

Journal of Organometallic Chemistry, 423 (1992) 163–171
 Elsevier Sequoia S.A., Lausanne
 JOM 22214

Synthesis of bis(pentachlorophenyl)silanediol and related compounds. Crystal structure of diethoxybis(pentachlorophenyl)silane

José Carilla, Lluís Fajará, Luis Juliá *, Juan Riera

Departament de Materials Orgànics Halogenats, Centre d'Investigació i Desenvolupament (C.S.I.C.), Jordi Girona 18-26, 08034 Barcelona (Spain)

Joaquín Lloveras, Nuria Verdager and Ignacio Fita

Departament d'Enginyeria Química, ETSEIB, Universitat Politècnica de Catalunya (UPC), Diagonal 647, 08028 Barcelona (Spain)

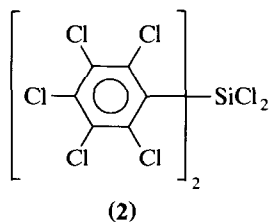
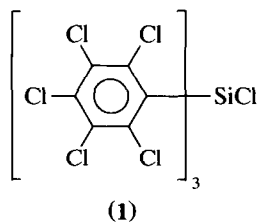
(Received June 24, 1991)

Abstract

Bis(pentachlorophenyl) silanediol (**3**) has been prepared by neutral hydrolysis of perchlorodiphenylsilane (**2**). Reduction of **2** with LiAlH_4 gives bis(pentachlorophenyl)silane (**4**) which upon treatment with bromine gives dibromobis(pentachlorophenyl)silane (**5**). Reaction of **2** with methanol and ethanol leads to dimethoxybis(pentachlorophenyl)silane (**6**) and diethoxybis(pentachlorophenyl)silane (**7**), respectively. The IR spectra of **2–7**, as well as the UV and ^1H NMR spectra of some of these compounds, are reported. The results of thermogravimetric and differential scanning calorimetric studies on silanediol **3** are discussed. The structure of the silane **7** has been established by X-ray crystallography.

Introduction

As part of our programme aimed at making organosilicon compounds with pentachlorophenyl groups as substituents [1,2], we previously described the first route to the highly sterically hindered perchlorotriphenylsilane (**1**) [1]. This was synthesized by photochemical chlorination of tris(pentachlorophenyl)silane, which in turn was obtained by reaction between trichlorosilane (SiHCl_3) and pentachlorophenylmagnesium chloride ($\text{C}_6\text{Cl}_5\text{Mg Cl}$).

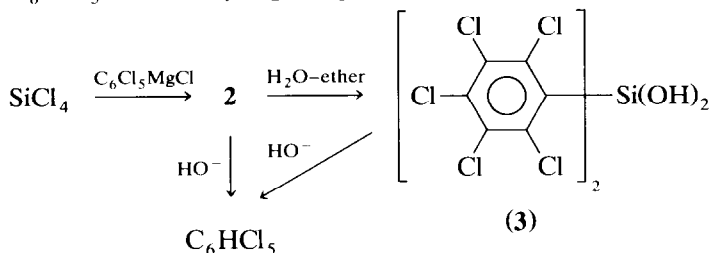


Two routes to perchlorodiphenylsilane (**2**) have been described previously. The better one, reported by Gilman *et al.* [3], involves the condensation between C_6Cl_5MgCl and tetrachlorosilane ($SiCl_4$) in 2:1 molar ratio. More recently, the action of the general and powerful aromatic perchlorinating reagent BMC [4] (a mixture of S_2Cl_2 and $AlCl_3$ in SO_2Cl_2) on triphenylsilane has given mixtures of hexachlorobenzene, **2** and traces of **1** [5].

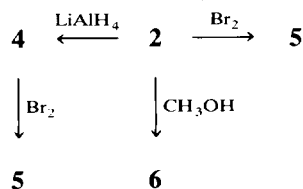
We describe below a modification of Gilman's method which gives a better yield of **2**, and the neutral hydrolysis of the latter gives the elusive bis(pentachlorophenyl)silanediol (**3**). This new silanediol **3** has been subjected to thermogravimetry (TG) and differential scanning calorimetry (DSC). Some related compounds, obtained by replacement of α -chlorines of **2** by other functional groups, are also reported. The crystal structure of diethoxybis(pentachlorophenyl)silane (**7**) has also been determined.

