Reaction of $(C_6F_5)_2HGeGeH(C_6F_5)_2$ with triethylbismuth: molecular structure of $[(C_6F_5)_2Ge]_4Bi_2$

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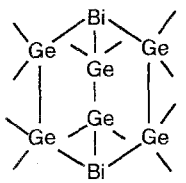
The reaction of $(C_6F_5)_2HGeGeH(C_6F_5)_2$ with triethylbismuth affords a new polynuclear germylbismuth derivative, $[(C_6F_5)_2Ge]_4Bi_2$ (**1**). The metal framework of molecule **1** has the form of a gable roof built by two central Bi atoms and four peripheral Ge atoms with covalent Bi—Bi bonds [3.045(3) Å], Bi—Ge [2.724(5)—2.755(4) Å] and Ge—Ge [2.444(6), 2.465(6) Å].

Key words: polynuclear compounds, synthesis; pentafluorophenyl groups; germylbismuth complex, X-ray structural analysis.

Hydride synthesis[1] is one of the most general methods for preparing linear, cage and cluster organometallic compounds. This method was used for preparing a series of polynuclear products with different numbers and combinations of heteroatoms.[2—4] For example, when Et_3Bi reacts with R^F_3GeH (hereinafter, $R^F = C_6F_5$), compounds $(R^F_3Ge)_nBiEt_{3-n}$ are formed, $n = 1$ or 2 depending on the ratio of the reagents;[5] the reaction of Et_3Bi with $R^F_2GeH_2$ affords compound $(R^F_2Ge)_3Bi_2$, which contains a five-nuclear Ge_3Bi_2 skeleton in the form of a trigonal bipyramid; the Ge atoms occupy the equatorial plane and are covalently bonded to the Bi atoms in the apical positions.[6]

The aim of this work was to attempt to apply hydride methodology to the synthesis of a germylbismuth cluster of larger nuclearity by reacting Et_3Bi with a dinuclear derivative of germanium $R^F_2HGeGeHR^F_2$ (instead of $R^F_2GeH_2$), which can form ($R^F_2Ge—GeR^F_2$) dinuclear bridges between the Bi atoms.



Results and Discussion

The reaction of Et_3Bi with $R^F_2HGeGeHR^F_2$ in toluene at 100 °C yields the germylbismuth polynuclear derivative $(R^F_2Ge)_4Bi_2$ (**1**) after 5 h.

$$3\ R^F_2HGe—GeHR^F_2 + 2\ Et_3Bi \xrightarrow{PhMe} \longrightarrow 6\ EtH + \frac{1}{n}(R^F_2Ge)_{2n} + (R^F_2Ge)_4Bi_2$$

1

It should be noted that elimination of ethane is a stepwise process starting at 80 °C (~2 out of 6 moles of EtH are eliminated in 1 h; the reaction mixture remains colorless). When the temperature is raised to 100 °C, further formation of EtH occurs (after 3 h, the color of the solution becomes light yellow), which is terminated after 5 h (the reaction mixture turns red); the Ge—H stretching band disappears in the IR spectra of the reaction products. In our opinion, the stepwise elimination of ethane and the color change during the reaction indicate that the formation of the final products is preceded by the formation of germilbismuth intermediates, as in the reaction of the mononuclear dihydride $R^F_2GeH_2$ with Et_3Bi.

Perfluorophenylated polygermane $(R^F_2Ge)_n$ was isolated from the reaction products; this compound was identified by IR spectroscopy. The desired germylbismuth compound **1** was prepared in the form of bright-red crystals, which are stable in air for several days, readily soluble in aromatic hydrocarbons, but almost insoluble in alkanes. An attempt to dissolve **1** in THF at room temperature resulted unexpectedly in its complete decomposition with the formation of metallic Bi in quantitative yield (unlike $(R^F_2Ge)_3Bi_2$).

