Synthesis and structure of 1,1′-bis(pentafluorophenyl)tetrahydrodigermane

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Dehydrogenation of pentafluorophenylgermane in the presence of catalytic amounts of a Wilkinson complex, certain Rh^I *ortho*-benzosemiquinolate complexes, or $(Ph_3P)_4Pt$ leads to tetrahydrodigermane, $C_6F_5H_2GeGeH_2C_6F_5$. X-ray analysis has confirmed the *trans*-arrangement of the C_6F_5-cycles at the Ge atoms. The Ge—Ge bond length is 2.394(1) Å. The doublet pattern of the band due to the Ge—H bonds (ν 2090 and 2104 cm^{-1}) in the IR spectrum is probably associated with nonequivalence of the hydrogen atoms in the molecule.

Key words: synthesis; 1,1'-bis(pentafluorophenyl)tetrahydrodigermane; X-ray analysis.

Catalytic dehydrogenation of organometallic dihydrides R_2EH_2 (E = Si, Ge; R = Me, Et, Ph) is one of the methods for preparing binuclear compounds of the group IVA elements with $\mathrm{H{-}\overset{\vdots}{\underset{\vdots}{E}}{-}\overset{\vdots}{\underset{\vdots}{E}}{-}H}$ fragments.[1,2] At the present time, only those processes involving silicon dihydrides and rhodium, platinum, and palladium triphenylphosphine complexes and alkyl bis(cyclopentadienyl)titanium derivatives have been studied in detail.[3,4] Attempts at preparing tetrahydrodisilanes, $-RH_2Si-SiH_2R-$, in the reactions of $RSiH_3$ with different dehydrogenation catalysts have led only to complex mixtures of oligomeric polysilanes, $\mathrm{[{-}\overset{|}{\underset{|}{Si}}{-}\overset{|}{\underset{|}{Si}}(H)]}_n$ (n = 5÷10).[5]

Previously we studied catalytic reactions of $R^F{}_2GeH_2$ (hereinafter $R^F = C_6F_5$) with L_3RhCl and L_2RhSQ_2 (L = Ph_3P; SQ = 3,6-di-*tert*-butyl-*o*-benzosemiquinone or 3,6-di-*tert*-butyl-4,5-dimethoxy-*o*-benzosemiquinone) leading to the formation of $R^F{}_2HGeGeHR^F{}_2$ in a quantitative yield.[6] Intermediate binuclear rhodium-germanium adducts were detected by ESR, their structure was established, and a scheme for the dehydrogenation was suggested. It was found that these paramagnetic intermediates were formed in the reactions of R^FGeH_3 with L_3RhCl and L_2RhSQ_2; in this case, however, the final germanium-containing product was not isolated.[6] The present work reports the synthesis of digermane $R^FH_2GeGeH_2R^F$ by dehydrogenation of R^FGeH_3 in the presence of catalytic amounts of rhodium and platinum complexes, and its X-ray and IR-spectroscopic data.

Results and Discussion

We found that R^FGeH_3 interacts with catalytic amounts of Wilkinson complex and L_2RhSQ_2 to give $R^FH_2GeGeH_2R^F$ (38 % yield)

$$2R^FGeH_3 \longrightarrow \underset{\mathbf{1}}{R^FH_2GeGeH_2R^F} + H_2$$

The reaction occurs when a toluene solution is heated at 60 °C for 25—30 h. The moderate yield of the target product could be caused by several reasons. As has already been mentioned,[4] organogermanium hydrides readily eliminate hydrogen in the presence of different complex catalysts to give oligomeric polygermanes. Since the yield of hydrogen in this reaction exceeds 100 %, we assume that under these conditions the dehydrogenation of product **1** leading to polygermanes takes place. Inaddition, a mixture of products of the nucleophilic substitution of *ortho*-F atoms in the C_6F_5-rings, which is difficult to separate, is formed along with **1**. Thus, unlike the smooth catalytic dehydrogenation of R^FGeH_2, the reaction of trihydride R^FGeH_3 in the presence of the above catalysts is complicated by side-processes lowering the yield of the target product.

We also isolated tetrahydrodigermane in the interaction of pentapfluorophenylgermane with PtL_4. To bring this reaction to completion, it was necessary to heat the reactants in toluene at 80—90 °C for 40—50 h. The yield of the final product was no more than 20 %.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 315—318, February, 1994.