Results and discussion

As reported by [3] reaction between C_6Cl_5MgCl and $SiCl_4$ (2:1) in THF gave **2**, for which the elemental analysis and spectral details are reported here for the first time. The main effect of the C_6Cl_5 groups in **2** is to act as electronegative substituents with considerable steric requirements. Thus there is marked ease of cleavage of the aryl-silicon bond of **2** to give pentachlorobenzene (C_6HCl_5), and it was reported previously that **2** is readily hydrolysed under acidic, basic and neutral conditions, to give C_6HCl_5 [3]. We have been able to hydrolyse the silicon-chlorine bonds preferentially by treating **2** with moist ether for a short time to give bis(pentachlorophenyl)silanediol (**3**), synthesis of which has been attempted in the past without success [3]. Silanediol **3** is quantitatively reconverted into **2** on treatment with thionyl chloride. Hydrolysis of **2** in water-acetone mixtures give C_6HCl_5 as the only organic product.



Perchlorosilane **2** is reduced to bis(pentachlorophenyl)silane (**4**) by $LiAlH_4$ in THF at low temperatures ($0^\circ C$). At room temperature, nucleophilic substitution at silicon with C_6Cl_5-Si cleavage takes place, to give C_6HCl_5 . The dimethoxy- and diethoxy-silane derivatives **6** and **7** were obtained by boiling a solution of **2** in methanol and ethanol, respectively; **6** was also isolated from solutions of silanediol **3** in methanol. Bromination of **4** with bromine in boiling tetrachloroethylene gave dibromobis(pentachlorophenyl)silane (**5**) which was hydrolysed to **3** when treated with moist ether, as described for **2**.



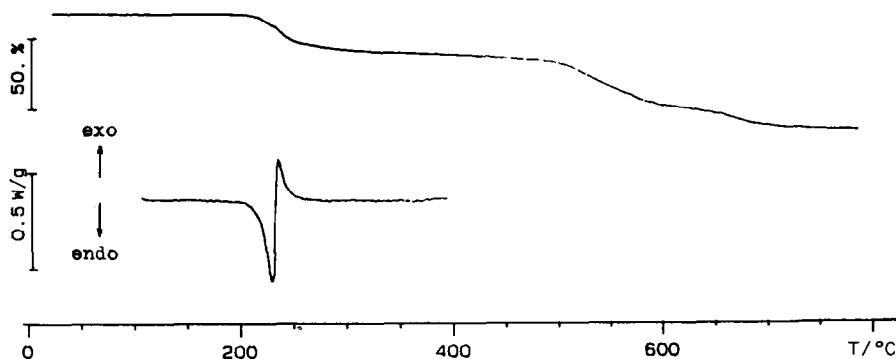


Fig. 1. TG and DSC curves for bis(pentachlorophenyl)silanediol (**3**) recorded at heating rates of 20.0 °C/min and 10.0 °C/min, respectively.

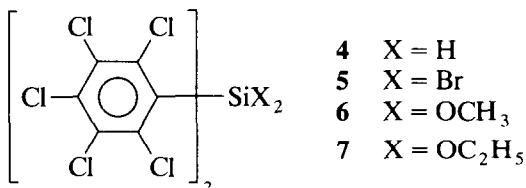
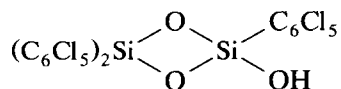


Figure 1 shows the TG and DSC traces for a sample of silanediol **3**. The TG trace shows an initial weight loss of ~22% between 215 and 260 °C, during which, pentachlorobenzene (IR spectrum) is collected as a sublimated compound. A second weight loss revealed by the TG trace starting at 500 °C, until 750 °C there is left a residue, the weight of which corresponded to complete degradation to SiO₂.

