Journal of Organometallic Chemistry, 384 (1990) 41–47
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20510

Concerning the silicon–germanium bond. The structures of isomeric $Ph_3E–E'Me_3$, E = Ge, E′ = Si and E = Si, E′ = Ge.

Keith H. Pannell, Ramesh N. Kapoor, Raphael Raptis,
Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968-0513 (U.S.A.)

László Párkányi and Vilmos Fülöp
Central Research Institute of Chemistry of the Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17 (Hungary)

(Received July 24th, 1989)

Abstract

The synthesis and structure of the unknown trimethylgermyltriphenylsilane (I, $Ph_3SiGeMe_3$) is reported. The molecular geometry is compared to that of the isomeric $Me_3SiGePh_3$ (II) and the related $Ph_3SiSiMe_3$ (III) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2GePh_3$ (IV). The Si–Ge bond of I is significantly longer than that for II. We suggest that this is due to expansion of Ge bonding orbitals by the relatively electron-donating methyl groups in conjunction with the contraction of the corresponding orbitals of Si due to the electron-withdrawing phenyl groups. The overall result is a better orbital overlap between the Si and Ge atoms for II.

Introduction

Whereas there are many crystallographic data published concerning the nature of the Si–Si bond [1–3], there exists only a single report on the Si–Ge bond [4]. Compounds of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_2EPh_3$ (E = Si, Ge) were compared to the non-metal containing analogs $Me_3Si–EPh_3$. From such studies, it was concluded that the germyl group was capable of electron release to silicon and that the transition metal was responsible for elongation of the Si–Ge bond. Since there is current interest in the nature of Si–Ge systems in the semi-conductor area, we have extended our investigations into the nature of the Si–Ge bond by now synthesizing and structurally characterizing $Ph_3Si–GeMe_3$ (I). This permits us to compare the nature of the Si–Ge bond in an isomeric pair in which the substituents on the two group 14 elements have been interchanged. We know of no other structural analysis of a pair of isomeric compounds involving exchange of the ligands on the core atoms bound to each other.

0022-328X/90/$03.50

Experimental

Synthesis of $Ph_3Si-GeMe_3$

To a slurry of sodium dispersion, 0.46 g (20 mmol) in 25 ml THF, was added 1.87 g (5 mmol) of Ph_3SiCl and 0.13 g (1 mmol) of naphthalene. The resulting mixture was stirred for 20 h after which time it had become a deep green/black solution of $Ph_3Si^- Na^+$. This solution was then added dropwise at 0 ° C to a stirred solution of Me_3GeCl (0.8 g, 5.2 mmol, in 25 ml THF). After complete addition, 15 min, the solution was stirred for 1 h and permitted to warm to room temperature. The solvent was removed under reduced pressure and the resulting oily solid was extracted and recrystallized from a 2/1 hexane/methylene chloride solvent mixture. An initial crop of 0.45 g of the title compound was obtained, uncorrected m.p. 102 ° C. No effort was made to collect a second fraction or optimize the yield. Spectroscopic data: NMR (ppm relative to TMS in C_6D_6): ^1H, 0.5 (Me_3Ge), 7.32, 7.76 (m, SiPh_3); ^{13}C: −1.26 (Me_3Ge), 128.5, 129.6, 135.6, 136.2 (SiPh_3); ^{29}Si: −13.7; UV (hexane): 266 nm (ϵ 1440), 273 nm (ϵ 890); IR (CCl_4): 3051(s), 2970(s), 2906(s), 1953(w), 1882(w), 1819(w), 1484(m), 1428(m), 1102(s) cm^{-1}.

X-ray structure analysis

Intensity data were collected at room temperature on an Enraf–Nonius CAD-4 computer controlled four circle diffractometer with graphite monochromated Cu-K_α radiation. Crystal data, data collection and least squares parameters are given in Table 1.

