Synthesis and Molecular Structure of Decamethyl-1,4-dibismutha-2,3,5,6,7-pentasilabicyclo[2.2.1]heptane

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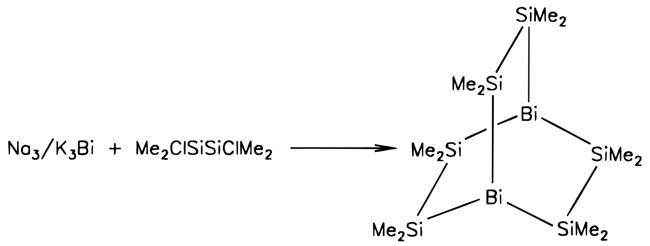
Summary: In the reaction between dichlorodimethylsilane and sodium potassium bismuthide, which was prepared from the elements in dimethoxyethane, the previously unknown cage $Bi_2(SiMe_2)_5$ is formed. It was isolated by crystallization from heptane, and its molecular structure was confirmed by X-ray analysis.

Introduction

Some years ago we reported on the synthesis of dodecamethyl-1,4-dibismutha-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane,[1] formed in the reaction between 1,2-dichlorotetramethyldisilane and sodium potassium bismuthide.



This was the first cage composed exclusively of silicon and bismuth atoms. Its structure was confirmed by mass spectroscopy and infrared and Raman vibrational spectroscopy, as well as by elemental analysis.

Further experiments revealed that cages with SiSi bonds are also formed when monosilanes react with sodium potassium bismuthide. If dichlorodimethylsilane is used, the title compound results, but small amounts of the bicyclo[2.2.2]octane $Bi_2(SiMe_2)_6$ were also detected. Both cages decompose quickly at room temperature forming metallic bismuth. Crystals decompose faster than do solutions. At −70 °C, the crystals decompose within a few hours, whereas a solution in DME or *n*-heptane is stable over a period of several days. At room temperature, the decomposition of the crystals is complete within 20 min.

Experimental Section

General Comments. All operations were carried out under a nitrogen atmosphere using Schlenk techniques. Sodium potassium alloy and sodium potassium bismuthide must be handled with care, since they are highly flammable when exposed to air or moisture.

Synthesis. An 8.7 mL (264.86 mmol) amount of 4:3 sodium potassium alloy was slowly added to a suspension of 36.9 g (176.5 mmol) of finely powdered bismuth in 200 mL of dimethoxyethane (DME). Several times a day, the mixture was activated using an ultrasonic bath. By doing this, the reaction time reported in the literature (5 days[2]) can be shortened considerably.

The reaction mixture was allowed to cool to room temperature after this time, and approximately 3 mL of mercury was added to remove all excess sodium potassium alloy. The suspension of Na_3/K_3Bi was decanted from the amalgam, and 17.09 g (132.4 mmol) of Me_2SiCl_2 in 50 mL of DME was added dropwise to the refluxing mixture. The reaction mixture was stirred overnight at room temperature and the salts were filtered. After removal of the solvent at −10 °C under reduced pressure, the residue was dissolved in 50 mL of *n*-heptane and filtered again to remove the remaining salts. At −70 °C, pale yellow crystals of the bicyclo[2.2.1]heptane precipitated. The yield was 0.8 g (4.3%). We were not able to record NMR, infrared, and Raman spectra, but a mass spectrum could be obtained.

Mass spectrum (EI, *m*/*e* (%)): 708 (84.3, M^+); 635 (44.8, $M^+ - SiMe_3$); 577 (24.2, $M^+ - Si_2Me_5$); 519 (10.8, $M^+ - Si_2Me_7$); 499 (8.5, $M^+ - Bi$); 426 (4.2, $M^+ - BiSiMe_3$); 353 (6.3, $M^+ - BiSi_2Me_6$); 73 (100, $SiMe_3$).