The DSC curve shows two peaks, one endothermic (230 °C, fusion of the sample) and the other exothermic (238 °C). Taking into account the information from the TG trace, these peaks suggest that silanediol **3** undergoes a chemical transformation on melting to give a new compound that is stable at temperatures as high as 500 °C. In order to identify this new compound some isothermal experiments were carried out at 250 °C. The elemental analysis and infrared and mass spectra of the residue are in good agreement with the following cyclodisiloxane:



The data support the view that at the melting temperature a substitution at silicon by an OH of a second molecule of silanediol takes place with a C₆Cl₅-Si cleavage, and this is followed or preceded by dehydration to give 2,2,4-tris(pentachlorophenyl)-4-hydroxycyclodisiloxane. Work is now in progress to determine fully the structure of this cyclic oxide and to examine the possibilities of getting linear polysiloxanes.

Attempts to determine the molecular structure of silanediol **3** have so far been frustrated by the failure to grow suitable crystals. However, we were able to determine the structure of the diethoxy derivative **7** by X-ray diffraction, shown in

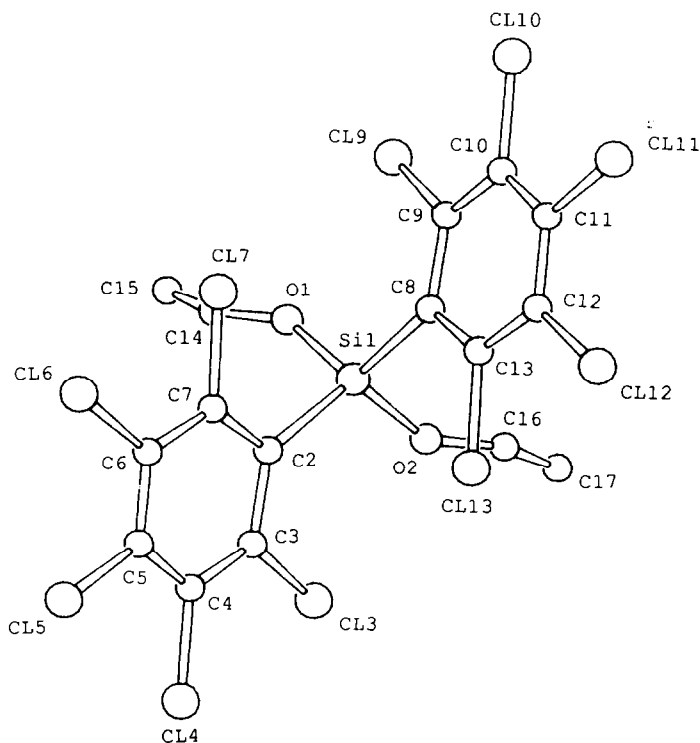


Fig. 2. The molecular structure of diethoxybis(pentachlorophenyl)silane (7) with the atom numbering.

Fig. 2. The fractional atomic coordinates are listed in Table 1 and the bond distances and angles in Table 2.

Two noteworthy features are observed in the molecular structure of 7. First, the Si–O–C angles ($151.7(2.4)^\circ$) are larger than in other silyl ethers ($120\text{--}131^\circ$) [6]

Table 1

Fractional atomic coordinates with estimated standard deviations in parentheses and equivalent isotropic thermal parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Si(1)	0.0000(0)	0.2500(0)	−0.1539(5)	9.5
C(2)	−0.0554(10)	0.3181(8)	−0.0834(11)	7.6
C(3)	−0.1351(11)	0.3343(10)	−0.0880(11)	7.6
C(4)	−0.1705(9)	0.3831(10)	−0.0295(15)	8.2
C(5)	−0.1305(11)	0.4202(8)	0.0333(12)	7.6
C(6)	−0.0519(10)	0.4091(8)	0.0403(10)	7.0
C(7)	−0.0186(7)	0.3577(9)	−0.0172(12)	6.3
Cl(3)	−0.1868(2)	0.2912(2)	−0.1661(3)	12.2
Cl(4)	−0.2671(2)	0.3962(2)	−0.0360(3)	12.1
Cl(5)	−0.1758(2)	0.4795(2)	0.1054(3)	11.0
Cl(6)	−0.0008(2)	0.4578(2)	0.1179(2)	9.2
Cl(7)	0.0798(2)	0.3475(2)	−0.0052(2)	9.1
C(1)	−0.0531(7)	0.1978(10)	−0.2133(10)	15.7
Cl(4)	−0.0630(24)	0.1453(15)	−0.2570(23)	25.4
Cl(5)	−0.0783(16)	0.0986(13)	−0.3078(21)	18.4

