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SYNTHESIS OF TRIMETHYLSILYLATED GERMANOCENES; X-RAY STRUCTURE OF AND STERIC EFFECTS IN HEXAKIS(TRIMETHYLSILYL)GERMANOCENE *

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Summary

Reaction of $GeCl_2 \cdot$ dioxane with mono-, bis- and tris-(trimethylsilyl)cyclopentadienyllithium yields bis-, tetrakis- and hexakis-(trimethylsilyl)germanocene. A single-crystal X-ray diffraction study shows the metallocene species with six silyl groups to consist of nearly parallel C_5-units, bound symmetrically to the germanium center. The eclipsed conformation of the rings and the 1,2,4-silyl substitution pattern leave only two silyl groups face to face, effecting a small bending of the molecule. The molecular structure has been examined with the steric energy program EENY2. The conformation found in the crystal is close to the lowest minimum given by the calculations.

Group IVB metallocenes have to change their typical angular sandwich structure if bulky substituents on both cyclopentadienyl rings come into contact. This could effect an increase in the metal to carbon bond lengths, not only in a symmetric manner, but also asymmetrically, distorting the molecule towards ionic dissociation, a feature which was considered [1] for the solid state structure of $(H_5C_5)_2Pb$ [2] and verified in the case of $Me_5C_5M^+ (MeOOC)_5C_5^-$ (M = Ge, Sn) [3,4]. There is also the possibility of decreasing the angle between the ring planes towards a ferrocene-like structure of parallel cyclopentadienyl ligands, resulting in the lone pair at the metal center having no stereochemical activity, as found in $(Ph_5C_5)_2Sn$ [5].

We thought that an increasing number of trimethylsilyl groups bound to the cyclopentadienyl rings of Group IVB metallocenes would be likely to have the largest effect on the structure in the case of the smallest available central atom. On

(Continued on p. 288)

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* Dedicated to Professor Max Schmidt on the occasion of his 60th birthday.

TABLE 1

BOND LENGTHS (A) FOR 3

C(001)–Ge(1) [a]	2.261	C(002)–Ge(1)	2.256	C(003)–Ge(2)	2.252	C(004)–Ge(2)	2.250
C(110)–Ge(1)	2.661(19)	C(120)–Ge(1)	2.574(15)	C(310)–Ge(2)	2.608(16)	C(320)–Ge(2)	2.559(12)
C(130)–Ge(1)	2.458(13)	C(140)–Ge(1)	2.528(17)	C(330)–Ge(2)	2.496(12)	C(340)–Ge(2)	2.532(17)
C(150)–Ge(1)	2.614(20)	C(210)–Ge(1)	2.629(15)	C(350)–Ge(2)	2.602(18)	C(410)–Ge(2)	2.633(16)
C(220)–Ge(1)	2.653(15)	C(230)–Ge(1)	2.568(19)	C(420)–Ge(2)	2.591(14)	C(430)–Ge(2)	2.490(14)
C(240)–Ge(1)	2.485(18)	C(250)–Ge(1)	2.496(17)	C(440)–Ge(2)	2.518(19)	C(450)–Ge(2)	2.568(19)
C(110)–Si(11)	1.877(16)	C(111)–Si(11)	1.901(23)	C(310)–Si(31)	1.877(14)	C(311)–Si(31)	1.877(20)
C(112)–Si(11)	1.910(18)	C(113)–Si(11)	1.885(21)	C(312)–Si(31)	1.866(16)	C(313)–Si(31)	1.868(23)
C(120)–Si(12)	1.875(16)	C(121)–Si(12)	1.877(22)	C(320)–Si(32)	1.868(14)	C(321)–Si(32)	1.891(18)
C(122)–Si(12)	1.892(21)	C(123)–Si(12)	1.889(16)	C(322)–Si(32)	1.888(15)	C(323)–Si(32)	1.902(20)
C(140)–Si(14)	1.868(14)	C(141)–Si(14)	1.900(28)	C(340)–Si(34)	1.888(14)	C(341)–Si(34)	1.900(17)
C(142)–Si(14)	1.906(19)	C(143)–Si(14)	1.914(19)	C(342)–Si(34)	1.884(21)	C(343)–Si(34)	1.859(18)
C(210)–Si(21)	1.851(15)	C(21)–Si(21)	1.887(23)	C(410)–Si(41)	1.864(15)	C(411)–Si(41)	1.792(42)
C(212)–Si(21)	1.916(17)	C(213)–Si(21)	1.870(15)	C(412)–Si(41)	1.887(21)	C(413)–Si(41)	1.851(35)
C(220)–Si(22)	1.864(13)	C(221)–Si(22)	1.893(16)	C(420)–Si(42)	1.859(15)	C(421)–Si(42)	1.858(27)
C(222)–Si(22)	1.886(19)	C(223)–Si(22)	1.908(23)	C(422)–Si(42)	1.926(19)	C(423)–Si(42)	1.876(21)
C(240)–Si(24)	1.851(14)	C(241)–Si(24)	1.900(23)	C(440)–Si(44)	1.853(15)	C(441)–Si(44)	1.899(20)
C(242)–Si(24)	1.889(19)	C(243)–Si(24)	1.885(17)	C(442)–Si(44)	1.894(22)	C(443)–Si(44)	1.896(18)
C(120)–C(110)	1.444(22)	C(150)–C(110)	1.414(19)	C(320)–C(310)	1.444(19)	C(350)–C(310)	1.439(17)
C(130)–C(120)	1.451(17)	C(140)–C(130)	1.415(22)	C(330)–C(320)	1.428(15)	C(340)–C(330)	1.431(18)
C(150)–C(140)	1.431(19)			C(350)–C(340)	1.418(18)		
C(220)–C(210)	1.455(18)	C(250)–C(210)	1.428(16)	C(420)–C(410)	1.450(20)	C(450)–C(410)	1.435(18)
C(230)–C(220)	1.430(17)	C(240)–C(230)	1.443(16)	C(430)–C(420)	1.441(18)	C(440)–C(430)	1.429(20)
C(250)–C(240)	1.450(19)			C(450)–C(440)	1.435(17)	C(440)–C(450)	1.435(17)

