 0.99-g yield (81%); mp 146–147 °C. ^{1}H NMR (C_6D_6): δ 1.73 (s, 6 H, *p*-Me), 2.10 (s, 12 H, *o*-Me), 6.51 (s, 4 H, arom Mes), 6.70–8.18 (m, 14 H, CH, Ph, and CR_2). ^{19}F NMR (C_6D_6): δ −91. IR: ν(OH) 3530 cm^{-1}. Anal. Calcd for $C_{38}H_{37}FGeO$: C, 75.90; H, 6.20. Found: C, 76.14; H, 6.33.

Reaction of 1 with Acetone. Acetone (0.21 g, 3.57 mmol), in 5 mL of Et_2O, was added to a solution of germene 1 (1.70 g, 3.57 mmol) in 20 mL of Et_2O. The orange solution became immediately colorless. The solvents were removed in vacuo to afford crude 9 (yield ~90%). 9 was purified by recrystallization in pentane: white crystals; mp 182–183 °C, 1.05 g (55% after recrystallization). ^{1}H NMR (C_6D_6): δ 1.22 (s, 3 H, Me), 1.97 (s, 6 H, *p*-Me), 2.00 (s, 12 H, *o*-Me), 2.97 (s, 2 H, CH_2), 5.37 (s, 1 H, CH), 6.52 (s, 4 H, arom Mes), 7.08–8.03 (m, 8 H, CR_2). ^{13}C NMR ($CDCl_3$): δ 20.88 (*p*-Me), 24.84 (*o*-Me), 32.33 (CH_3), 37.39 (CH_2), 46.0 (CH), 119.63 (C_4, C_5 (CR_2)), 125.34, 125.65, 125.79, (C_1, C_2, C_3, C_6, C_7, C_8 (CR_2)), 142.54, 145.21 (C_{10}, C_{11}, C_{12}, C_{13} (CR_2)), 209.53 (C=O). IR (KBr): ν(CO) 1676 cm^{-1}. MS (EI, 70 eV, ^{74}Ge): *m/z* 533 (M − 1, 10), 477 (M − CH_2COCH_3, 15), 415 (M − Mes, 5), 369 (M − R_2CH, 100), 313 (Mes_2Ge + H, 13), 43 (CH_3CO, 60). Anal. Calcd for $C_{34}H_{36}GeO$: C, 76.56; H, 6.80. Found: C, 76.68; H, 6.91.

Synthesis of Digermoxane 6. To a solution of 1 (1.36 g, 2.86 mmol) in Et_2O (15 mL) at room temperature was slowly added a solution of water (0.025 g, 1.43 mmol) in THF. The orange starting solution turned yellow. After the mixture was stirred overnight, most of the Et_2O was eliminated in vacuo. Crystallization at −20 °C afforded yellow crystals of 6 (1.17 g, 85%), mp 299–300 °C. ^{1}H NMR (C_6D_6): δ 2.02 (v broad s, 36 H, Me), 5.38 (s, 2 H, CH), 6.44 (v broad s, 8 H, arom Mes) 6.95–7.81 (m, 16 H, CR_2). ^{13}C NMR ($CDCl_3$): δ 20.99 (*p*-Me), 24.69 (broad s, *o*-Me), 47.67 (CH), 119.26, 125.81 (CH, arom fluorenyl), 128.75 (broad s, *m* C, Mes), 138.23, 138.67 (C_{10}, C_{11}, C_{12}, C_{13} (CR_2)), 141.73 (*p* C, Mes), 143.79 (broad s, *o* C, Mes). The very broad singlets observed in ^{1}H and ^{13}C NMR spectra are explained by the slow rotation of mesityl groups due to the very large steric hindrance. MS (EI, 70 eV, ^{74}Ge): *m/z* 803 (M − CHR_2, 75), 684 (M − CHR_2 − Mes, 30), 638 ($Mes_2GeOGeMes_2$, 5) 477 (Mes_2GeCHR_2, 40), 431 (Mes_2GeCR_2 − 3Me, 80), 329 (Mes_2GeO + H, 100). Anal. Calcd for $C_{62}H_{62}Ge_2O$: C, 76.90; H, 6.45. Found: C, 77.19; H, 6.58.

Structure Determination of 3, 4, and 6. Crystal data as well as details of intensity data collections and refinements are given in Table II. The densities were obtained from neutral buoyancy (Thoulet for 3 and 4, sodium polywolframate for 6). Crystals were fixed by gravity and sealed in glass capillaries. Crystals of 4 are always thin and small; the crystal quality of 6 is generally poor.[25] The quality and symmetry of the crystals was examined by Weissenberg exposures. Integrated intensities were measured by means of $\omega/2\theta$ scans on a CAD4 diffractometer (Enraf-Nonius).

The structures were solved by Patterson synthesis (Ge atoms) and completed by Fourier syntheses (O and C atoms). The refinements were by full-matrix methods (one block only). Hydrogen positions are considered as riding on carbon atoms (separate refinement only for H(32) of 3). 4 and 6 contain $^1/_4$ mol of *n*-pentane and $^1/_2$ mol of diphenylacetylene,[25] respectively, both of which are statistically ordered around a center of symmetry. The atom positions (10 and 16 definite positions for *n*-pentane and diphenylacetylene (4 positions for C≡C), respectively, with site occupation factors (sof) of 0.5 or 0.25) have been determined from difference Fourier syntheses and tested for a rough reasonability of their isotropic thermal parameters by refinement: after this consideration, no difference Fourier maximum of the solvent molecules remains. A further phenyl group of 4 (Ph(22)) is partially disordered. All three refinements come out with a good convergence and an even distribution of the variances. The quality of the structure determination of 4 is limited because of the small ratio of reflections used to variables refined (5.1). Besides several locally written routines, local versions of SHELX-76 and SHELX-86 were used for the calculations and PLUTO-78 was used for the figures (HB-DPS-8/70 equipment at Zentrum für Datenverarbeitung, Universität Mainz). Tables III–V contain the final parameters.

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Supplementary Material Available: Tables of anisotropic thermal parameters and H atom coordinates for 3 (4 pages); tables of observed and calculated structure factor amplitudes for 3, 4, and 6 (61 pages). Ordering information is given on any current masthead page.

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[25] The only acceptable crystals of 6 for the X-ray determination were obtained by slow recrystallization in Et_2O of the hydrolysis byproduct isolated in the attempted reaction between germene 1 and diphenylacetylene; this explains the surprising presence of diphenylacetylene in the crystal of 6.