Table 2

Bond distances (Å) and angles (deg) with standard deviations in parentheses

Si(1)–C(2)	1.881(16)	O(1)–C(14)–C(15)	171.2(4.2)
C(2)–C(3)	1.429(18)	C(2)–Si(1)–O(2)	105.3(0.8)
C(3)–Cl(3)	1.680(14)	C(2)–Si(1)–C(8)	110.1(0.7)
C(3)–C(4)	1.385(18)	O(2)–Si(1)–C(8)	113.0(0.7)
C(4)–Cl(4)	1.714(16)	Si(1)–C(8)–C(9)	127.2(1.6)
C(4)–C(5)	1.355(18)	C(8)–C(9)–C(10)	122.1(1.5)
C(5)–Cl(5)	1.711(15)	C(9)–C(10)–C(11)	121.4(1.5)
C(5)–C(6)	1.398(17)	C(10)–C(11)–C(12)	119.9(1.5)
C(6)–Cl(6)	1.715(14)	C(11)–C(12)–C(13)	117.3(1.4)
C(6)–C(7)	1.389(15)	C(12)–C(13)–C(8)	126.2(1.3)
C(7)–Cl(7)	1.746(13)	C(13)–C(8)–C(9)	113.1(1.4)
C(7)–C(2)	1.387(15)	C(13)–C(8)–Si(1)	119.7(1.4)
Si(1)–O(1)	1.591(12)	C(8)–C(9)–Cl(9)	118.3(1.9)
O(1)–C(14)	1.152(20)	Cl(9)–C(9)–C(10)	119.6(1.7)
C(14)–C(15)	1.160(27)	C(9)–C(10)–Cl(10)	119.3(1.8)
Si(1)–C(8)	1.881(16)	Cl(10)–C(10)–C(11)	119.3(1.9)
C(8)–C(9)	1.429(18)	C(10)–C(11)–Cl(11)	120.4(1.7)
C(9)–Cl(9)	1.680(14)	Cl(11)–C(11)–C(12)	119.6(1.8)
C(9)–C(10)	1.385(18)	C(11)–C(12)–Cl(12)	120.0(1.7)
C(10)–Cl(10)	1.714(16)	Cl(12)–C(12)–C(13)	122.7(1.5)
C(10)–C(11)	1.355(18)	C(12)–C(13)–Cl(13)	114.6(1.5)
C(11)–Cl(11)	1.711(15)	Cl(13)–C(13)–C(8)	119.1(1.4)
C(11)–C(12)	1.398(17)	C(8)–Si(1)–O(1)	105.3(0.8)
C(12)–Cl(12)	1.715(14)	Si(1)–O(2)–C(16)	151.7(2.4)
C(12)–C(13)	1.389(15)	O(2)–C(16)–C(17)	171.2(4.2)
C(13)–Cl(13)	1.746(13)	O(1)–Si(1)–O(2)	110.5(0.9)
C(13)–C(8)	1.387(15)		
Si(1)–O(2)	1.591(12)		
O(2)–C(16)	1.152(20)		
C(16)–C(17)	1.160(27)		
O(1)–Si(1)–C(2)	112.9(0.7)		
Si(1)–C(2)–C(3)	127.2(1.6)		
C(2)–C(3)–C(4)	122.1(1.5)		
C(3)–C(4)–C(5)	121.4(1.5)		
C(4)–C(5)–C(6)	119.9(1.5)		
C(5)–C(6)–C(7)	117.3(1.4)		
C(6)–C(7)–C(2)	126.2(1.3)		
C(7)–C(2)–C(3)	113.1(1.4)		
C(7)–C(2)–Si(1)	119.7(1.4)		
C(2)–C(3)–Cl(3)	118.3(1.9)		
Cl(3)–C(3)–C(4)	119.6(1.7)		
C(3)–C(4)–Cl(4)	119.3(1.8)		
Cl(4)–C(4)–C(5)	119.3(1.9)		
C(4)–C(5)–Cl(5)	120.4(1.7)		
Cl(5)–C(5)–C(6)	119.6(1.8)		
C(5)–C(6)–Cl(6)	120.0(1.7)		
Cl(6)–C(6)–C(7)	122.7(1.5)		
C(6)–C(7)–Cl(7)	114.6(1.5)		
Cl(7)–C(7)–C(2)	119.1(1.4)		
Si(1)–O(1)–C(14)	151.7(2.4)		

