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An unusual cyclization reaction in the chemistry of perchloroorganic compounds of silicon and germanium. Synthesis and crystal structure of perchloro(2,2′-biphenylene)diphenyl-silane and -germane

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Abstract

The reactions of $SiCl_4$ and $GeCl_4$ (or $(Ph_{Cl})_3SiCl$ and $(Ph_{Cl})_3GeCl$ where Ph_{Cl} denotes Cl_5C_6) with $Ph_{Cl}MgCl$ give perchloro(2,2′-biphenylene)diphenyl-silane (**2**) and -germane (**3**), respectively. The structure of both strained compounds have been determined by X-ray crystallography of their benzene solvates. The photobromination of germane **3** with Br_2 results in cleavage of one germanium–biphenylene bond to give the highly crowded bromo(2-(2′-bromooctachlorobiphenyl))bis(pentachlorophenyl)germane (**4**).

Introduction

As part of our programme aimed at making highly sterically hindered organosilicon [1] and germanium [2] compounds of high thermal stability we described the first route to perchlorotriphenylgermane [2], involving the condensation between $GeCl_4$ and pentachlorophenyllithium. In the course of the work, we saw no indication of the substitution of the fourth chlorine atom attached to germanium, and this can reasonably be attributed to steric hindrance.

Many years ago, Gilman et al. [3] reported the synthesis of tetrakis(pentachlorophenyl)silane (**1**) in very small yield by treating pentachlorophenylmagnesium chloride with silicon tetrachloride. Feeling rather doubtful about this report, we decided to reexamine the reaction, and we have now shown that the product, characterized by an X-ray study, is in fact perchloro(2,2′-biphenylene)diphenylsilane (**2**) and not **1**.

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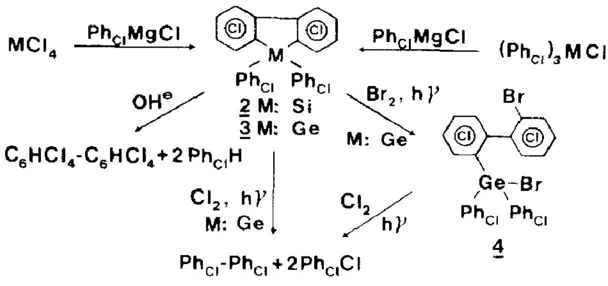
In order to gain more information about the scope of this unusual cyclodechlorination we also examined involving germanium tetrachloride and have found that it gives the corresponding perchloro(2,2′-biphenylene)diphenylgermane (**3**), which has also been characterized by an X-ray diffraction study.

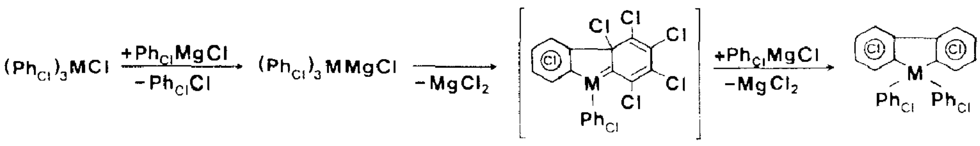
Results and discussion

In contrast to the reactions of $SiCl_4$ and $GeCl_4$ with pentafluorophenylmagnesium bromide, which give tetrakis(pentafluorophenyl)-silane [4] and -germane [5], respectively, the reactions with pentachlorophenylmagnesium chloride, in the absence of magnesium give perchloro(2,2′-biphenylene)diphenyl-silane (**2**) and -germane (**3**), respectively (see Scheme 1). Both compounds, **2** and **3**, have been shown to give 2,3,4,5,2′,3′,4′,5′-octachlorobiphenyl and pentachlorobenzene upon hydrolysis by aqueous NaOH in THF. While photochlorination of germane **3** with Cl_2 causes complete decomposition to perchlorobiphenyl and perchlorobenzene, photobromination of the same germane with Br_2 affords bromo(2-(2′-bromooctachlorobiphenyl))bis(pentachlorophenyl)germane (**4**) by cleavage of one of the germanium–biphenylene bonds. Compound **4** has been characterized by spectroscopic and elemental analysis, and shown to give perchlorobiphenyl and perchlorobenzene (molar ratio 1/2) upon photochlorination with Cl_2 in CCl_4. In connection with the aromatic substitution of bromine by chlorine in this photochlorination reaction, it is noteworthy that perbromobenzene gives perchlorobenzene under similar conditions [6].