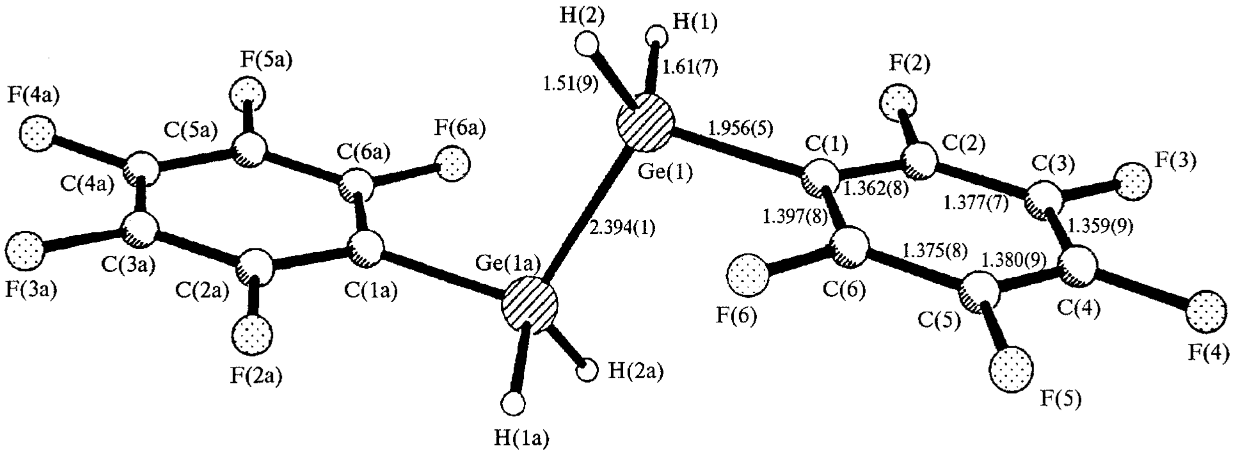

Fig. 1. The general view and bond lengths in molecule **1**.

Digermane **1** is obtained as colorless crystals stable in air for several days. The compound is readily soluble in ethers, aromatic hydrocarbons, and alkanes.

X-ray structural investigation showed that molecule **1** in the crystal is centrosymmetric (the symmetry center is in the middle of the Ge(1)—Ge(1a) bond, *i.e.*, it has a *trans* structure (Fig. 1)). The Ge—Ge bond in **1**, 2.394(1) Å, is markedly shorter than the Ge—Ge distance in $R^F{}_3$Ge—GeEt$_3$, 2.436 Å (see Ref. 7), and the sum of the covalent radii of these atoms according to Pauling, is 2.44 Å (see Ref. 8). The Ge(1)—C(1) distance, 1.956(5) Å, is, on the contrary, virtually equal to the sum of the Ge and C(sp^3) covalent radii, 1.96 Å. A similar length was found for the Ge—C bond in the $R^F{}_4$Ge molecule, 1.956 Å (see Ref. 9). The C—C and C—F bond lengths in the pentafluorophenyl fragment vary over the range of 1.359(9)—1.397(8) Å and 1.329(7)—1.350(7) Å (the mean values are 1.375 and 1.338 Å, respectively). The Ge—C_6F_5 fragment is planar: the maximum deviation of the F atoms from the average plane of the C(1)—C(6) ring is 0.034 Å for F(6); Ge(1) is 0.005 Å out of this plane.

The hydrogen atoms at the Ge atom differ in their arrangement relative to the ring plane. Unlike H(2), H(1) lies nearly in the plane: the deviation from the plane is 0.24 Å, and the H(1)—Ge(1)—C(1)—C(2) torsion angle is −10°. The H(2) atom is 1.08 Å out of the plane and the H(2)—Ge(1)—C(1)—C(2) torsion angle is −123.3°. The Ge(1)—C(1)—C(2) angle, 123.3(4)°, is somewhat larger than the Ge(1)—C(1)—C(6) angle, 120.4(4)°, which is likely to be connected with the repulsion of H(1) and F(2). The Ge(1) · · · F(2) and Ge(1) · · · F(6) distances (3.148 and 3.093 Å) also differ somewhat. The Ge(1)—H(1) 1.61(7) Å and Ge(1)—H(2) 1.51(9) Å bonds in the digermane molecule are comparable with the Ge—H bonds in GeH_4 (1.527 Å) (see Ref. 10), and $(CH_3)_2GeH_2$ (1.532 Å) (see Ref. 11). Despite the above-mentioned asymmetry in the arrangement of the H(1) and H(2) atoms relative to the C_6F_5-ring, the conformation of molecule **1** in the crystal corresponds to the minimum nonvalent repulsion of the H(1)and H(2) atoms and the atoms of the C_6F_5 group. As can be seen from Fig. 2, which shows the interatomic repulsion energy plotted against the H(1)—Ge(1)—C(1)—C(2) torsion angle in molecule **1** calculated by the MOLDRAW program,[12] the value of the H(1)—Ge(1)—C(1)—C(2) torsion angle, 10°, for the real conformation of molecule **1** in the crystal corresponds to the energy minimum of the interatomic repulsion in the molecule.