and the Si–O bond distances (1.591(12) Å) are much shorter than the sum of the covalent radii (0.74 Å for oxygen and 1.17 Å for silicon) [7]. These differences can, at least in part, be interpreted in terms of a dative π bond involving the lone electron pairs on oxygen and the 3*d* orbitals of silicon. It is noteworthy that the presence of the two electron-withdrawing C₆Cl₅ groups on silicon (C₆Cl₅ acts as a good nucleofuge in many substitution reactions at silicon) may facilitate this (*p* → *d*) π interaction [8]. The mean Cl–C and C–C bond distances in the pentachlorophenyl groups are in good agreement with those previously reported for **1** [1] and perchloro(2,2'-biphenylene)diphenylsilane [2]. The C(14), C(15), C(16) and C(17) atoms have a high temperature factor, reflecting a strong vibration of these chains and this leads to uncertainty in their bond distances and angles. The angle between the least square planes of the two phenyl rings is 79.15°.

Experimental

Melting points were determined with a Köfler microscope. Infrared and UV spectra were recorded on Perkin–Elmer 682 and Beckmann Acta M–VI spectrometers, respectively. A Bruker WP805Y instrument was used for ¹H NMR spectroscopy. TG analyses were carried out with a Mettler TG-50-M3 thermobalance under nitrogen at a heating rate of 20°C/min, and DSC analyses with a Mettler DSC 25 instrument at a heating rate of 10°C/min. Mass spectral data were obtained with a double focusing AEI M5-9025 instrument (70 eV, 100 μ A emission). THF was freshly distilled from sodium, and other solvents were used as received.

Perchlorodiphenylsilane (2)

A THF solution of pentachlorophenylmagnesium chloride (made from hexachlorobenzene (29.0 g; 0.1 mol) and Mg (3.6 g; 0.15 atg) in 100 ml) was filtered through glass wool and added dropwise to a stirred solution of SiCl₄ (8.5 g; 0.05 mol) in THF (40 ml) under argon. The mixture was stirred for 18 h at room temperature, and the solvent then distilled off. Benzene (120 ml) was added to the residue and the mixture boiled for 1 h and the insoluble material then filtered off. The solution yielded crystals of bis(pentachlorophenyl)dichlorosilane (8.25 g; 28%), m.p. 242–246°C (sublimed at 280°C, 760 mmHg). IR (KBr): 1515m, 1345m, 1325s, 1300s, 1200w, 1168m, 1098s, 872s, 862s, 715w, 682m, 658w, 618m, 608w, 590w, 565m, 530s, 415m cm⁻¹. Mass spectrum: *m/z* 598 (8%, *M*⁺), 561 (3%, (C₆Cl₅)₂SiCl⁺), 526 (1%, (C₆Cl₅)₂Si⁺), 347 (12%, C₆Cl₅SiCl₂⁺), 312 (3%, C₆Cl₅SiCl⁺). Anal. Found: C, 24.3; Cl, 71.3. C₁₂Cl₁₂Si calc.: C, 24.1; Cl, 71.2%.