Table 1

Crystal data, data collection, and least-squares parameters

Empirical formula	$C_{21}H_{24}GeSi$
M (a.m.u.)	377.1
a (Å)	11.307(1)
c (Å)	8.910(1)
V (Å^3)	986.5(3)
Space group	$P3$
Z	2
F(000)	392
D_c (g cm^{-3})	1.27
λ(Cu-K_α) (Å)	1.54184
μ(Cu-K_α) (cm^{-1})	26.4
2θ limits (deg.)	3–150
Scan technique	$\theta-2\theta$
No. of reflections collected	4254
No. of unique data	1362
No. of reflections used in least-squares (NO)	1269 [$I \geq 3\sigma(I)$]
No. of variables (NV)	70
Weighting scheme	$w = 4F_o^2/\sigma(F_o^2)^2$
R_o	0.031
R_w	0.055
$(\Sigma w(\|F_o\| - \|F_c\|)^2/(NO-NV))^{1/2}$	2.208
Approx. crystal size (mm)	0.15 × 0.40 × 0.50

Table 2

Final positional parameters$\times 10^4$ ($\times 10^3$ for the hydrogen atoms), B_{eq} [a] (Å^2) values (B_{iso} for the hydrogen atoms) and C–H distances (Å$\times 10^2$)

Atom	x	y	z	B_{eq}/B_{iso}	C–H
Ge	2/3	1/3	−1007.4(3)	2.983(8)	
Si	2/3	1/3	1679.0(7)	2.29(1)	
C(1)	7220(1)	2115(1)	2389(1)	2.69(2)	
C(2)	6692(1)	1357(1)	3698(2)	3.05(3)	
C(3)	7082(1)	437(1)	4190(2)	3.79(3)	
C(4)	7997(1)	239(1)	3356(2)	3.58(4)	
C(5)	8547(1)	989(1)	2068(2)	3.31(4)	
C(6)	8165(1)	1918(1)	1589(2)	3.04(3)	
C(7)	6166(3)	1526(2)	−1176(3)	5.79(6)	
H(2)	609(1)	149(1)	420(1)	4.6(4)	89(2)
H(3)	658(2)	−13(1)	512(2)	4.9(4)	103(2)
H(4)	829(2)	−43(2)	371(2)	5.8(5)	102(2)
H(5)	919(2)	94(2)	163(2)	6.6(6)	85(2)
H(6)	852(2)	237(2)	66(2)	15.0(4)	95(2)
H(7a)	604(3)	148(3)	−271(4)	12(1)	84(4)
H(7b)	695(4)	149(4)	−184(5)	13(1)	91(2)
H(7c)	530(4)	85(4)	−141(6)	13(1)	95(4)

[a] B_{eq} is defined as 4/3 trace (**BG**) where **B** is the thermal motion tensor and **G** is the direct metric tensor.

From a total number of collected intensities 3604 reflections were averaged giving 1362 unique data. The close relationship between the unit cells of I, II, and III, the identical space group and Z, suggested the isomorphism of I and II. A structure factor calculation using the appropriate model (the coordinates of silicon and germanium exchanged in the atomic coordinate set of II) clearly indicated no isomorphism existed. The structure was therefore solved by direct methods.

At the end of isotropic refinement of the structure a non empirical absorption correction was applied to the original, unaveraged data set (maximum, minimum, and average absorption corrections were 0.789, 1.233, and 0.998). The data set was then averaged again. The agreement factor on intensity and on $F_{(obs)}$ for 3604 averaged reflections were 0.032 and 0.021, respectively. This reflection set was used for the anisotropic refinement of the structure. The hydrogen atoms were also refined with individual isotropic temperature factors in two final cycles. Final atomic parameters are listed in Table 2 *.

Results and discussion

There is a single report in the literature concerning the title complex $Ph_3Si–GeMe_3$ (I), as an identification product from the reaction of GeF_2 with Ph_3SiCl (eq. 1) [5].

$$Ph_3SiCl + GeF_2 \rightarrow Ph_3Si\text{–}GeF_2Cl \xrightarrow{MeMgI} Ph_3Si\text{–}GeMe_3 \qquad (1)$$

---

* Lists of observed and calculated structure factors and anisotropic thermal parameters may be obtained from the authors.