The structure of compound **1** was established by X-ray diffraction. It was shown that the metal skeleton of molecule **1** has the form of a gable roof built by two

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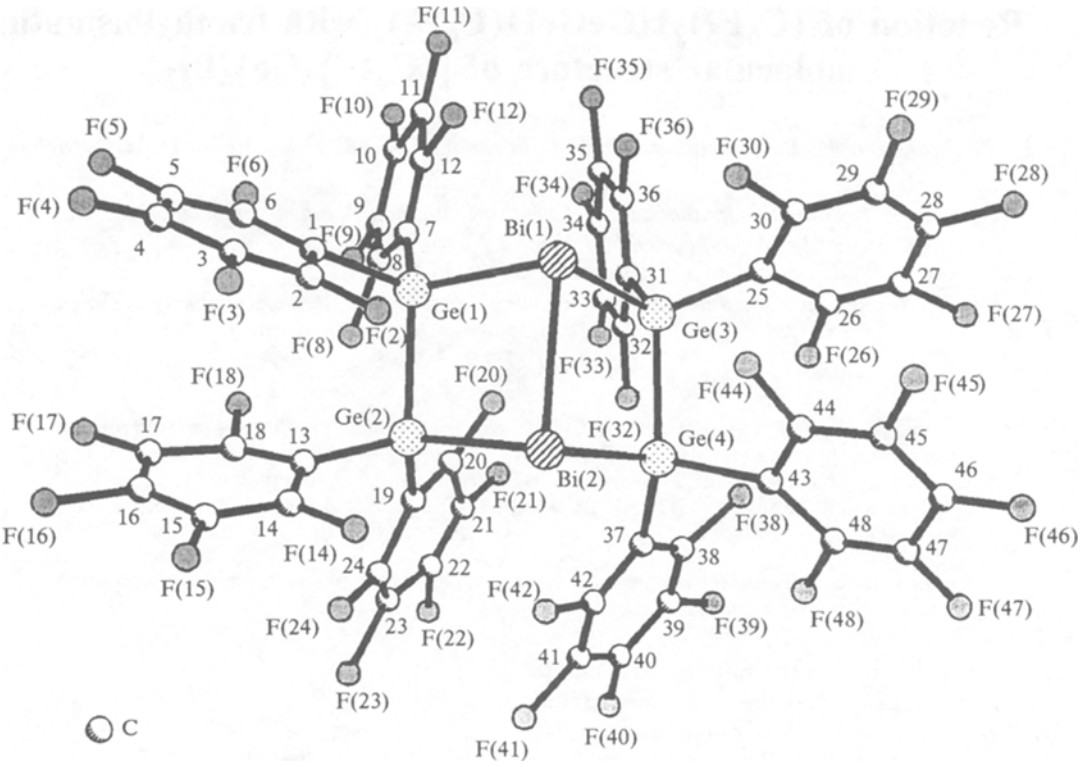

Fig. 1. The overall view and the atomic numbering scheme for molecule **1**.

covalently bonded Bi atoms and four Ge atoms (Fig. 1). Therefore, instead of the three expected $R^F_2Ge—GeR^F_2$ bridges, only two bridges are present in molecule **1**; the third bridge is "replaced" by a Bi—Bi bond.

The Bi—Bi [3.045(3) Å], Ge—Ge [aver. 2.455(6) Å], and Bi—Ge [aver. 2.743(4) Å] bond lengths (Table 1) are close to the corresponding sums of the Pauling[7] covalent radii for the Bi (1.50 Å) and Ge (1.22 Å) atoms. Similar Bi—Ge bond lengths are observed in $(R^F_2Ge)_3Bi_2$ [2.733(1)—2.749(1) Å] and $(R^F_2Ge)_3Bi_2Pt(PPh_3)_2$ (2.736—2.707 Å) molecules.[6]

The Bi atoms are in the distorted pyramidal coordination (see Fig. 1). The Bi—Bi—Ge bond angles [83.0—84.2(1)°] are significantly smaller than the Ge—Bi—Ge bond angles [97.2(1) and 97.1(1)°, see Table 1]. The average values of the bond angles at the Bi atoms (88.2°) is smaller than the ideal value of 90°.

The coordination environment of the Ge atoms in molecule **1** is significantly distorted compared to that of an ideal tetrahedron. The Bi—Ge—Ge bond angles are in the range 95.0—97.4(2)°, *i.e.*, they are slightly larger than the Bi—Ge—Bi bond angles in the $(R^F_2Ge)_3Bi_2$ molecule (93.85—94.03°), but smaller than the analogous angles in the $(R^F_2Ge)_3Bi_2Pt(PPh_3)_2$ molecule (see Ref. 6). The C—Ge—C angles in **1** [103—106(2)°] are also contracted compared to the ideal tetrahedral value (109.4°). The average Ge—C bond length is 1.95 Å. The pentafluorophenyl groups in molecule **1** have normal geometric parameters: the average C—C and C—F bonds are 1.40 and 1.35 Å, respectively.