Bis(pentachlorophenyl)silane diol (3)

A solution of perchlorodiphenylsilane (0.50 g) in moist ether (70 ml) was stirred at room temperature for 20 min and then evaporated under vacuum to leave bis(pentachlorophenyl)silane diol (0.448 g; 96%), m.p. 208°C (dec). IR (KBr) 3665m, 3440m, br, 1520m, 1342m, 1325s, 1298s, 1200w, 1165m, 1095s, 970w, 940w, 870s, 820m, br, 715w, 680s, 660w, 635w, 608w, 590w, 445m, cm⁻¹. UV-vis (CHCl₃) 286(sh) nm, 296, 306 (ϵ 1150, 1895, 2200). Mass spectrum: *m/z* 560 (13%, *M*⁺), 311 (37%, C₆Cl₅ Si(OH)₂⁺). Anal. Found: C, 26.0; H, 0.4; Cl, 63.4. C₁₂H₂Cl₁₀O₂Si calc.: C, 25.7; H, 0.4; Cl, 63.2%.

Hydrolysis of 3

A mixture of bis(pentachlorophenyl)silanediol (0.457 g) and aqueous NaOH (10%) (2.5 ml) in THF (15 ml) was stirred at room temperature for 1 h, then added to an excess of water. The mixture was extracted with ether and the extract was washed with water, dried over Na₂SO₄ and evaporated under vacuum, to leave a residue. This was passed through silica gel with hexane as eluant to give pentachlorobenzene (0.385 g; 94%).

Reaction of 3 with SOCl₂

A solution of bis(pentachlorophenyl)silanediol (0.124 g) in distilled thionyl chloride (20 ml) was heated under reflux for 48 h in a dry atmosphere and then evaporated to dryness to give a quantitative yield of perchlorodiphenylsilane (0.131 g) (IR spectrum identical with that of an authentic sample).

Bis(pentachlorophenyl)silane (4)

Powdered LiAlH₄ (0.073 g; 1.92 mmol) was added to a stirred mixture of bis(pentachlorophenyl)dichlorosilane (3.360 g; 5.62 mmol) in THF (90 ml) at 0 °C under argon. The mixture was left under the same conditions for 30 min then more LiAlH₄ (0.091 g; 2.39 mmol) was added and the mixture stirred for a further 1 h at 0 °C and then at room temperature, overnight. It was then treated with CHCl₃-water, and the organic layer was washed with water, dried over Na₂SO₄, and evaporated under vacuum, to give a residue, which was treated with boiling CCl₄ to remove soluble fractions. The residue consisted of bis(pentachlorophenyl)silane (1.903 g), m.p. 261.5–262.5 °C (from hexane). IR (KBr) 2230m, 1518m, 1338m, 1325s, 1300s, 1200w, 1170w, 1162m, 1092s, 940s, 875s, 860m, 835s, 705w, 680s, 670m, 640m, 575w, 520m cm⁻¹, UV-vis (CHCl₃) 285 nm, 296, 306 (ε 830, 1660, 2010). ¹H NMR (CDCl₃): δ 5.53 (s, 2H). Anal. Found: C, 27.3; H, 0.4; Cl, 67.6. C₁₂H₂Cl₁₀Si calc.: C, 27.3; H, 0.4; Cl, 67.1%. The CCl₄ solution gave by recrystallization more **4** (0.325 g). The overall yield was 75%.

Dimethoxybis(pentachlorophenyl)silane (6)

(a) *From 2.* A mixture of dichlorobis(pentachlorophenyl)silane (0.100 g) and boiling methanol (15 ml) was stirred for 1 h and then evaporated under vacuum to leave dimethoxybis(pentachlorophenyl)silane (0.087 g; 89%), m.p. 197–205 °C (from methanol). IR (KBr) 2970w, 2940w, 2840w, 1515m, 1460w br, 1395w, 1342m, 1325m, 1295s, 1190m, 1165m, 1130m, 1095s, 862s, 805w, 738m, 710w, 678m, 660w, 625w, 590w, 470s cm⁻¹. UV-vis (CHCl₃) 286(sh) nm, 296, 306 (ε 935, 1850, 2220). ¹H NMR (CDCl₃): δ 3.67 (s, 6H). Anal. Found: C, 28.6; H, 0.9; Cl, 59.8. C₁₄H₆Cl₁₀O₂Si calc.: C, 28.6; H, 1.0; Cl, 60.2%.