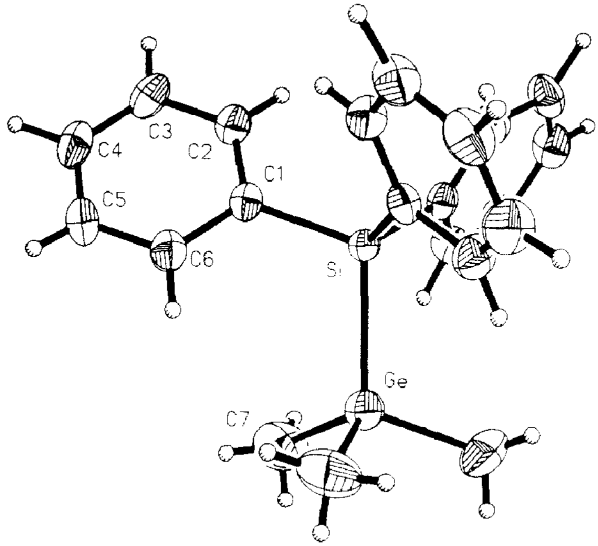

Fig. 1. The diagram of compound I with the numbering of atoms. Thermal ellipsoids are drawn at the 45% probability level.

No spectral, analytical or experimental detail was provided. We have prepared the compound via a standard salt elimination reaction outlined in eq. 2.

$$Ph_3Si^- \ Na^+ + Me_3GeCl \rightarrow Ph_3Si{-}GeMe_3 \qquad (2)$$

The spectroscopic data on the compound are unremarkable, and the ^{29}Si chemical shift at -13.7 ppm compares to a value of -20.4 ppm for the Ph_3Si group in III.

Crystals suitable for X-ray analysis were obtained and the molecular structure of I is shown in Fig. 1, and is similar to that previously described for $Me_3Si{-}GePh_3$ (II) [4], and $Me_3Si{-}SiPh_3$ (III) [6]. The molecules in the crystal are situated on the symmetry axes $\pm 1/3$, $\pm 2/3$, $\pm z$, therefore they possess threefold symmetry. The z coordinates of all atoms of I differ from those of the corresponding II and III. Relevant bond angles and distances are presented in Table 3.

The Si–Ge bond in I is significantly longer than that in the isomeric compound II, i.e. 2.394(1) vs. 2.384(1) Å, but shorter than the elongated Si–Ge bond in $(\eta^5\text{-}C_5H_5)Fe(CO)_2{-}SiMe_2{-}GePh_3$ (IV) [4]. The elongation of Si–Si bonds when one of the Si atoms is bonded to a transition metal is now well documented [7] and the longer Si–Ge bond of IV fits into this category. Thus, the elongation of the bond in I reflects a real difference from that in the isomeric II.

The $Si{-}C_{methyl}$ bond distances in I, II, and III are significantly shorter than the $Si{-}C_{phenyl}$ bond distances, 1.862(2) vs. 1.886(1) Å. This trend is not so apparent with the limited data set of the Ge compounds where the two bonds $Ge{-}C_{methyl}$ and $Ge{-}C_{phenyl}$ are comparable, 1.952(3) and 1.958(1) Å respectively. The shortening of $Si{-}C_{methyl}$ bonds relative to the sum of the tetrahedral covalent radii has been noted previously in electron diffraction studies of $SiMe_4$ and Si_2Me_6 [8]. The shortening was attributed to either electronegativity differences between Si and C or occupancy of *d*-orbitals by electron donation from the methyl group. While we have no comments to make upon the source of the short $Si{-}C_{methyl}$ bonds it is of interest

Table 3

Relevant bond distances and angles (with e.s.d.'s) for compounds I, II, III and IV