[a] C(001) etc. = centroid of C_5 unit.

TABLE 2. BOND ANGLES (deg.) FOR 3

C(001)–Ge(1)–C(002)	169.48			C(003)–Ge(2)–C(004)	171.77		
C(112)–Si(11)–C(111)	108.6(11)	C(113)–Si(11)–C(110)	114.1(10)	C(311)–Si(31)–C(310)	114.2(9)	C(312)–Si(31)–C(310)	108.2(7)
C(112)–Si(11)–C(111)	108.6(11)	C(113)–Si(11)–C(110)	114.1(10)	C(312)–Si(31)–C(311)	108.8(9)	C(313)–Si(31)–C(310)	109.8(8)
C(113)–Si(11)–C(111)	111.4(9)	C(113)–Si(11)–C(112)	108.0(9)	C(313)–Si(31)–C(311)	109.1(9)	C(313)–Si(31)–C(312)	106.4(12)
C(121)–Si(12)–C(120)	112.8(8)	C(122)–Si(12)–C(120)	111.1(9)	C(321)–Si(32)–C(320)	111.3(8)	C(322)–Si(32)–C(320)	106.6(7)
C(122)–Si(12)–C(121)	109.2(9)	C(123)–Si(12)–C(120)	108.4(7)	C(322)–Si(32)–C(321)	108.7(8)	C(323)–Si(32)–C(320)	111.6(6)
C(123)–Si(12)–C(121)	108.5(10)	C(123)–Si(12)–C(122)	106.7(8)	C(323)–Si(32)–C(321)	109.7(8)	C(323)–Si(32)–C(322)	108.9(9)
C(141)–Si(14)–C(140)	107.6(8)	C(142)–Si(14)–C(140)	110.2(7)	C(341)–Si(34)–C(340)	107.9(6)	C(342)–Si(34)–C(340)	112.4(8)
C(142)–Si(14)–C(141)	108.4(10)	C(143)–Si(14)–C(140)	108.4(8)	C(342)–Si(34)–C(341)	106.7(8)	C(343)–Si(34)–C(340)	108.6(7)
C(143)–Si(14)–C(141)	109.2(10)	C(143)–Si(14)–C(142)	112.9(9)	C(343)–Si(34)–C(341)	108.9(10)	C(343)–Si(34)–C(342)	112.1(8)
C(211)–Si(21)–C(210)	111.3(7)	C(121)–Si(21)–C(210)	107.3(7)	C(411)–Si(41)–C(410)	115.5(12)	C(412)–Si(41)–C(410)	108.6(8)
C(212)–Si(21)–C(211)	107.1(10)	C(213)–Si(21)–C(210)	112.3(8)	C(412)–Si(41)–C(411)	109.5(14)	C(413)–Si(41)–C(410)	108.4(12)
C(213)–Si(21)–C(211)	110.2(8)	C(213)–Si(21)–C(212)	108.3(9)	C(413)–Si(41)–C(411)	113.6(18)	C(413)–Si(41)–C(412)	100.1(15)
C(221)–Si(22)–C(220)	108.5(6)	C(222)–Si(22)–C(220)	111.1(8)	C(421)–Si(42)–C(420)	112.3(8)	C(442)–Si(42)–C(420)	108.2(8)
C(222)–Si(22)–C(221)	107.1(9)	C(223)–Si(22)–C(220)	111.7(8)	C(422)–Si(42)–C(421)	107.2(11)	C(423)–Si(42)–C(420)	110.3(11)
C(223)–Si(22)–C(221)	108.0(8)	C(223)–Si(22)–C(222)	110.3(9)	C(423)–Si(42)–C(421)	111.2(10)	C(423)–Si(42)–C(422)	107.4(11)
C(241)–Si(24)–C(240)	109.8(7)	C(242)–Si(24)–C(240)	108.7(9)	C(441)–Si(44)–C(440)	109.9(9)	C(442)–Si(44)–C(440)	109.2(7)
C(242)–Si(24)–C(241)	109.1(8)	C(243)–Si(24)–C(240)	109.8(7)	C(442)–Si(44)–C(441)	107.4(9)	C(443)–Si(44)–C(440)	108.8(8)
C(243)–Si(24)–C(241)	110.1(10)	C(243)–Si(24)–C(242)	109.4(9)	C(443)–Si(44)–C(441)	111.2(9)	C(443)–Si(44)–C(442)	110.5(12)
C(120)–C(110)–Si(11)	131.8(10)	C(150)–C(110)–Si(11)	120.1(33)	C(320)–C(310)–Si(31)	132.5(8)	C(350)–C(310)–Si(31)	119.0(11)
C(110)–C(120)–Si(12)	132.2(9)	C(130)–C(120)–Si(12)	121.6(11)	C(310)–C(320)–Si(32)	132.2(8)	C(350)–C(320)–Si(32)	121.0(10)
C(130)–C(140)–Si(14)	129.1(0)	C(150)–C(140)–Si(14)	123.5(13)	C(330)–C(340)–Si(34)	126.3(9)	C(350)–C(340)–Si(34)	125.8(11)
C(220)–C(210)–Si(21)	132.8(8)	C(250)–C(210)–Si(21)	120.9(10)	C(420) C(410)–Si(41)	134.3(9)	C(450)–C(410)–Si(41)	118.5(11)
C(210)–C(220)–Si(22)	132.0(8)	C(230)–C(220)–Si(22)	120.2(10)	C(410)–C(420)–Si(42)	132.5(9)	C(430)–C(420)–Si(42)	120.6(11)
C(230)–C(240)–Si(24)	127.5(11)	C(250)–C(240)–Si(24)	127.0(9)	C(430)–C(440)–Si(44)	126.5(10)	C(450)–C(440)–Si(44)	126.5(11)
C(150)–C(110)–C(120)	107.8(12)	C(130)–C(120)–C(110)	106.0(12)	C(350)–C(310)–C(320)	107.8(11)	C(330)–C(320)–C(310)	106.7(11)
C(140)–C(130)–C(120)	109.9(13)	C(150)–C(140)–C(130)	106.3(11)	C(340)–C(330)–C(320)	109.5(11)	C(350)–C(340)–C(330)	107.3(10)
C(140)–C(150)–C(110)	110.0(13)			C(340)–C(350)–C(310)	108.7(12)		
C(250)–C(210)–C(220)	106.2(11)	C(230)–C(220)–C(210)	107.7(10)	C(450)–C(410)–C(420)	107.1(11)	C(430)–C(420)–C(410)	106.8(12)
C(240)–C(230)–C(220)	110.4(12)	C(250)–C(240)–C(230)	104.5(10)	C(440)–C(430)–C(420)	110.0(12)	C(450)–C(440)–C(430)	106.2(11)
C(240)–C(250)–C(210)	111.2(11)			C(440)–C(450)–C(410)	109.9(12)		