(b) *From 3.* A solution of bis(pentachlorophenyl)silanediol (0.202 g) in methanol (25 ml) was kept at room temperature overnight, and crystallization gave **6** (0.171 g; 81%) m.p. 190–197 °C.

Diethoxybis(pentachlorophenyl)silane (7)

A mixture of dichlorobis(pentachlorophenyl)silane (0.252 g) and boiling ethanol (30 ml) was stirred for 2 h. Crystallization gave diethoxybis(pentachlorophenyl)silane (0.100 g; 39%), m.p. 180 °C (dec). IR (KBr) 2980m, 2925w, 2895w, 1518m, 1478w, 1438w, 1390w, 1345m, 1325s, 1298s, 1200w, 1160s, 1105s, 1090s, 970m,

Table 3

Space group	$I4_1/a$
Z	8
$a = b$ (Å)	17.56
c (Å)	15.27
V (Å ³)	4708.56
Molecular formula	$C_{16}H_{10}Cl_{10}O_2Si$
Formula weight (g/mol)	616.87
μ (cm ⁻¹)	11.4
Asymmetric unit content	1/2 molecule
Calculated density (g/cm ³)	1.74

955m, 868s, 775w, 728m, 675s, 655w, 625w, 605w, 592w, 465m, 450m cm⁻¹. UV-vis (CHCl₃) 286(sh) nm, 296, 306 (ϵ 940, 1820, 2180). ¹H NMR (CDCl₃): δ 1.26 (t, 6H, $J = 7.16$ Hz, -CH₂-), 3.92 (q, 4H, $J = 7.16$ Hz, -CH₃). Anal. Found: C, 31.2.; H, 1.4; Cl, 57.5. $C_{16}H_{10}Cl_{10}O_2Si$ calc.: C, 31.2; H, 1.6; Cl, 57.5%.

X-Ray crystallography of 7

Space group and cell parameters were determined (Table 3) from both precession photographs and 25 reflections ($5 < \theta < 20^\circ$) measured on an Enraf-Nonius CAD-4 diffractometer with Cu- K_α radiation ($\lambda = 1.5418$ Å) and graphite monochromator. The intensities of 843 independent reflections were then measured at 4 °C from a crystal $0.6 \times 0.4 \times 0.4$ mm³ in size, in the ω -scan mode. Three reflections measured every hour during the data collection showed no significant change. Lorentz, polarization, decay and absorption corrections were applied in derivation of the structure factor amplitudes.

The structure was solved by direct methods using the SHELXS 86 computer program package [9]. Cycles of least squares refinement and difference Fourier syntheses, with the SHELX 76 computer program [10] revealed all the non-hydrogen atoms; hydrogen atoms were then added in calculated positions. Full-matrix refinement, anisotropic for non-hydrogen atoms and isotropic for hydrogen, converged to a standard agreement factor $R = 5.12\%$ ($R_w = 5.31\%$) for 571 reflections with $I > 4\sigma(I)$. The weighting scheme used in the last cycle was $(\sigma^2(F) + 0.000757|F|^2)^{-1}$. The maximum and minimum heights in the final difference Fourier map were 0.56 and -0.48 e Å⁻³, respectively. MicroVax 2000 and 3100 computers were used for the calculations.

Tables of hydrogen atom coordinates, thermal parameters and structure factors are available from the authors.