Table 1. The basic bond lengths (d) and bond angles (ω) in molecule **1**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Bi(1)—Bi(2)	3.045(3)	Bi(2)—Bi(1)—Ge(1)	83.0(1)	Ge(2)—Ge(1)—C(7)	128(2)	Ge(4)—Ge(3)—C(25)	109(1)
Bi(1)—Ge(3)	2.755(4)	Bi(2)—Bi(1)—Ge(3)	83.9(1)	C(1)—Ge(1)—C(7)	106(2)	Bi(1)—Ge(3)—C(31)	117(1)
Ge(1)—Bi(1)	2.724(5)	Ge(1)—Bi(1)—Ge(3)	97.2(1)	Bi(2)—Ge(2)—Ge(1)	95.0(2)	Ge(4)—Ge(3)—C(31)	124(1)
Bi(2)—Ge(2)	2.743(5)	Bi(1)—Bi(2)—Ge(2)	84.2(1)	Bi(2)—Ge(2)—C(13)	115(2)	C(25)—Ge(3)—C(31)	103(2)
Bi(2)—Ge(4)	2.752(4)	Bi(1)—Bi(2)—Ge(4)	83.8(1)	Ge(1)—Ge(2)—C(13)	106(2)	Bi(2)—Ge(4)—Ge(3)	96.1(2)
Ge(1)—Ge(2)	2.444(6)	Ge(2)—Bi(2)—Ge(4)	97.1(1)	Bi(2)—Ge(2)—C(19)	118(2)	Bi(2)—Ge(4)—C(37)	117(2)
Ge(3)—Ge(4)	2.465(6)	Bi(1)—Ge(1)—Ge(2)	97.4(2)	Ge(1)—Ge(2)—C(19)	117(1)	Ge(3)—Ge(4)—C(37)	124(2)
		Bi(1)—Ge(1)—C(1)	109(1)	C(13)—Ge(2)—C(19)	106(2)	Bi(2)—Ge(4)—C(43)	108(1)
		Ge(2)—Ge(1)—C(1)	102(1)	Bi(1)—Ge(3)—Ge(4)	95.8(2)	Ge(3)—Ge(4)—C(43)	106(1)
		Bi(1)—Ge(1)—C(7)	114(2)	Bi(1)—Ge(3)—C(25)	108(1)	C(37)—Ge(4)—C(43)	104(2)

Table 2. Atomic coordinates ($\times 10^4$) and thermal parameters U_{iso}^{eq} ($\times 10^3$) in structure **1**