Crystal Structure of Decamethyl-1,4-dibismutha-2,3,5,6,7-pentasilabicyclo[2.2.1]heptane. Crystals grown from *n*-heptane were used for the X-ray experiments. The data collection was performed under a stream of N_2 at −186 °C, using a modified STOE four-circle diffractometer and graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The crystal was mounted on the tip of a glass fiber in an inert oil. Hydrogen atoms were included into the model at their calculated positions. Anisotropic displacement parameters were assigned to all non-hydrogen atoms; isotropic displacement parameters were used for hydrogen atoms.

Selected intramolecular distances and angles are summarized in Table 2. The estimated standard deviations in parentheses refer to the last digit. Detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Center, Cambridge, UK.

Results

$Bi_2(SiMe_2)_5$ crystallizes in the space group *Pbca* with eight molecules in the unit cell. The structure of the cage and the arrangement of the molecules in the unit cell are shown in Figure 1. The molecule consists of a six-membered Bi_2Si_4 ring in a boat conformation, bridged by a $SiMe_2$ group, and belongs, apart from small deviations, to the point group C_{2v}. The mean silicon-bismuth bond distances are 2.6585(40) Å for the bonds with the bridging Si atom and 2.6565(40) Å for the bonds within the six-membered ring. The distances are somewhat smaller than in tetrakis(trimethysilyl)dibismuthane (2.683(16) Å[3]) but longer than in lithium bis(trimethylsilyl)bismuthide (2.633(14) Å[3]). These are the

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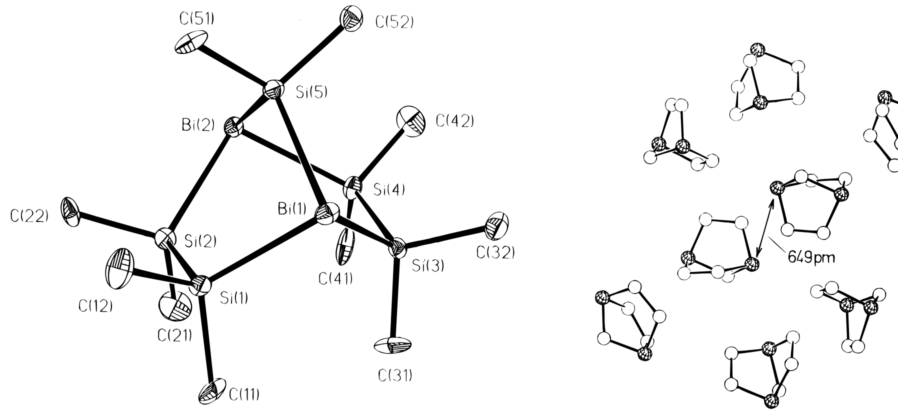

Figure 1. View of the molecular structure of $Bi_2(SiMe_2)_5$ and arrangement of the molecules in the unit cell.

Table 1. Crystal Data Collection and Refinement of Decamethyl-1,4-dibismutha-2,3,5,6,7-pentasilabicyclo[2.2.1]heptane

empirical formula	$C_{10}H_{30}Bi_2Si_5$
fw	708.75
cryst system	orthorhombic
space group	*Pbca*
a (pm)	1447.9(4)
b (pm)	1479.3(4)
c (pm)	2058.2(6)
α (deg)	90.0
β (deg)	90.0
γ (deg)	90.0
V (nm^3)	4.408(2)
Z	8
temp (K)	88
d (calc) (g cm^{-3})	2.136
F(000)	2608
cryst size (mm)	0.15 × 0.10 × 0.10
ab coeff (mm^{-1})	16.202
index ranges	$-17 \le h \le 17$, $-12 \le k \le 17$, $-22 \le l \le 24$
reflcns collcd	4440
indepdt reflcns	3881
data/restraints/params	3880/0/164
goodness of fit on F^2	1.063
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0494$, w$R2 = 0.0860$
R indices (all data)	$R1 = 0.0967$, w$R2 = 0.1020$
largest diff peak and hole [e nm^{-3}]	1254 and −1453
software	SHELX-93[8]

