

choice would have demanded mirror, twofold or inversion symmetry for the molecule. The polar space group $Pca2_1$ was assumed and confirmed by the analysis. Refinement of the model and its enantiomorph yielded no significant differences in R , wR , goodness of fit or molecular dimensions. All H atoms were visible in difference maps and were included as riding atoms (C—H 0.95 Å) during the refinement.

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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 55594 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1013]

References

- Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
- Browne, C. M., Ferguson, G., McKervey, M. A., Mulholland, D. L., O'Connor, T. & Parvez, M. (1985). *J. Am. Chem. Soc.* **107**, 2703–2712.
- Ferguson, G., Kaitner, B., Browne, C. M. & McKervey, M. A. (1988). *J. Chem. Soc. Perkin Trans. 2*, pp. 1725–1728.
- Gabe, E. J., Le Page, Y., Charland, J. P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, p. 291. Copenhagen: Munksgaard.
- Tomat, G., Valle, G., Cassol, A. & di Bernardo, P. (1983). *Inorg. Chim. Acta*, **76**, L13–L14.

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Structure of 1,1,2,2,3,3-Hexamethyl-4-(2-ethynylphenyl)-1,2,3-trigermacyclopent-4-ene

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Abstract

This is the first crystal structure determination of a member of the new germacyclic system of 1,2,3-trigermacyclopent-4-enes. The five-membered heterocycle is nearly planar with a maximum deviation of 0.139(10) Å from the least-squares plane through these

atoms. The Ge—Ge, Ge—C and C—C distances in the ring are 2.411(3), 2.406(2), 1.979(9), 1.954(8) and 1.30(1) Å and the bond angles in the ring are Ge—Ge—Ge 92.8(1), Ge—Ge—C 99.4(3), 99.3(3) and Ge—C—C 125.3(7), 122.4(7)°. The remaining exocyclic bond angles at the three Ge atoms are in the range 108.2(5)–116.0(4)°. The tetrahedral coordination around the Ge atoms is mainly distorted because of the conditions imposed by the ring geometry. The exocyclic Ge—C bond distances are in the range 1.92(1)–1.95(1) Å [mean value 1.94(1) Å]. The dihedral angle between the heterocycle and the phenyl ring is 99.5(3)°.

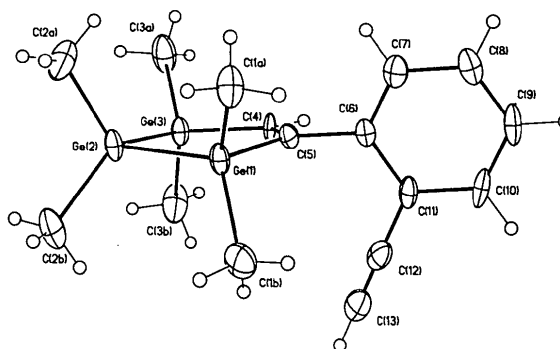
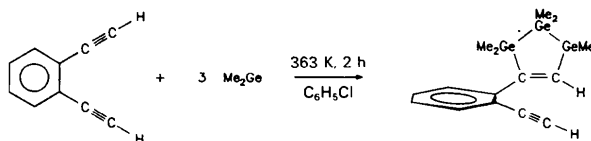


Fig. 1. General view (*SHELXTL-Plus* graphic) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii.

Comment

The title compound is the first crystalline member of the fascinating germacyclic system of 1,2,3-trigermacyclopent-4-enes. The reaction and the recrystallization was carried out under dry argon because the crystals are air sensitive. The exact mechanism is unknown. A cyclotrigermane (Me_2Ge)₃ is proposed as a reaction intermediate (Neumann, 1991). *Ab initio* quantum-mechanical determinations of the strain enthalpy of a hexamethylcyclotrigermane show a strong instability (Horner, Grev & Schäfer, 1992). This reactive intermediate reacts with 1,2-diethynylbenzene to give a trigermacyclopentene. The second ethynyl group does not react with another dimethylgermylene or cyclotrigermane. Presumably additional steric hindrance prevents access to the triple bond and prevents the reaction. Surprisingly the remarkable five-membered germaheterocycle is nearly planar. Evidence of this has also been provided by NMR spectroscopy (¹H NMR: only three GeMe resonance signals).