Atom	x	y	z	U_{iso}^{eq}/Å^2	Atom	x	y	z	U_{iso}^{eq}/Å^2
Bi(1)	−3050(2)	−845(1)	−1263(1)	52(1)	C(42)	−1508(37)	−4867(38)	−2875(26)	69(23)
Bi(2)	−1033(2)	−1880(1)	−1330(1)	53(1)	C(43)	−1352(35)	−2617(27)	−3699(20)	54(19)
Ge(1)	−3760(4)	−1963(3)	−347(2)	47(2)	C(44)	−1135(37)	−1575(30)	−3539(24)	63(21)
Ge(2)	−2248(4)	−2922(3)	−512(3)	53(2)	C(45)	−565(45)	−1116(33)	−4015(33)	94(28)
Ge(3)	−3859(4)	−2324(3)	−2813(2)	50(2)	C(46)	−240(38)	−1711(36)	−4747(30)	92(26)
Ge(4)	−2143(4)	−3057(3)	−2917(3)	50(2)	C(47)	−362(40)	−2700(32)	−4857(22)	74(22)
C(1)	−3374(29)	−1078(22)	874(20)	33(16)	C(48)	−893(38)	−3099(28)	−4429(27)	74(23)
C(2)	−2254(30)	−498(27)	1131(23)	48(18)	F(2)	−1610(16)	−407(13)	604(12)	60(10)
C(3)	−1969(30	59(27)	1967(35)	50(23)	F(3)	−862(19)	623(15)	2211(12)	87(11)
C(4)	−2620(53)	−31(33)	2570(26)	85(25)	F(4)	−2242(23)	488(17)	3346(13)	113(14)
C(5)	−3622(47)	−589(33)	2283(26)	74(24)	F(5)	−4353(22)	−706(21)	2847(15)	130(16)
C(6)	−4022(33)	−1127(29)	1466(33)	72(24)	F(6)	−5072(19)	−1718(17)	1228(12)	91(12)
C(7)	−5376(37)	−2479(42)	−561(24)	63(25)	F(8)	−5260(19)	−4089(17)	−504(16)	100(14)
C(8)	−5992(46)	−3450(34)	−633(23)	57(23)	F(9)	−7532(20)	−4758(16)	−863(18)	117(15)
C(9)	−7098(49)	−3810(28)	−804(24)	70(22)	F(10)	−8945(18)	−3518(20)	−983(17)	117(16)
C(10)	−7812(33)	−3196(41)	−830(28)	71(26)	F(11)	−7966(22)	−1628(17)	−781(22)	147(19)
C(11)	−7372(41)	−2239(41)	−771(29)	68(29)	F(12)	−5725(20)	−966(14)	−548(17)	106(14)
C(12	−6167(40)	−2010(27)	−610(24)	48(20)	F(14)	289(18)	−1846(16)	468(14)	93(12)
C(13)	−1549(44)	−2678(26)	568(31)	61(23)	F(15)	1135(22)	−1440(17)	2951(16)	121(15)
C(14)	−427(43)	−2193(34)	893(27)	73(24)	F(16)	−190(30)	2000(16)	3057(15)	152(18)
C(15)	40(36)	−1954(35)	1714(33)	83(26)	F(17)	−2306(25)	−2995(18)	2440(15)	127(16)
C(16)	−630(46)	−2216(39)	2176(29)	68(26)	F(18)	−3211(20)	−3373(16)	890(14)	89(13)
C(17)	−1660(62)	−2669(36)	1955(46)	111(37)	F(20)	−4216(21)	−4197(16)	−1896(14)	95(13)
C(18)	−2012(64)	−2916(35)	1110(31)	112(35)	F(21)	−4977(25)	−6164(20)	−2681(19)	159(18)
C(19)	−2754(39)	−4440(30)	−1083(31)	52(23)	F(22)	−3701(33)	−7442(17)	−2262(17)	181(20)
C(20)	−3766(61)	−4797(30)	−1644(28)	107(32)	F(23)	−1897(33)	−6664(19)	−1076(16)	161(20)
C(21)	−4046(54)	−5858(52)	−2135(48)	161(55)	F(24)	−1140(21)	−4676(16)	−349(14)	98(13)
C(22)	−3475(60)	−6345(32)	−1919(26)	116(28)	F(26)	−4173(21)	−3237(13)	−4683(11)	89(11)
C(23)	−2646(51)	−6100(37)	−1342(32)	90(29)	F(27)	−4097(32)	−2416(20)	−5877(14)	165(20)
C(24)	−2107(37)	−5054(39)	−894(25)	76(23)	F(28)	−3722(29)	−380(21)	−5387(17)	149(19)
C(25)	−3946(31)	−1684(31)	−3582(26)	54(21)	F(29)	−3538(24)	785(17)	−3804(15)	114(15)
C(26)	−4019(42)	−2214(29)	−4436(28)	76(26)	F(30)	−3621(23)	−23(15)	−2658(13)	98(13)
C(27)	−3988(45)	−1873(30)	−4998(24)	96(26)	F(32)	−4966(18)	−4754(14)	−3533(12)	76(11)
C(28)	−3879(43)	−866(37)	−4810(24)	88(29)	F(33)	−7150(22)	−5673(16)	−3788(17)	113(14)
C(29)	−3667(39)	−215(26)	−4014(25)	76(22)	F(34)	−8794(22)	−4600(19)	−3370(20)	145(17)
C(30)	−3778(37)	−637(28)	−3450(23)	59(22)	F(35)	−8238(22)	−2581(20)	−2698(21)	153(19)
C(31)	−5439(29)	−3123(26)	−2987(20)	35(17)	F(36)	−6086(22)	−1620(17)	−2489(17)	120(15)
C(32)	−5711(34)	−4201(29)	−3364(21)	48(20)	F(38)	−3392(19)	−4886(14)	−4556(12)	78(11)
C(33)	−6802(46)	−4704(25)	−3453(26)	67(23)	F(39)	−3394(21)	−6855(15)	−5023(16)	108(14)
C(34)	−7680(34)	−4169(42)	−3280(31)	82(27)	F(40)	−2230(24)	−7548(16)	−4065(17)	119(16)
C(35)	−7431(51)	−3109(45)	−2888(34)	98(31)	F(41)	−871(23)	−6246(17)	−2615(16)	113(15)
C(36)	−6309(64)	−2602(31)	−2826(31)	105(31)	F(42)	−820(19)	−4300(14)	−2150(12)	76(11)
C(37)	−2179(43)	−4534(27)	−3304(35)	77(25)	F(44)	−1433(17)	−906(13)	−2833(12)	63(10)
C(38)	−2771(33)	−5205(30)	−4016(30)	61(23)	F(45)	−392(23)	−89(16)	−3828(16)	112(14)
C(39)	−2769(44)	−6173(33)	−4244(25)	75(24)	F(46)	354(28)	−1254(18)	−5166(16)	141(17)
C(40)	−2180(35)	−6570(31)	−3820(40)	66(28)	F(47)	−59(24)	−3289(18)	−5552(15)	122(15)
C(41)	−1556(51)	−5911(48)	−3110(30)	96(32)	F(48)	−1038(18)	−4115(14)	−4575(13)	76(11)

