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## Structure of Dimethyl *trans*-3,3'-(1,1-Dimethylgermacyclopentane-3,4-diyl)-bis[(*E*)-2-methylpropenoate]

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### Abstract

This is the first crystal structure determination of a 3,4-dialkenyl-1-germacyclopentane. In the crystal this molecule resides around a twofold axis with Ge on this axis. The bond distances in the five-membered heterocycle are Ge—C 1.950(5), C—C 1.539(6), 1.550(6) Å and the exocyclic Ge—C bond distance is 1.929(4) Å. The ring torsion angles C—Ge—C—C, Ge—C—C—C, C—C—C—C are 14.1(3), 39.2(3),  $-53.2(4)^\circ$  and the bond angles around Ge are 92.1(2) (ring), 113.5(2), 110.6(2), 113.1(2)°. Bond distances and angles in the alkenyl group are in the normal range.

### Comment

This is the first example of an electron-deficient 1,3-diene that reacts with dimethylgermylene to give a 3,4-dialkenyl-1-germacyclopentane. A number of 1,3-dienes, bearing no functional group (Neumann, Michels & Köcher, 1987; Bobbitt, Maloney & Gaspar, 1991) also give germacyclopentanes but no crystal structures have been obtained so far. The well known 1,2-cycloaddition of silylenes to alkenes or dienes (Gaspar, 1978, 1981, 1985) has not yet been observed in the case of the heavier carbene analogue, the germylene. Styrene and its derivatives are the only alkenes that react with dimethylgermylene to give a cycloaddition product, which consists of two moles of the alkene and one mole of germylene. The reaction is assumed to proceed *via* an unstable 1:1 intermediate, a 2-phenylgermirane (Neumann, 1991). Conjugated 1,3-dienes may give a 1,4-cycloaddition with  $\text{Me}_2\text{Ge}$  or may react like styrene with only one double bond of the conjugated system to give 3,4-dialkenyl-1-germacyclopentanes with a molar ratio of diene/germylene of 2/1 (Neumann, 1991). The substitution pattern of methyl (*E*)-2-methyl-2,4-pentadienoate favours the latter reaction type, resulting in the formation of the title compound. *Ab initio*

quantum-mechanical determination of the strain enthalpy of a germirane shows a comparative instability of germiranes relative to the homologous cyclopropanes and siliranes (Horner, Grev & Schaefer, 1992). This may explain the experimental observation that no 1,2-addition product of germylens to alkenes or dienes is formed.

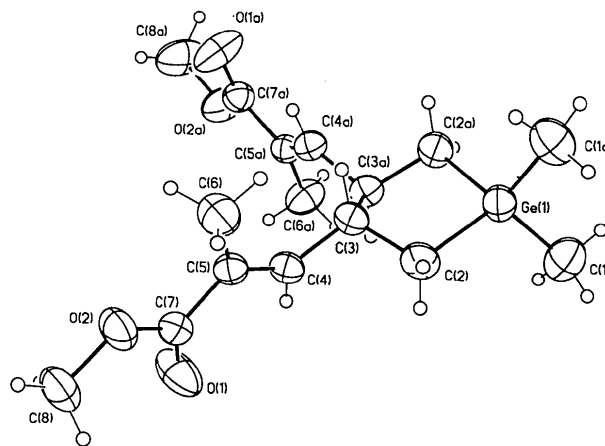
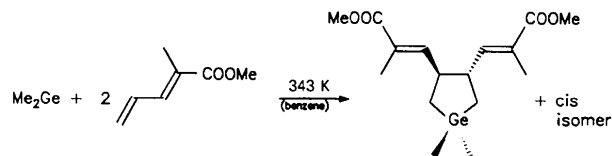


Fig. 1. General view (SHELXTL-Plus graphic) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii.

### Experimental

#### Crystal data

$\text{C}_{16}\text{H}_{26}\text{GeO}_4$   
 $M_r = 354.97$   
 Monoclinic  
 $C2/c$   
 $a = 20.373(9)$  Å  
 $b = 8.707(4)$  Å  
 $c = 12.637(6)$  Å  
 $\beta = 126.91(3)^\circ$   
 $V = 1792(2)$  Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.315$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 16  
 reflections  
 $\theta = 9.4\text{--}20.5^\circ$   
 $\mu = 1.70$  mm<sup>-1</sup>  
 $T = 293(1)$  K  
 Platelet  
 $0.44 \times 0.44 \times 0.28$  mm  
 Colourless

#### Data collection

Nicolet R3m/V diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction:  
 none  
 2628 measured reflections  
 1171 independent reflections  
 997 observed reflections  
 $[F > 4.0 \sigma(F)]$

$R_{\text{int}} = 0.0382$   
 $\theta_{\text{max}} = 22.5^\circ$   
 $h = -22 \rightarrow 22$   
 $k = 0 \rightarrow 10$   
 $l = -14 \rightarrow 14$   
 6 standard reflections  
 frequency: 150 min  
 intensity variation: none