Experimental*Crystal data*C₁₆H₂₄Ge₃M_r = 434.14

Monoclinic

P2₁/n

a = 7.237 (7) Å

b = 14.952 (9) Å

c = 17.071 (20) Å

β = 95.11 (8)°

V = 1840 (3) Å³

Z = 4

Data collection

Nicolet R3m/V diffractometer

θ/2θ scans

Absorption correction:
none

4379 measured reflections

3250 independent reflections

2297 observed reflections

[F > 4.0 σ(F)]

Refinement

Refinement on F

Final R = 0.068

wR = 0.083

S = 0.87

2297 reflections

173 parameters

Only H-atom U's refined

Calculated weights

w = 1/[σ²(F) + 0.007F²]

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 (Å²)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
Ge(1)	0.07107 (14)	0.14797 (6)	0.43819 (5)	213
Ge(2)	-0.04309 (14)	0.08593 (6)	0.31272 (6)	231
Ge(3)	-0.02950 (14)	0.22783 (6)	0.24704 (5)	216
C(1a)	-0.091 (2)	0.1300 (7)	0.5209 (6)	334
C(1b)	0.322 (1)	0.1147 (7)	0.4768 (7)	378
C(2a)	-0.292 (2)	0.0439 (9)	0.3195 (7)	445
C(2b)	0.117 (2)	-0.0058 (8)	0.2744 (7)	422
C(3a)	-0.263 (2)	0.2696 (7)	0.1935 (7)	437
C(3b)	0.165 (2)	0.2371 (9)	0.1754 (6)	465
C(4)	0.035 (1)	0.3042 (6)	0.3382 (5)	187
C(5)	0.071 (1)	0.2764 (6)	0.4100 (5)	202
C(6)	0.121 (1)	0.3402 (6)	0.4775 (5)	180
C(7)	-0.010 (1)	0.3689 (6)	0.5248 (6)	256
C(8)	0.034 (2)	0.4291 (7)	0.5857 (6)	314
C(9)	0.209 (2)	0.4605 (7)	0.5997 (6)	314

C(10)	0.347 (1)	0.4324 (6)	0.5532 (5)	279
C(11)	0.304 (1)	0.3723 (6)	0.4916 (5)	238
C(12)	0.447 (1)	0.3440 (7)	0.4435 (7)	304
C(13)	0.562 (2)	0.3218 (8)	0.4049 (7)	386

Table 2. Geometric parameters (Å, °)

Ge(1)—Ge(2)	2.411 (3)	C(4)—C(5)	1.30 (1)
Ge(1)—C(1a)	1.93 (1)	C(5)—C(6)	1.52 (1)
Ge(1)—C(1b)	1.94 (1)	C(6)—C(7)	1.37 (1)
Ge(1)—C(5)	1.979 (9)	C(6)—C(11)	1.41 (1)
Ge(2)—Ge(3)	2.406 (2)	C(7)—C(8)	1.39 (1)
Ge(2)—C(2a)	1.92 (1)	C(8)—C(9)	1.35 (2)
Ge(2)—C(2b)	1.95 (1)	C(9)—C(10)	1.39 (2)
Ge(3)—C(3a)	1.95 (1)	C(10)—C(11)	1.40 (1)
Ge(3)—C(3b)	1.95 (1)	C(11)—C(12)	1.44 (1)
Ge(3)—C(4)	1.954 (8)	C(12)—C(13)	1.16 (2)
C(1b)—Ge(1)—C(5)	108.2 (5)	C(3a)—Ge(3)—C(3b)	109.0 (5)
C(1a)—Ge(1)—C(5)	108.9 (4)	Ge(3)—C(4)—C(5)	125.3 (7)
C(1a)—Ge(1)—C(1b)	109.1 (5)	Ge(1)—C(5)—C(4)	122.4 (7)
Ge(2)—Ge(1)—C(5)	99.4 (3)	C(4)—C(5)—C(6)	122.0 (8)
Ge(2)—Ge(1)—C(1b)	116.0 (4)	Ge(1)—C(5)—C(6)	115.5 (6)
Ge(2)—Ge(1)—C(1a)	114.4 (4)	C(5)—C(6)—C(11)	120.1 (8)
Ge(1)—Ge(2)—C(2b)	113.7 (4)	C(5)—C(6)—C(7)	121.0 (8)
Ge(1)—Ge(2)—C(2a)	108.8 (4)	C(7)—C(6)—C(11)	118.9 (8)
Ge(1)—Ge(2)—Ge(3)	92.8 (1)	C(6)—C(7)—C(8)	121 (1)
C(2a)—Ge(2)—C(2b)	112.3 (5)	C(7)—C(8)—C(9)	120 (1)
Ge(3)—Ge(2)—C(2b)	114.5 (4)	C(8)—C(9)—C(10)	120 (1)
Ge(3)—Ge(2)—C(2a)	113.2 (4)	C(9)—C(10)—C(11)	120 (1)
Ge(2)—Ge(3)—C(4)	99.3 (3)	C(6)—C(11)—C(10)	119.2 (9)
Ge(2)—Ge(3)—C(3b)	114.6 (4)	C(10)—C(11)—C(12)	119.9 (9)
Ge(2)—Ge(3)—C(3a)	115.6 (4)	C(6)—C(11)—C(12)	120.9 (9)
C(3b)—Ge(3)—C(4)	108.9 (5)	C(11)—C(12)—C(13)	179 (1)
C(3a)—Ge(3)—C(4)	108.8 (4)		
Ge(2)—Ge(1)—C(5)—C(4)	-6.8 (9)		
C(5)—Ge(1)—Ge(2)—Ge(3)	7.1 (3)		
Ge(1)—Ge(2)—Ge(3)—C(4)	-6.6 (3)		
Ge(2)—Ge(3)—C(4)—C(5)	4.5 (9)		
Ge(3)—C(4)—C(5)—Ge(1)	2 (1)		
C(4)—C(5)—C(6)—C(7)	97 (1)		
Ge(1)—C(5)—C(6)—C(7)	-84 (1)		
C(4)—C(5)—C(6)—C(11)	-80 (1)		
Ge(1)—C(5)—C(6)—C(11)	96.7 (9)		