	I	II	III	IV
	this work	[7]	[6]	[7]
Bond distances (Å)				
Si–Si			2.355(1)	
Si–Ge	2.394(1)	2.384(1)		2.405(2)
Si–C_{phenyl}	1.885(1)		1.886(1)	
Si–C_{methyl}		1.863(3)	1.862(2)	1.877(6) 1.885(6)
Ge–C_{phenyl}		1.958(1)		1.959(5) 1.960(4) 1.966(5)
Ge–C_{methyl}	1.958(1)			
Bond angles (°)				
C_{phenyl}–Si–C_{phenyl}	109.3(1)		108.7(1)	
C_{methyl}–Si–C_{methyl}		110.1(1)	109.0(2)	105.5(5)
C_{phenyl}–Ge–C_{phenyl}		107.9(1)		106.9(3) 108.2(3) 107.4(3)
C_{methyl}–Ge–C_{methyl}	108.4(2)			
Si–Si–C_{phenyl}			110.3(1)	
Si–Si–C_{methyl}			109.9(1)	
Si–Ge–C_{phenyl}		110.0(1)		114.4(2) 106.5(2) 113.1(3)
Si–Ge–C_{methyl}	110.5(1)			
Ge–Si–C_{phenyl}	109.6(1)			
Ge–Si–C_{methyl}		108.9(1)		102.9(4) 104.1(4)

that such shortening is not a uniform phenomenon. It should be borne in mind that such shrinkage of the Si–C bonds can be partly due to the greater thermal motion of the methyl carbon atoms. However, no unusually high B_{eq} values were observed and the range of values are comparable to those reported for compounds II, III, and IV. Analysis of the X-ray crystallographic data available via the Cambridge data base reveals that the shortening of the Si–C_{methyl} bond relative to that of the Si–C_{aryl} bond is only apparent for linear systems. If the methylsilicon species is part of a cyclic structure then the Si–C_{methyl} and Si–C_{phenyl} bonds are almost identical. This situation is illustrated graphically in Fig. 2. Similar "normal" Si–C_{methyl} bond lengths are observed for the $SiMe_n$, $n = 2,3$ in transition metal substituted LM–$SiMe_nR_{3-n}$ [4].

Based upon a simple valence shell electron pair repulsion concept (VSEPR) the shortening of the Si–Me bond lengths should increase the steric requirement about the Si atom in such systems, and one might expect a relief of such congestion by elongation of the remaining bonds and an increase in the C_{methyl}–Si–C_{methyl} bond angles. In compound II this angle is indeed larger than the expected tetrahedral angle, and also larger than that in compound III as noted in Table 3. The corresponding angle in the transition metal complex IV (which exhibits a long Si–Ge bond as noted above, and longer Si–C_{methyl} bonds (1.881(5) Å) is signifi-