Since **2** and **3** are also formed, in even better yields, from $(Ph_{Cl})_3MCl$ (M = Si, Ge) in similar Grignard reactions, it seems that the ring closure process takes place at the very last stage of the reaction, after the substitution of the first three chlorine atoms of MCl_4, the probable reaction mechanism is that shown in Scheme 2. The first step involves ligand exchange at magnesium with formation of equimolecular amounts of hexachlorobenzene. There is some evidence for this type of exchange in



Scheme 1



Scheme 2

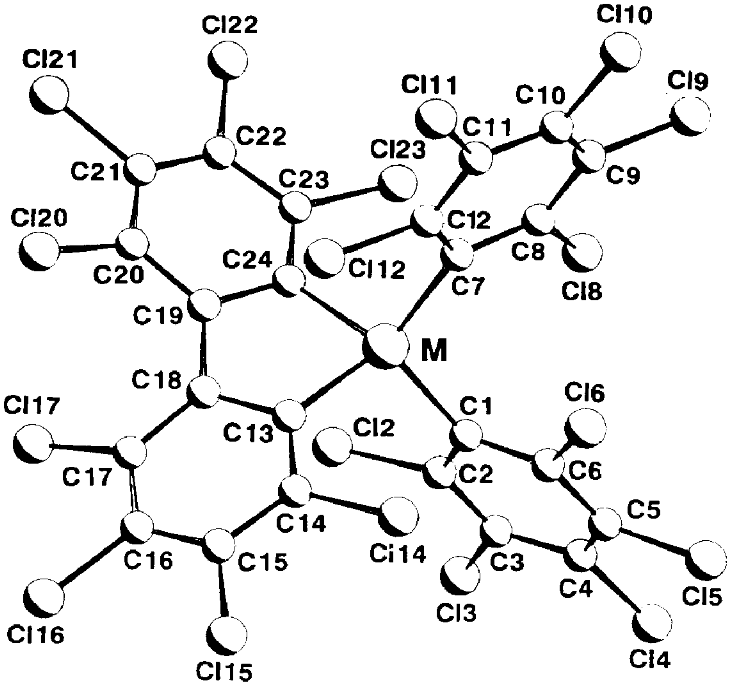


Fig. 1. The molecular structures of perchloro(2,2′-biphenylene)diphenyl-silane (**2**) and -germane (**3**) with the atom numbering.

cases in which the halides R_3MX are sterically hindered towards the introduction of a fourth R group [7],

Good transparent crystals of composition $\mathbf{2} \cdot 2C_6H_6$ and $\mathbf{3} \cdot 2C_6H_6$ were obtained by recrystallization from hexane/benzene mixtures.

A perspective view of the structure of both molecules, which are very similar, is shown in Fig. 1, and the bond distances and angles are listed in Tables 1 and 2. The mean values of Cl–C, C–C and M–C bond distances do not differ from those revealed by the X-ray studies of perchlorotriphenylsilane [1] and perchlorotriphenylgermane [2], and are close to the average literature values.

In the five-membered rings of both molecules, the very acute C(13)SiC(24) (90.6°) and C(13)GeC(24) (87.9°) angles, arising from the "bite" of the chelating biphenyl mean that the coordination about silicon and germanium is considerably distorted from the usual tetrahedral arrangement. The constraints imposed by the other angles in these rings contributes to make the angles SiC(13)C(14) (132.1°), SiC(24)C(23) (132.4°), GeC(13)C(14) (129.9°) and GeC(24)C(23) (129.8°) much larger than the normal sp^2 value.

The chlorine atoms Cl(17) and Cl(20) in the octachlorobiphenylene group are found to be well separated (3.382 and 3.404 Å, for M = Si, Ge, respectively) owing to a torsion of 34° about the C(18)–C(19) bond and in-plane bending about this bond. The torsion in the C(18)–C(19) bond introduces a considerable twist between the two benzene rings 3 and 4, in both the silicon and germanium derivative (Table 3; Fig. 2), and the in-plane bending results in angles C(17)C(18)C(19) (Si, 126.2° and Ge, 126.0°) and C(18)C(19)C(20) (Si, 127.4° and Ge, 126.5°) which are considerably larger than the sp^2 value of 120°.

Table 1

Bond distances (Å) and bond angles (°) with their e.s.d.'s for perchloro(2,2′-biphenylen)diphenylsilane (**2**)