this basis we decided to synthesize the bis- (**1**), tetrakis- (**2**) and hexakis(trimethylsilyl)metallocene (**3**) derivatives of germanium. These complexes were prepared by treatment of the silylated cyclopentadienyllithium compounds with $GeCl_2 \cdot$ dioxane in THF, by analogy with the synthesis of the corresponding tin [6] and lead [7] compounds.

$$2\,(Me_3Si)_nH_{5-n}C_5Li \xrightarrow[-2\,LiCl,\ -C_4H_8O_2]{GeCl_2 \cdot C_4H_8O_2} [(Me_3Si)_nH_{5-n}C_5]_2Ge$$

$$(\mathbf{1},\ n = 1;\ \mathbf{2},\ n = 2;\ \mathbf{3},\ n = 3)$$

Compound **1** was isolated by distillation as a pale yellow liquid, b.p. $97^\circ C/10^{-5}$ mmHg, whereas **2** and **3** crystallized (from hexane) as yellow needles, m.p. 72°C (**2**) and pale-yellow cubes, m.p. 98°C (**3**); the air-sensitive compounds are soluble in benzene, THF, CH_2Cl_2 and hexane; their thermal stability and resistance to oxidation increase with the number of silyl groups as expected. The germanocenes **1**, **2** and **3** are monomeric in benzene and also in the gas phase. They have been analysed and characterized by C and H analysis, mass spectra and ^1H and ^{13}C NMR spectra, and in the case of **3** also by an X-ray structure analysis.

No hindrance to rotation was observed for the trimethylsilylated cyclopentadienyl rings about the ring centroid–germanium axis in the compounds **1**, **2** and **3**. Only one signal for the trimethylsilyl groups in **1** and **2** and two signals for these groups in **3** appear in the ^1H or ^{13}C NMR spectra even at lower temperatures. The ^1H and ^{13}C data for the cyclopentadienyl ring protons and carbons also give no indication of rotational isomers.