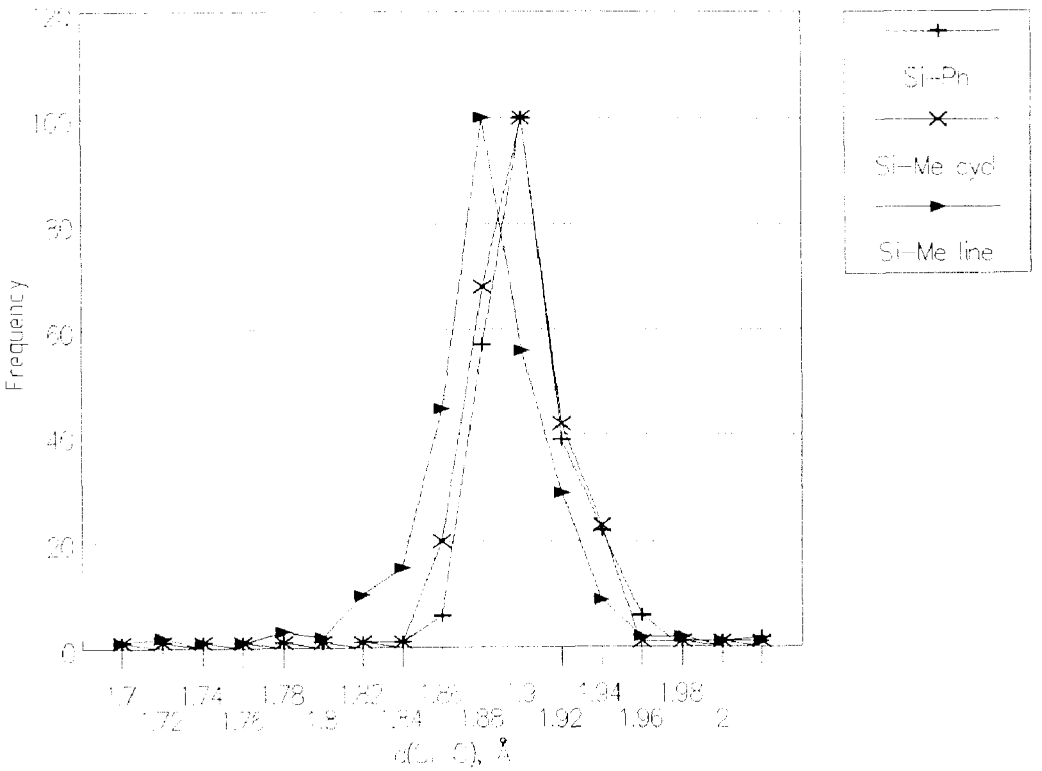

Fig. 2. The distribution of Si–C bond distances in polysilanes. 266 Si–Me distances in linear molecules (mean 1.871(36) Å), 211 Si–Me distances in cyclic molecules (mean 1.889(23) Å), and 125 Si–Ph distances (1.896(35) Å) were retrieved from the Cambridge Crystallographic Data files and used to construct the diagram. The curves were normalized to give the same maximum frequency.

cantly reduced to 105.5(5)°. Bond angles are less sensitive to thermal motion than bond lengths, hence the increased bond angles noted for II further support our contention that the short Si–C_{methyl} lengths noted above are not due to increased thermal motion. Overall, the short bond distances and increased angles in II, do not cause an elongation of the fourth bond in II, i.e. the Si–Ge bond. The simple VSEPR approach to the analysis of these structures is inappropriate.

An alternative approach to the features of this interesting isomeric pair of compounds is to consider the effect of the substituents upon the energy levels and radial distributions of the bonding orbitals of the two elements Si and Ge. In general it is well established that phenyl groups tend to be electron withdrawing while methyl groups tend to be electron donating. The former situation should cause a contraction in the radial distribution of the bonding orbitals of the E atom for a Ph_3E group, and the latter a expansion of the orbitals of the E atom in a Me_3E group. In the case of I, the radial distribution of Ge orbitals should be increased and those on Si decreased. These effects will cause an increased disparity in the two sets of combining orbitals which are already non-equivalent since the two atoms are in different rows of the periodic table. On the other hand, for II the effect will be the opposite, i.e. decreasing the radial distribution of orbitals on Ge and increasing those on Si will tend to make the two sets of orbitals more compatible and thereby enhance overlap and bonding. It is on this basis that the lengthening of the Si–Ge bond in I may best be understood.

The principle discussed above should be general for other isomeric pairs of compounds containing a bond between elements in different rows of the periodic table and we are currently attempting to verify this expectation.

Acknowledgements

Support of this research by the Robert A. Welch Foundation, Houston, Texas, and by the National Science Foundation via the establishment of a Minority Research Center of Excellence in Materials Science is gratefully acknowledged. We thank Ms. Elvira Delgado for technical assistance.

References

1 W. Wojnowski, K. Peters, E-M. Peters, H.G. von Schnering, B. Becker, Z. Anorg. Allg. Chem., 553 (1987) 287.
2 W. Wojnowski, B. Dręczewski, K. Peters, E-M. Peters, H.G. von Schnering, Z. Anorg. Allg. Chem., 540/541 (1986) 271.
3 N. Wiberg, H. Schuster, A. Simon, K. Peters, Angew. Chem. Int. Ed. 25 (1986) 79.
4 L. Parkanyi, C. Hernandez, K.H. Pannell, J. Organomet. Chem., 301 (1986) 145.
5 P. Riviere, J. Satgé, A. Boy, J. Organomet. Chem., 83 (1970) 25.
6 L. Parkanyi, E. Hengge, J. Organomet. Chem., 235 (1982) 273.
7 (a) J. Drahnak, R. West, J.C. Calabrase, J. Organomet. Chem. 198 (1980) 55; (b) L. Parkanyi, K.H. Pannell, C. Hernandez, J. Organomet. Chem., 252 (1983) 127.
8 B. Beagley, J.J. Monoghan, T.G. Hewitt, J. Mol. Struct., 8 (1971) 401.