Dibromobis(pentachlorophenyl)silane (5)

A solution of bromine (0.608 g; 3.80 mmol) and bis(pentachlorophenyl)silane (0.968 g; 1.83 mmol) in tetrachloroethylene (30 ml) was refluxed with exclusion of moisture for 7 h and then evaporated to dryness under vacuum to give dibromobis(pentachlorophenyl)silane (1.244 g; 99%), m.p. 232–234.5 °C (sublimated at 220 °C, 0.2 mmHg). IR (KBr) 1515m, 1342m, 1325s, 1298s, 1215w, 1200w, 1165m, 1095s, 870s, 860m, 715w, 682s, 662w, 648w, 608m, 585w, 465s, 455s, 405m cm⁻¹. Mass spectrum: m/z 686 (16.3%, M^+), 607 (100%, $(C_6Cl_5)_2SiBr^+$).

Anal. Found: C, 20.9; H, 0.1; Br, 23.4; Cl, 51.2. $C_{12}Br_2Cl_{10}Si$ calc.: C, 21.0; H, 0.0; Br, 23.0; Cl, 51.6%.

Thermal analysis of 3

Several thermogravimetric experiments on silanediol **3** were carried out with a Perkin Elmer TGS-1 instrument (sample weights, 3.1–4.6 mg; starting temperature 150 °C at 20 °C/min up to 250 °C and then at this temperature for 25 min). An average weight loss of 29.0% was observed. The sublimated product was identified as pentachlorobenzene (IR). The residue was tentatively characterized as 2,2,4-tris-(pentachlorophenyl)-4-hydroxycyclodisiloxane; IR (KBr) 3660w, br, 1520m, 1400w, 1350m, 1332m, 1305s, 1215w, 1205w, 1170m, 1105s, 1030s, br, 940w, 878s, 820w, 800w, br, 720w, 685s, 610w, 555w, 470s, 455m cm^{-1} . UV-vis ($CHCl_3$) 288(sh) nm, 298, 308 (ϵ 1800, 3130, 3520). Mass spectrum: m/z 852 (3%, M^+), 250 (100%, $C_6Cl_5^+$). Anal. Found: C, 25.9; H, 0.2; Cl, 62.6. $C_{18}HCl_{15}O_3Si_2$ calc.: C, 25.3; H, 0.1; Cl, 62.3.

Acknowledgements

This work was supported by DGICYT of MEC (Spain) through project PB87-0388. One of us (L.F.) is grateful to Vallés Industrias Orgánicas, S.A. for a studentship.

References

- 1 L. Fajará, L. Juliá, J. Riera, C. Miravittles and E. Molins, *J. Chem. Soc., Chem. Commun.*, (1987) 143.
- 2 L. Fajará, L. Juliá, J. Riera, E. Molins and C. Miravittles, *J. Organomet. Chem.*, 381 (1990) 321.
- 3 F.W.G. Fearon and H. Gilman, *J. Organomet. Chem.*, 6 (1966) 577.
- 4 M. Ballester, C. Molinet and J. Castañer, *J. Am. Chem. Soc.*, 82 (1960) 4254; L.F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Wiley, New York, 1967, p. 1131.
- 5 C. Glidewell and J.C. Walton, *J. Chem. Soc., Chem. Commun.*, (1977) 915.
- 6 C. Glidewell, D.W.M. Rankin, A.G. Robiette, G.M. Sheldrick, B. Beagley and J.M. Freeman, *J. Mol. Struct.*, 5 (1970) 417; L.H. Boonstra, F.C. Mijlhoff, G. Renes, A. Spelbos and I. Hargittai, *Ibid.*, 28 (1975) 129; K. Gergo, I. Hargittai and G.Y. Schultz, *J. Organomet. Chem.*, 112 (1976) 29.
- 7 V. Chomaker and D.P. Stevenson, *J. Am. Chem. Soc.*, 63 (1941) 37; N.N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1984, p. 382.
- 8 K.A.R. Mitchell, *Chem. Rev.*, 69 (1969) 157; T.B. Brill, *J. Chem. Educ.*, 50 (1973) 392.
- 9 G.M. Sheldrick, *SHELXS 86 Program for Crystal Structure Determination*, University of Oxford, 1986.
- 10 G.M. Sheldrick, *SHELX 76 Program for Crystal Structure Determination*, University of Cambridge, 1976.