In the studies of the properties of compound **1**, we found that elemental bromine readily cleaves the Bi—Bi, Bi—Ge, and Ge—Ge bonds. Addition of a benzene solution of Br_2 at 10 °C after 5 min affords $BiBr_3$ and $R^F{}_2GeBr_2$ in a quantitative yield.

$$\mathbf{1} + 7\,Br_2 \xrightarrow{C_6H_6} 4\,R^F{}_2GeBr_2 + 2\,BiBr_3$$

Experimental

Synthesis of tetraperfluorophenyldigermane was performed according to the procedure described previously.[8] IR spectra were recorded on a Perkin-Elmer 577 instrument.

Synthesis of $(R^F{}_2Ge)_4Bi_2$. A solution of 2 g (2.45 mmol) of tetraperfluorophenyldigermane in 20 mL of toluene was added to a solution of 0.484 g (1.63 mol) of triethylbismuth.

109 mL (100 %) of ethane was evolved after 5 h at 100 °C. The toluene solution was concentrated and cooled to 0 °C to yield 0.44 g of a colorless amorphous powder of $(R^F_2Ge)_n$, which was identified from the IR spectrum (ν/cm^{-1}: 430, 950, 1230, 2130).[9] Addition of hexane to the mother liquor gave 1.2 g (72 %) of red crystals of **1** with m. p. 215 °C (decomp.). Found: C, 28.31 %. $C_{48}Bi_2F_{40}Ge_4$. Calculated: C, 28.2 %.

Reaction of compound 1 with bromine. A solution of 1.5 g (0.733 mmol) of compound **1** in 10 mL of benzene was added to a benzene solution of 0.82 g (5.13 mmol) of Br_2 precooled to 5 °C. The reaction mixture decolorized in 10 min, and the 0.71 g (99 %) of $BiBr_3$ that formed was isolated by centrifugation. The benzene solution was decanted from the precipitate and the solvent was evaporated *in vacuo*; the residue (1.6 g) contained 95 % of $R^F_2GeBr_2$ according to GLC data.

X-ray structural analysis. The X-ray diffraction study was performed on a Hilger—Watts diffractometer at ~20 °C (λ(Mo-Kα) radiation, θ/2θ-scan technique, $0 < 2\theta < 50°$, 3036 independent reflections with $F > 3\sigma(F)$). Crystals are triclinic, a = 12.009(2) Å, b = 14.466(3) Å, c = 17.338(4) Å, α = 110.23(2)°, β = 95.19(2)°, γ = 99.68(2)°, V = 2750(2) Å^3, d_{calc} = 2.47 g cm^{-3}, Z = 2, space group $P\bar{1}$. The structure was solved using the Patterson function and was refined by the full-matrix least-squares procedure with anisotropic thermal parameters for nonhydrogen atoms. The corrections for absorption were made using the DIFABS program.[10] The weighting scheme $w^{-1} = \sigma^2(F) + 0.00023F^2$ was used in the refinement. The final values of the R factors are R = 0.106, R_w = 0.062. All calculations were performed on an IBM PC/AT computer using the SHELXTL PLUS program package. Atomic coordinates are given in Table 2.

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