## Refinement

Refinement on $F$	$(\Delta/\sigma)_{\max} = 0.168$
Final $R = 0.037$	$\Delta\rho_{\max} = 0.3 \text{ e } \text{\AA}^{-3}$
$wR = 0.050$	$\Delta\rho_{\min} = -0.7 \text{ e } \text{\AA}^{-3}$
$S = 0.55$	Atomic scattering factors
997 reflections	from <i>International Tables</i>
98 parameters	for <i>X-ray Crystallography</i>
Only H-atom $U$ 's refined	(1974, Vol. IV, Table
Calculated weights $w =$	2.2B)
$1/[\sigma^2(F) + 0.0070F^2]$	

Data collection: Nicolet *R3m/V* software, release 4.11. Cell refinement: Nicolet *R3m/V* software. Data reduction: Nicolet *R3m/V* software. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1987). Program(s) used to refine structure: *SHELXTL-Plus*. Software used to prepare material for publication: *PARST* (Nardelli, 1983), *PLATON* (Spek, 1982), *MISSYM* (Le Page, 1987).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
Ge(1)	0.0	0.02457 (6)	0.25	0.0448
O(1)	-0.0965 (2)	-0.6461 (4)	0.3928 (3)	0.0768
O(2)	-0.2113 (2)	-0.7006 (3)	0.1983 (3)	0.0654
C(1)	0.0672 (3)	0.1507 (5)	0.4059 (4)	0.0686
C(2)	-0.0620 (2)	-0.1309 (4)	0.2672 (4)	0.0479
C(3)	-0.0457 (2)	-0.2816 (4)	0.2228 (3)	0.0378
C(4)	-0.0657 (2)	-0.4168 (4)	0.2729 (3)	0.0380
C(5)	-0.1316 (2)	-0.5059 (4)	0.2025 (3)	0.0359
C(6)	-0.1970 (3)	-0.4918 (4)	0.0571 (4)	0.0573
C(7)	-0.1412 (2)	-0.6234 (4)	0.2774 (3)	0.0416
C(8)	-0.2282 (4)	-0.8154 (6)	0.2618 (5)	0.0908

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ge(1)—C(1)	1.929 (4)	C(3)—C(3 <sup>i</sup> )	1.550 (6)
Ge(1)—C(2)	1.950 (5)	C(3)—C(4)	1.504 (6)
O(1)—C(7)	1.184 (4)	C(4)—C(5)	1.327 (5)
O(2)—C(7)	1.332 (4)	C(5)—C(6)	1.492 (5)
O(2)—C(8)	1.447 (8)	C(5)—C(7)	1.483 (6)
C(2)—C(3)	1.539 (6)		
C(1)—Ge(1)—C(2)	113.1 (2)	C(2)—C(3)—C(4)	110.0 (3)
C(1)—Ge(1)—C(1 <sup>i</sup> )	110.6 (2)	C(3)—C(4)—C(5)	126.6 (3)
C(1)—Ge(1)—C(2 <sup>i</sup> )	113.5 (2)	C(4)—C(5)—C(7)	116.3 (3)
C(2)—Ge(1)—C(2 <sup>i</sup> )	92.1 (2)	C(4)—C(5)—C(6)	124.9 (3)
C(7)—O(2)—C(8)	115.9 (3)	C(6)—C(5)—C(7)	118.7 (3)
Ge(1)—C(2)—C(3)	104.8 (3)	O(2)—C(7)—C(5)	111.2 (3)
C(2)—C(3)—C(3 <sup>i</sup> )	107.6 (3)	O(1)—C(7)—C(5)	127.0 (4)
C(4)—C(3)—C(3 <sup>i</sup> )	111.7 (3)	O(1)—C(7)—O(2)	121.7 (4)

C(2)—Ge(1)—C(2<sup>i</sup>)—C(3<sup>i</sup>) -14.1(3)

Ge(1)—C(2<sup>i</sup>)—C(3<sup>i</sup>)—C(3) 39.2(3)

C(2<sup>i</sup>)—C(3<sup>i</sup>)—C(3)—C(2) -53.2(4)

Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ .

The title compound was obtained from free singlet dimethylgermylene, which is generated by thermolysis of a 7-germanorbornadiene (Neumann, 1991), and methyl (*E*)-2-methyl-2,4-pentadienoate at 343 K in benzene (Wienken & Neumann, 1992) and is separated from the isomeric *cis*-3,4-dialkenyl-1-germacyclopentane by repeated crystallization. The crystals were obtained from methanol at room temperature, m.p. 384 K (yield 16%). The lattice parameters were determined from a symmetry-constrained least-squares fit. Refinement was based on full-matrix least-squares methods with H atoms in calculated positions (C—H 0.96  $\text{\AA}$ ). One common isotropic temperature

factor was refined for the H atoms of the methyl groups and another was refined for the remaining H atoms.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55576 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1027]

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## Structure of a *syn*-Aldol Addition Product of Benzaldehyde and a Prolinol-Derived *O*-Silacyclopentyl Ketene *N,O*-Acetal

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## Abstract

The compound (5*S*,6*S*,11*aS*)-hexahydro-6-methyl-5-phenylspiro[1*H*,7*H*-pyrrolo[2,1-*e*][1,3,6,2]dioxasilone-3,1'-silacyclopentan]-7-one (1) results from the silicon-directed condensation of the prolinol-derived

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