The intramolecular distances Ge(1) · · · F(2) and Ge(1a) · · · F(6), 4.602 and 3.966 Å, as well as the shortest intermolecular contact Ge(1) · · · F(3), 3.496 Å, exceed the sum of the van der Waals radii of the Ge and F atoms. Thus, no geometric features that would point to the presence of intramolecular Ge · · · F interactions, as has been postulated for $(R^F{}_3Ge)_2Hg$ (see Ref. 13), were found in the molecular structure of **1**.

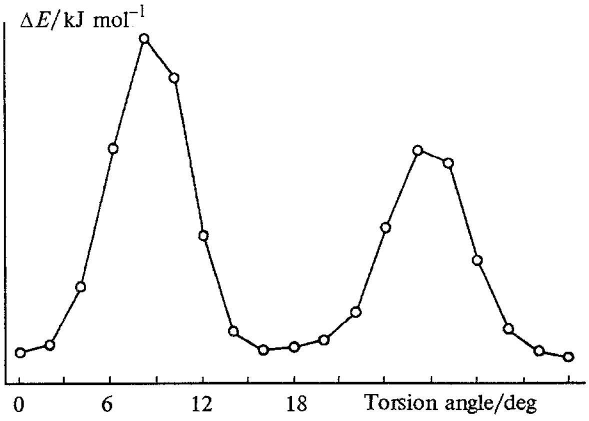

Fig. 2. The plot of the conformational energy against the value of the H(1)—Ge(1)—C(1)—C(2) torsion angle in molecule **1**.

The IR spectrum of **1** (suspension in vaseline oil) showed bands characteristic of the C_6F_5—Ge fragment: 1630, 1500, 1280, 1075, 960, 810, 720, 600, 490 and 350 cm^{-1} and bands due to the vibrations of the Ge—H bond: doublet 2090 and 2140 (ν(Ge—H)), 855 (δ GeH_2) and 655 cm^{-1} (ρ GeH_2). The doublet character of the ν(Ge—H) absorption band is of note. Such anomalies in the IR spectra of silicon and germanium hydrides have been accounted for by the presence of *trans-* and *gauche-*conformers,[14] symmetric and asymmetric M—H vibrations, and intramolecular coordination between a halogen atom and an M atom that are not linked by an ordinary chemical bond. However, the experimental results and calculations indicate that the ν(Ge—H) absorption band is split into a doublet neither by the presence of geometric conformers nor by the presence of two types of vibrations. Usually, the symmetric and asymmetric frequencies of the stretching vibrations of the MH_2 and MH_3 groups are observed as a single band.[15] The splitting of the ν(Ge—H) band in the IR spectrum is assumed to arise because of the above mentioned nonequivalence of the H(1) and H(2) atoms in **1**.

Experimental

The syntheses of perfluorinated germane and of the catalysts were carried out using known procedures.[1,16—18] IR spectra were recorded on a Perkin Elmer 577 spectrometer. X-ray structural analysis was performed on a Siemens P3/PC diffractometer at room temperature (λ(Mo-K_α)-radiation, θ/2θ-scan in the range $2° < 2\theta < 50°$, 8148 independent reflections with $F > 4.0\sigma(F)$). Crystals **1** are monoclinic, a = 9.082(2), b = 5.290(2), c = 15.396(4) Å; β = 96.20(2)°, V = 735.4(3) $Å^3$, d_{calc} = 1.09 g cm^{-3}, Z = 2, space group $P2_1/n$. The structure was solved by a combination of direct methods and Fourier syntheses and refined by a full-matrix least-squares approximation with anisotropic parameters of the thermal vibrations for nonhydrogen atoms and isotropic parameters for hydrogen atoms. In the refining, the following weight scheme was used: $w^{-1} = \sigma^2(F) + 0.0007F^2$. The residual R-factors were R = 0.046, R_W= 0.049. The atomic coordinates and parameters of thermal vibrations in **1** are given in Table 1. Bond lengths are given in Fig. 1, and bond angles in Table 2. All calculations were performed using the SHELXTL PLUS package of programs.