The mass spectra of **1**, **2** and **3** show intense peaks for the cyclopentadienylgermanium(II) cations $(Me_3Si)_nH_{5-n}C_5Ge^+$. Attempts to stabilize these cations chemically have so far failed. Upon reaction of the silylated germanocenes with electrophiles (H^+, CH_3^+) only decomposition products were isolated.

Discussion of the structure of compound 3

The structure contains two crystallographically independent molecules which have very similar geometries and conformations. The bond lengths and angles are given in Tables 1 and 2, and the molecular structures and atom numbering schemes are shown in Fig. 1a and 1b. The common structure can be described as a very slightly distorted parallel and symmetrical metallocene sandwich. The distortion is a combination of a small bending of the Cp(centroid)–Ge–Cp(centroid) angle from linearity (10.5° in molecule 1 and 8.2° in molecule 2) and small tilts of the Cp ring planes relative to the Ge–centroid vectors (5.2°, 5.1° in molecule 1 and 3.1°, 3.6° in molecule 2). These tilts correspond to a spread in the Ge–C distances between 2.46 and 2.63 Å. However, the basic symmetry of the sandwich structure can be seen from the very small variation in the Ge–centroid distances, 2.250–2.256 Å and in the average Ge–C distances for the four independent Ge–Cp interactions, 2.556–2.574 Å, which are similar to those found in the crystal structure of $Ge(C_5H_5)_2$ [8] and in the gas phase structure of $Ge[(CH_3)H_4C_5]_2$ [9] and $[(CH_3)_5C_5]_2Ge$ [10].

Although the sterically crowded $(Me_3Si)_3C_5H_2$ ligands were used in the hope that interactions between the two substituted Cp systems might lead to a "locking in" of some particular configuration, our NMR studies show that the molecule is fluxional, even down to −40°C. However, since the two independent molecules found in the

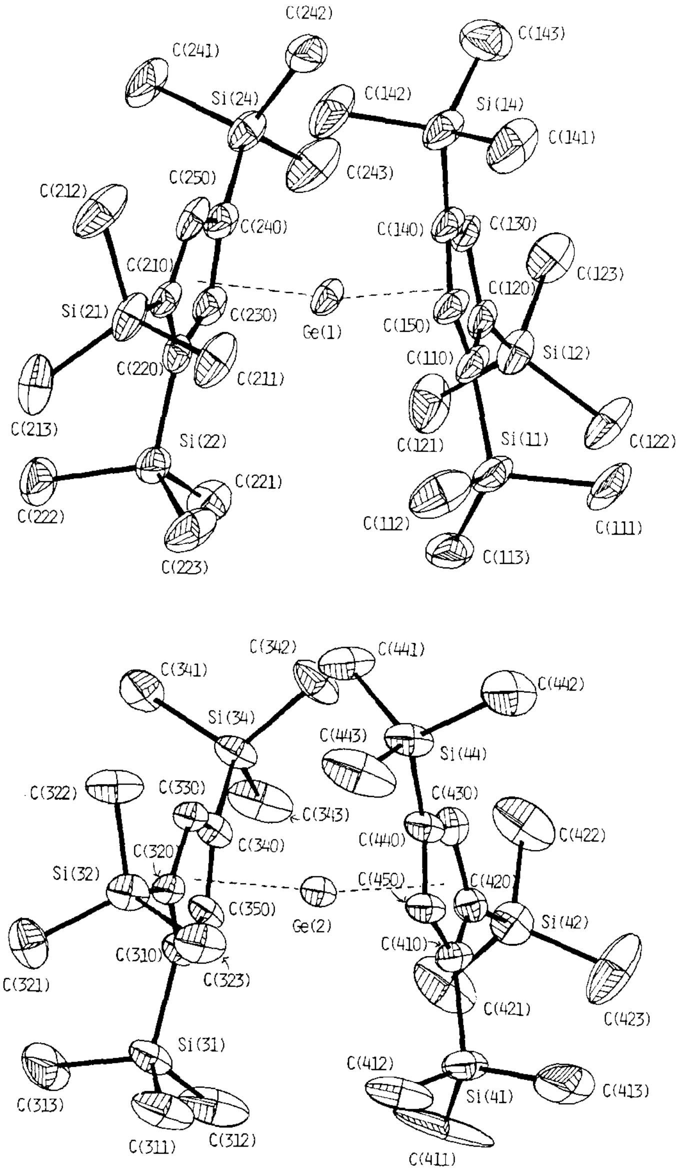

Fig. 1. Molecular structure of **3**.

solid state structure of our complex adopt approximately the same configuration, at least as far as the mutual orientation of the two $C_5H_2Si_3$ fragments is concerned (see Fig. 2), we felt that it would be of interest to explore the steric situation in more detail.