Table 2. Bond Distances (Å) and Selected Angles (deg) of Decamethyl-1,4-dibismutha-2,3,5,6,7-pentasilabicyclo[2.2.1]heptane

Distances			
Bi1Si1	2.647(4)	Si1C12	1.873(14)
Bi1Si3	2.656(4)	Si2C21	1.87(2)
Bi1Si5	2.653(4)	Si2C22	1.863(13)
Bi2Si2	2.662(4)	Si3C31	1.881(14)
Bi2Si4	2.661(4)	Si3C32	1.866(14)
Bi2Si5	2.664(4)	Si4C41	1.88(2)
Si1Si2	2.353(5)	Si4C42	1.88(2)
Si3Si4	2.355(5)	Si5C51	1.849(14)
Si1C11	1.870(14)	Si5C52	1.889(14)
Angles			
Si1Bi1Si5	89.14(11)	C22Si2Si1	108.1(5)
Si5Bi1Si3	90.82(11)	C31Si3Si4	108.6(5)
Si1Bi1Si3	95.25(11)	C32Si3Si4	111.2(5)
Si4Bi2Si5	87.90(11)	C41Si4Si3	109.4(6)
Si4Bi2Si2	96.63(12)	C42Si4Si3	110.3(5)
Si2Bi2Si5	89.83(11)	C51Si5Bi1	110.7(5)
Si2Si1Bi1	111.4(2)	C51Si5Bi2	109.5(5)
Si1Si2Bi2	113.3(2)	C52Si5Bi1	108.1(4)
Si4Si3Bi1	112.4(2)	C52Si5Bi2	109.3(4)
Si3Si4Bi2	111.7(2)	C11Si1Bi1	113.1(5)
C11Si1C12	106.6(7)	C12Si1Bi1	105.5(5)
C21Si2C22	108.8(7)	C31Si3Bi1	111.6(5)
C31Si3C32	107.0(7)	C32Si3Bi1	105.9(5)
C41Si4C42	106.8(7)	C21Si2Bi2	110.8(5)
C51Si5C52	107.8(7)	C22Si2Bi2	105.9(4)
C11Si1Si2	109.8(5)	C41Si4Bi2	110.9(5)
C12Si1Si2	110.3(5)	C42Si4Bi2	107.6(5)
C21Si2Si1	109.7(5)		

only two silicon−bismuth compounds that have been investigated by X-ray crystallography (apart from the cage described in this work). The SiSi bond lengths (2.355(5) Å) are within the range found for six-membered rings containing SiSi bonds (Si_6Me_{12}, 2.338(1) Å;[4] $Si_6Me_{11}-Si_6Me_{11}$, 2.347(7), 2.363(7), and 2.366(7) Å[5]). Steric repulsions between the nearly eclipsed methyl groups obviously do not cause a significant lengthening of the SiSi bond distances.

The intramolecular BiBi contact distance is 4.39 Å, which is just 1.39 Å longer than twice the covalent radius of the Bi atom (1.50 Å[6]). Typical BiBi bond distances are between 2.80 and 3.60 Å[7] (3.035(3) Å in $(Me_3Si)_2BiBi(SiMe_3)_2$).

The arrangement of the cages in the crystal is presented in Figure 1. The shortest intermolecular distance is 6.49 Å; it is much longer than in crystals of $(Me_3Si)_2BiBi(SiMe_3)_2$ with intermolecular BiBi distances of 3.804(3) Å.[3] The centrosymmetric molecules of $(SiMe_3)_4$-Bi_2 form nearly linear zigzag chains with shortened intermolecular contact distances. For $Bi_2(SiMe_2)_5$, no such shortening is observed.

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Supporting Information Available: Tables of X-ray data, atom positional and thermal parameters, and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

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