The title compound was obtained from free singlet dimethylgermylene, thermally generated from 7-germanorbomadiene (Neumann, 1991), and 1,2-diethynylbenzene at 363 K in chlorobenzene (Weisbeck & Neumann, 1992). The air-sensitive crystals were obtained from methanol at 243 K, m.p. 365 K. 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 Å).

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 55577 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1028]

References

- Homer, D. A., Grev, R. S. & Schaefer, H. F. III (1992). *J. Am. Chem. Soc.* **114**, 2093–2098.
 Le Page, Y. (1987). *J. Appl. Cryst.* **20**, 264–269.
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
 Neumann, W. P. (1991). *Chem. Rev.* **91**, 311–334.
 Sheldrick, G. M. (1987). *SHELXTL-Plus*. Release 3.4 for Nicolet R3m/V crystallographic system. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Spek, A. L. (1982). *The EUCLID Package*. In *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.
 Weisbeck, M. P. & Neumann, W. P. (1992). In preparation.

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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 Me₂Ge 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 germlyenes to alkenes or dienes is formed.

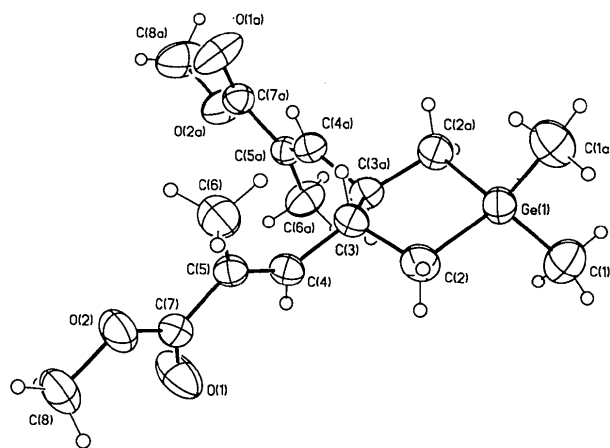
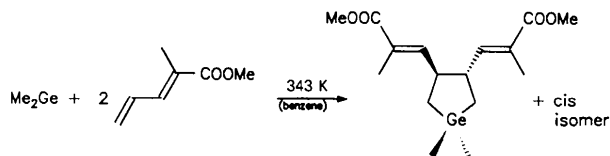


Fig. 1. General view (SHELXTL-Plus graphic) of the molecule, showing the atom-numbering scheme. Anisotropic ellipsoids represent 50% probability boundaries. H atoms are represented as spheres of arbitrary radii.

Experimental

Crystal data

C₁₆H₂₆GeO₄
M_r = 354.97
 Monoclinic
*C*2/*c*
a = 20.373 (9) Å
b = 8.707 (4) Å
c = 12.637 (6) Å
 β = 126.91 (3)°
V = 1792 (2) Å³
Z = 4

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 σ (*F*)]

D_x = 1.315 Mg m⁻³
 Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 18 reflections
 θ = 9.4–20.5°
 μ = 1.70 mm⁻¹
T = 293 (1) K
 Platelet
 0.44 × 0.44 × 0.28 mm
 Colourless

*R*_{int} = 0.0382
 θ_{\max} = 22.5°
h = -22 → 22
k = 0 → 10
l = -14 → 14
 6 standard reflections
 frequency: 150 min
 intensity variation: none