The 1,2,4-substitution pattern of the Cp rings gives rise to a number of possibilities for the relative orientations of the two rings in each molecule. For each of the two limiting possibilities, eclipsed and staggered, there are in fact three configurational isomers, and these are shown in Fig. 3. Obviously, intermediate configurations

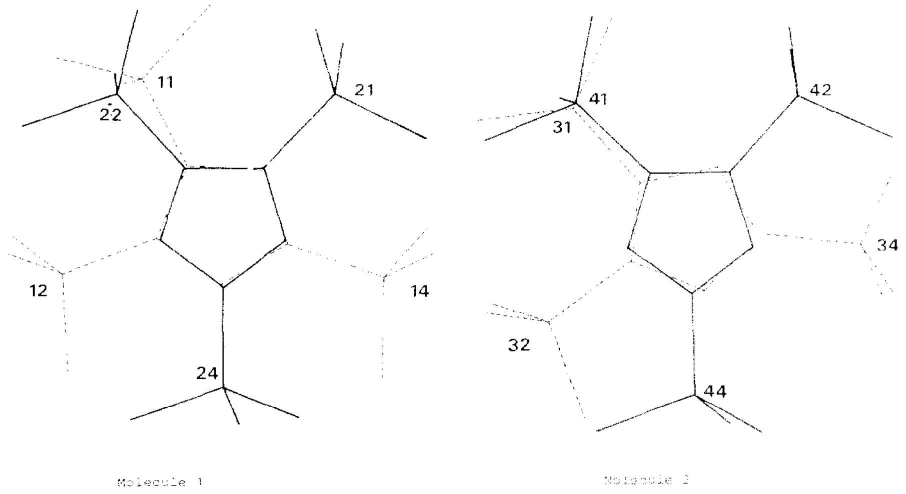

Fig. 2. Orientations of the Cp-fragments in 3.

are also possible, and during the systematic rotation of one ring relative to the other, configurations equivalent by symmetry to those shown will be produced. In the event, both independent molecules adopt structures which correspond very closely to isomer c, (see Fig. 2) which has maximum substituent staggering of an eclipsed Cp/Cp system. In an attempt to determine how these isomers are related in steric energies, we examined the molecular structure with our steric energy program

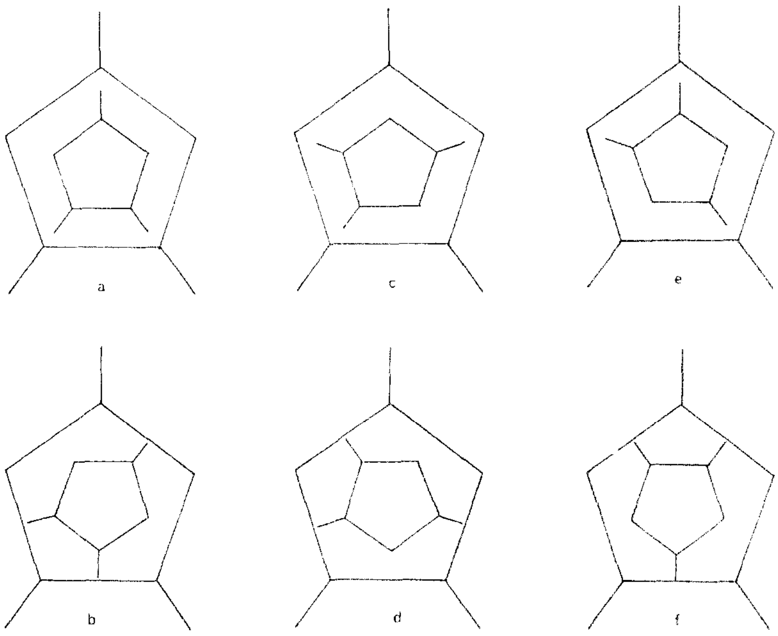

Fig. 3. Conformational isomers of 3.

EENY2 [11]. Full details of the way in which calculations are made with this program will be published shortly [12], but the application to the present problem can be summarised as follows.

The component atoms of the molecule (the coordinates of molecule 1 were used for these calculations) are assigned to residues and sub-residues. In this case, each ($C_5H_2R_3$) ligand is defined as one residue, whilst the R groups are defined as sub-residues. The coordinates of the Cp centroids are added to the list as dummy atoms. It is then possible to make changes to the molecular structure in a variety of ways:

(a) by varying the angle Cp(1)–Ge–Cp(2),
(b) by varying the tilt angles Ge–Cp–any ring carbon;
(c) by varying the orientations of the rings via changes in suitable torsion angles,
(d) by varying the orientations of the $SiMe_3$ groups, again via changes in suitable torsion angles.

It should be noted that changes involving sub-residues can be made whilst effecting changes in positions of whole residues.

The program can then compute the overall "steric energy" for any configuration of the molecule by summing all non-bonded atom–atom interactions calculated using a generalised 6/12 potential with the parameters of Pavel, Quagliata and Scarcelli [13], and can also allow the energy to be minimised against variations in chosen parameters. It is important to note that we are specifically examining only steric interactions, and that no account is taken of the electronic energies which might be associated with the geometry changes made, so that the subsequent assessment of the results must be considered with suitable care.