Synthesis of $R^FH_2GeGeH_2R^F$. A solution of 6 g (24 mmol) of pentafluorophenylgermane in 10 mL of toluene was poured into a solution of 0.2 g (0.0002 mmol) of the Wilkinson complex. 400 mL of H_2 was eliminated over 20 h at 80 °C. Toluene was evaporated in a vacuum, and the residue was extracted with hexane. Then the hexane was evaporated in a vacuum, and the residue was sublimed at 60 °C (0.01 Torr). Colorless crystals **1** (2.28 g, 38 %) were obtained, m. p. 64 °C. IR spectrum, ν/cm^{-1}; doublet 2090, 2104 (Ge—H). Found (%): C, 29.5; H, 0.9. $C_{12}H_4F_{10}Ge_2$. Calculated (%): C, 29.82; H, 0.83. The fraction insoluble in hexane contained 3g of polyphenylgermane $[(C_6F_4)_xGeH]_n$ identified by IR spectroscopy, ν/cm^{-1}: 430, 950, 1230, 2130,[19] and oligomeric polygermanes.

Reactions of R^FGeH_3 with L_2RhSQ_2 (L = Ph_3P; SQ = 3,6-di-*tert*-butyl-*o*-benzosemiquinone or 3,6-di-*tert*-butyl-4,5-dimethoxy-*o*-benzosemiquinone) and PtL_4 were carried out in the same way. The yield of tetrahydrodigermane in these reactions was 20 %.

Table 1. Atomic coordinates (×10^4) and equivalent isotropic parameters of the atomic thermal vibrations U ($Å^2$ ×10^3) in structure **1**

Atom	x	y	z	U
Ge(1)	8913	0780	5285	49(1)
C(1)	7251	0586	4367	35(2)
C(2)	6199	−1256	4332	39(2)
C(3)	5031	−1390	3684	46(2)
C(4)	4924	0362	3035	46(2)
C(5)	5962	2265	3029	49(2)
C(6)	7117	2343	3685	41(2)
F(2)	6257	−3047	4960	58(1)
F(3)	4018	−3228	3679	71(2)
F(4)	3807	0297	2392	81(2)
F(5)	5872	3963	2384	76(2)
F(6)	8127	4152	3660	66(1)
H(1)	8625	−1227	6033	71(20)
H(2)	9021	3452	5619	150(40)

Table 2. Bond angles (ω) in structure **1**

Angle	ω/deg
C(1)—Ge(1)—H(1)	108.1(20)
H(1)—Ge(1)—H(2)	112.8(52)
H(1)—Ge(1)—Ge(1a)	103.8(23)
Ge(1)—C(1)—C(2)	123.3(4)
C(2)—C(1)—C(6)	116.3(5)
C(1)—C(2)—F(2)	120.1(5)
C(2)—C(3)—C(4)	119.1(6)
C(4)—C(3)—F(3)	119.8(5)
C(3)—C(4)—F(4)	121.0(6)
C(4)—C(5)—C(6)	119.0(6)
C(6)—C(5)—F(5)	120.4(6)
C(1)—C(6)—F(6)	119.8(5)
C(1)—Ge(1)—H(2)	108.2(40)
C(1)—Ge(1)—Ge(1a)	108.6(2)
H(2)—Ge(1)—Ge(1a)	115.0(41)
Ge(1)—C(1)—C(6)	120.4(4)
C(1)—C(2)—C(3)	123.2(5)
C(3)—C(2)—F(2)	116.7(5)
C(2)—C(3)—F(3)	121.1(5)
C(3)—C(4)—C(5)	120.5(5)
C(5)—C(4)—F(4)	118.5(6)
C(4)—C(5)—F(5)	120.5(5)
C(1)—C(6)—C(5)	121.9(6)
C(5)—C(6)—F(6)	118.3(5)

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Received November 12, 1992