For the present calculations, in which we wished to explore the steric factors associated with the mutual rotation of the substituted Cp rings, we began with an idealised molecular structure. The Cp(1)–Ge–Cp(2) angle was changed to, and fixed at, 180°, and the tilts of the Cp rings were removed by setting the Ge–Cp vectors to be orthogonal to the ring planes. Then one of the rings was systematically rotated, in steps of 10°, using the idealised structure defined above as a starting point, for a full 360°. At each point including the starting point, the energy was minimised against the orientations of the $SiMe_3$ groups; that is, for each Cp/Cp orientation, the $SiMe_3$ groups were allowed to readjust their orientations to minimise any steric interactions. In this way, we are effectively mapping out the possible pathway for the rotation of one ring relative to the other.

The energy-angle relationship found for this calculation is shown in Fig. 4. On the angle scale we also indicate the configurational isomer in Fig. 3 to which the relevant structure corresponds.

Several notable features are apparent from this graph. First we see that the conformation found in the crystal does occur in a region of low energy, but not at a well-defined minimum. Secondly we note that there seems to be significant barrier to the complete rotation of the ring, in both positive and negative rotational directions. Finally we see that energies of configurations which should be equivalent by symmetry (based on the orientations of the $C_5H_2Si_3$ fragments, see above) are quite different. The latter two features are related, and we believe that they result from limitations in the "flexibility" of the model used. The barriers and the energy differences are almost certainly due to locking together of $SiMe_3$ groups. In order to escape from these situations and invoke the unrestricted Cp/Cp and $SiMe_3$ rota-

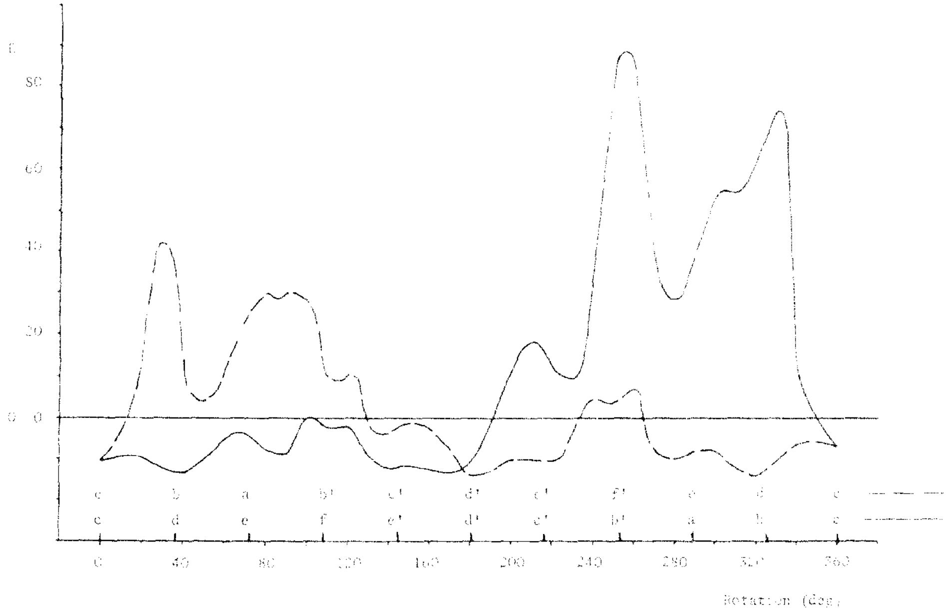

Fig. 4. Graphs showing variations of intramolecular steric energy, E (in kcal mol^{-1}) with rotation of one $C_5H_2(SiMe_3)_3$ residue relative to the other for a molecule of **3**. The full line corresponds to a "positive" rotation (clockwise rotation of the "inner" ring in Fig. 3), the dashed line a "negative" rotation.

tions inferred from from the NMR study, it would seem to be necessary to allow the ligands to tilt and/or the Cp–Ge–Cp angle to vary. That such deformations are possible is clearly indicated by the structures as found. An alternative possibility is that the ring rotations actually occur via slippage and tilting of the rings, i.e. a circumambulatory motion. Modelling of such a flexible system is not a trivial problem, and although we are attempting to tackle it a detailed discussion of such work is beyond the scope of this paper.

In a further calculation we began with the actual structure found and allowed minimization of the energy with respect just to the orientations of the $SiMe_3$ groups. Not surprisingly this showed that the structure was very close to a minimum, some 5 kcal mol^{-1} deeper than that found for the idealised structure. Most significantly, we found that important contributions were made to the energy sum by a number of small attractive interactions between methyl groups on different Cp units, and that these may be responsible, in part, for the tilting and bending. We hope that our further detailed calculations will provide more clarification on this point.

Experimental

All reactions were carried out under an inert atmosphere with exclusion of moisture. C, H analysis: Perkin–Elmer 240; melting points: Büchi 510, Mettler FP61; mass spectra: Varian 311A (70 eV, 300 μA, 200°C). NMR spectra: Varian EM 360 L, Bruker AM 300; chemical shifts (δ) in ppm.

Bis[(trimethylsilyl)cyclopentadienyl]germanium (1), bis[bis(trimethylsilyl)cyclopentadienyl]germanium (2) and bis[tris(trimethylsilyl)cyclopentadienyl]germanium (3)

General procedure. A suspension of germanium dichloride-dioxane adduct in tetrahydrofuran was added to a solution of the silylated cyclopentadienyllithium and stirred for 6 h. The solvent was evaporated off and 30 ml hexane were added to the residue. After stirring and filtration, compound **1** was isolated by fractional distillation and the compounds **2** and **3** by low temperature crystallization.

Compound **1**: 29.8 mmol $(Me_3Si)C_5H_4Li$ [14] in 10 ml THF; 3.18 g (14.9 mmol) $GeCl_2 \cdot$ dioxane; b.p. 97°C/10^{-5} Torr, yield 520 mg (10%). Found: C, 54.78; H, 7.87. $C_{16}H_{26}GeSi_2$ (346.8) calcd.: C, 55.37; H, 7.50%. ^1H NMR (CH_2Cl_2, TMS): $\delta(SiCH_3)$. 0.29 (s, 18H); δ(ring H) 6.7, 6.8 (pseudotripletts, 8H). ^{13}C NMR ($CDCl_3$, TMS): $\delta(SiCH_3)$: 0.4; δ(C(1)) 112.9; δ(C(2.5)) 115.5; δ(C(3.4)) 118.9. MS: 331 ($M^+ - CH_3$).

Compound **2**: 30.9 mmol $(Me_3Si)_2C_5H_3Li$ [14] in 40 ml THF; 3.58 g (15.4 mmol) $GeCl_2 \cdot$ dioxane; m.p. 72°C, yield: 4.41 g (45%). Found: C, 53.02; H, 8.06. $C_{22}H_{42}GeSi_4$ (490.95) calcd.: C, 53.77; H, 8.55%. ^1H NMR (CH_2Cl_2, TMS): $\delta(SiCH_3)$ 0.17 (s, 36H); δ(ring-H(4,5)) 6.17 (d, J 2.5 Hz, 4H); δ(ring-H(2)) 6.69 (t, J 2.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, TMS): $\delta(SiCH_3)$ 0.26; δ(C(4.5)) 120.1; δ(C(2)) 127.3; δ(C(1.3)) 136.5. MS: 417 ($M^+ - SiMe_3$).

Compound **3**: 14.9 mmol $(Me_3Si)_3C_5H_2Li$ [14] in 20 ml THF; 1.59 g (7.5 mmol) $GeCl_2 \cdot$ dioxane; m.p. 98°C, yield 1.54 g (42%). Found: C, 52.83; H, 9.66. $C_{28}H_{58}GeSi_6$ (635.88) calcd.: C, 52.90; H, 9.13%. ^1H NMR ($CDCl_3$, TMS): $\delta(SiCH_3)$ 0.30 (s, 18H), 0.33 (s, 36H); δ(ring-H) 6.90 (s, 4H). ^{13}C NMR ($CDCl_3$, TMS): $\delta(SiCH_3)$: 0.7, δ(C(1,2,4)) 125.6, 130.9; δ(C(3,5)) 133.6. MS: 562 ($M^+ - SiMe_3$).

Crystallography

The X-ray crystallographic study was made using an Enraf–Nonius CAD4 and graphite monochromated Mo-K_α radiation ($\lambda(K_{\alpha1})$, ($K_{\alpha2}$) 0.70930, 0.71359 Å) at room temperature (22 ± 2°C), following procedures previously outlined in detail [15]. The pale-yellow, air-sensitive crystals were mounted under argon in thin-walled glass capillaries. Data were recorded for a crystal of dimensions $0.3 \times 0.2 \times 0.07$ mm^3 using an $\omega/2\theta$ scan mode for $1.5 \leq \theta \geq 21°$ within the hemisphere $+h$, $\pm k$, $\pm l$, giving 8575 measured, 8384 unique and 5104 observed ($I > 1.5\sigma(I)$) reflections. An empirical absorption correction was made using ψ-scan data for the reflections $31\bar{1}$, $62\bar{1}$, $95\bar{2}$ with χ values of 83.06, 88.31 and 83.63° respectively.

Crystal data: $C_{28}H_{58}Si_6Ge$, $M = 635.88$, triclinic, space group $P1$ or $P\bar{1}$ (the latter confirmed by the analysis), a 11.377(3), b 19.520(3), c 20.780(3) Å, α 115.93(1), β 97.43(2), γ 74.34(2)°, V 3995.96 Å, $Z = 4$, D_c 1.06 g cm^{-3}, μ(Mo-K_α) 9.09 cm^{-1}.

The structure was solved via direct methods, developed via difference electron-density maps and refined using full matrix least-squares. All heavy atoms (C, Si, Ge) were refined with anisotropic thermal parameters. Hydrogen atoms were not reliably located in difference maps and none were included in the refinement, which was achieved through use of two blocks (one per molecule) in the final stages. The function minimised was $\omega(\Delta F)^2$ and weights were calculated according to the relationship $\omega = 1/[\sigma^2(F_0) + gF_0^2]$, with $g = 0.0002$ giving acceptable agreement analysis. The final R ($= \Sigma\Delta F/\Sigma F_0$) and R' ($= \Sigma w^{\frac{1}{2}} |\Delta F| / \Sigma w^{\frac{1}{2}} F_0$) values were 0.0647 and 0.0764, respectively, for a total of 649 parameters. Atomic positional

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR 3

	x	*y*	*z*		*x*	*y*	*z*
Ge(1)	1654(1)	10897(1)	7897(1)	Ge(2)	3820(1)	4976(1)	7099(1)
Si(11)	−1253(4)	10315(3)	8315(2)	Si(31)	1524(3)	6572(2)	6499(2)
Si(12)	−283(4)	9702(2)	6341(2)	Si(32)	1799(3)	6839(2)	8514(2)
Si(14)	3947(3)	9087(3)	8104(3)	Si(34)	6628(3)	5858(2)	7297(2)
Si(21)	2578(4)	12513(2)	9644(2)	Si(41)	1851(4)	3465(3)	5877(2)
Si(22)	−179(3)	13137(2)	8482(2)	Si(42)	5400(4)	3067(3)	5512(2)
Si(24)	3826(3)	10893(2)	6632(2)	Si(44)	4597(4)	4129(3)	8529(2)
C(110)	282(11)	9987(7)	7895(7)	C(310)	2855(10)	6332(6)	7063(6)
C(111)	−1846(14)	9404(10)	8050(10)	C(311)	61(11)	6424(10)	6683(8)
C(112)	−1006(15)	10766(12)	9328(8)	C(312)	1918(14)	5938(13)	5540(8)
C(113)	−2385(13)	11073(9)	8074(10)	C(313)	1283(17)	7607(10)	6624(11)
C(120)	632(11)	9752(7)	7171(7)	C(320)	2960(9)	6450(6)	7803(6)
C(121)	−844(16)	10683(9)	6309(9)	C(321)	752(13)	7803(9)	8584(8)
C(122)	−1629(13)	9267(10)	6248(8)	C(322)	2672(12)	7011(10)	9386(7)
C(123)	715(14)	9019(9)	5540(7)	C(323)	857(12)	6106(9)	8352(7)
C(130)	1952(11)	9480(7)	7159(7)	C(330)	4234(9)	6262(6)	7961(6)
C(140)	2399(11)	9530(7)	7842(7)	C(340)	4919(10)	6034(7)	7339(6)
C(141)	3735(15)	8532(10)	8620(10)	C(341)	7073(11)	6806(8)	7926(9)
C(142)	4749(13)	9890(10)	8717(10)	C(342)	7482(12)	5088(9)	7614(9)
C(143)	4838(15)	8365(10)	7252(10)	C(343)	7036(12)	5604(11)	6368(7)
C(150)	1357(11)	9856(7)	8293(7)	C(350)	4069(10)	6084(7)	6789(6)
C(210)	2349(11)	12207(7)	8668(6)	C(410)	3225(12)	3614(7)	6468(6)
C(211)	1840(14)	11966(9)	9969(7)	C(411)	1808(21)	3663(23)	5109(14)
C(212)	4298(13)	12234(11)	9818(8)	C(412)	446(18)	4093(17)	6430(12)
C(213)	2013(16)	13595(8)	10166(7)	C(413)	1650(27)	2476(16)	5659(19)
C(220)	1325(11)	12413(6)	8236(6)	C(420)	4510(12)	3476(7)	6343(6)
C(221)	−1208(12)	12914(9)	7661(8)	C(421)	4977(15)	3711(12)	5032(9)
C(222)	−9(14)	14166(8)	8777(9)	C(422)	7101(15)	2994(13)	5775(9)
C(223)	−955(13)	13071(10)	9207(8)	C(423)	5227(24)	2049(11)	4916(9)
C(230)	1665(11)	11971(7)	7501(7)	C(430)	5114(12)	3695(7)	7033(7)
C(240)	2877(11)	11470(7)	7443(6)	C(440)	4248(11)	3951(7)	7581(6)
C(241)	4782(14)	11512(9)	6549(8)	C(441)	5722(14)	4778(9)	8912(7)
C(242)	4874(13)	10003(9)	6717(10)	C(442)	5354(17)	3162(10)	8578(9)
C(243)	2814(15)	10567(11)	5815(8)	C(443)	3121(15)	4602(14)	9047(8)
C(250)	3272(11)	11636(7)	8177(7)	C(450)	3084(10)	3908(7)	7226(6)

parameters are given in Table 3. Neutral atom scattering factors, with corrections for anomalous dispersion, were based on data from ref. 16. All calculations were made using the SHELX programs [17] on a VAX II/750 computer. Tables of Thermal parameters and F_0/F_c values can be obtained from the authors at QMC.

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