C1...Si1	1.910(7)	C7-Si1-C1	112.6(0.4)	C15-C14-C13	122.9(1.0)
C7...Si1	1.903(10)	C13-Si1-C1	106.5(0.3)	C14-C15-Cl15	120.6(0.9)
C13...Si1	1.866(8)	C13-Si1-C7	120.2(0.4)	C16-C15-Cl15	120.3(0.7)
C24...Si1	1.881(11)	C24-Si1-C1	120.8(0.4)	C16-C15-C14	119.1(0.9)
C2...Cl2	1.730(12)	C24-Si1-C7	105.1(0.4)	C15-C16-Cl16	120.1(0.7)
C3...Cl3	1.717(11)	C24-Si1-C13	90.6(0.4)	C17-C16-Cl16	120.2(0.9)
C4...Cl4	1.719(8)	C2-C1-Si1	121.6(0.8)	C17-C16-C15	119.7(0.9)
C5...Cl5	1.721(12)	C6-C1-Si1	123.2(0.6)	C16-C17-Cl17	116.4(0.7)
C6...Cl6	1.730(10)	C6-C1-C2	115.2(0.7)	C18-C17-Cl17	123.4(0.8)
C8...Cl8	1.727(8)	C1-C2-Cl2	119.0(0.6)	C18-C17-C16	119.8(1.0)
C9...Cl9	1.732(9)	C3-C2-Cl2	117.8(0.8)	C17-C18-C13	121.4(0.8)
C10...Cl10	1.729(12)	C3-C2-C1	123.3(1.0)	C19-C18-C13	112.3(0.7)
C11...Cl11	1.726(9)	C2-C3-Cl3	120.9(0.9)	C19-C18-C17	126.2(1.0)
C12...Cl12	1.738(9)	C4-C3-Cl3	119.4(0.6)	C20-C19-C18	127.4(0.7)
C14...Cl14	1.729(12)	C4-C3-C2	119.6(0.9)	C24-C19-C18	113.1(0.7)
C15...Cl15	1.732(10)	C3-C4-Cl4	120.4(0.8)	C24-C19-C20	119.4(0.7)
C16...Cl16	1.719(10)	C5-C4-Cl4	120.2(0.9)	C19-C20-Cl20	120.1(0.6)
C17...Cl17	1.730(12)	C5-C4-C3	119.4(0.7)	C21-C20-Cl20	118.5(0.6)
C20...Cl20	1.731(8)	C4-C5-Cl5	119.2(0.6)	C21-C20-C19	120.5(0.7)
C21...Cl21	1.723(10)	C6-C5-Cl5	120.5(0.8)	C20-C21-Cl21	119.8(0.7)
C22...Cl22	1.710(9)	C6-C5-C4	120.3(1.0)	C22-C21-Cl21	119.4(0.7)
C23...Cl23	1.717(9)	C1-C6-Cl6	121.1(0.5)	C22-C21-C20	120.7(0.9)
C2...C1	1.402(13)	C5-C6-Cl6	116.9(0.8)	C21-C22-Cl22	120.7(0.8)
C6...C1	1.414(15)	C5-C6-C1	121.9(0.9)	C23-C22-Cl22	121.3(0.7)
C3...C2	1.375(10)	C8-C7-Si1	123.4(0.6)	C23-C22-C21	117.8(0.8)
C4...C3	1.385(17)	C12-C7-Si1	122.4(0.7)	C22-C23-Cl23	118.1(0.6)
C5...C4	1.387(15)	C12-C7-C8	114.2(0.8)	C24-C23-Cl23	119.1(0.7)
C6...C5	1.381(10)	C7-C8-Cl8	120.6(0.7)	C24-C23-C22	122.8(0.8)
C8...C7	1.413(12)	C9-C8-Cl8	116.7(0.6)	C19-C24-Si1	108.0(0.6)
C12...C7	1.409(11)	C9-C8-C7	122.5(0.7)	C23-C24-Si1	132.4(0.8)
C9...C8	1.352(13)	C8-C9-Cl9	121.8(0.6)	C23-C24-C19	117.6(0.9)
C10...C9	1.396(12)	C10-C9-Cl9	117.5(0.8)		
C11...C10	1.378(13)	C10-C9-C8	120.7(0.8)		
C12...C11	1.377(15)	C9-C10-Cl10	120.8(0.8)		
C14...C13	1.400(12)	C11-C10-Cl10	119.3(0.7)		
C18...C13	1.406(15)	C11-C10-C9	119.8(1.0)		
C15...C14	1.380(13)	C10-C11-Cl11	119.9(0.8)		
C16...C15	1.373(17)	C12-C11-Cl11	121.9(0.7)		
C17...C16	1.416(13)	C12-C11-C10	118.2(0.8)		
C18...C17	1.365(12)	C7-C12-Cl12	119.1(0.8)		
C19...C18	1.492(11)	C11-C12-Cl12	116.5(0.6)		
C20...C19	1.401(12)	C11-C12-C7	124.4(0.8)		
C24...C19	1.422(11)	C14-C13-Si1	132.1(0.8)		
C21...C20	1.393(12)	C18-C13-Si1	109.6(0.6)		
C22...C21	1.386(12)	C18-C13-C14	116.3(0.8)		
C23...C22	1.415(15)	C13-C14-Cl14	118.4(0.7)		
C24...C23	1.386(12)	C15-C14-Cl14	118.7(0.7)		

Experimental

Solvents were dried and purified by standard methods. Melting points were determined with a Köfler microscope. Infrared spectra were recorded on a Perkin

Table 2

Bond distances (Å) and bond angles (°) with their e.s.d.'s for perchloro(2,2′-biphenylen)diphenylgermane (3)

C1...Ge1	1.980(4)	C7-Ge1-C1	112.2(2)	C18-C13-C14	119.3(4)
C7...Ge1	1.979(5)	C13-Ge1-C1	106.6(2)	C13-C14-Cl14	119.5(4)
C13...Ge1	1.956(4)	C13-Ge1-C7	120.7(2)	C15-C14-Cl14	119.5(4)
C19...Ge1	2.749(6)	C19-Ge1-C1	130.8(2)	C15-C14-C13	120.9(6)
C24...Ge1	1.967(6)	C19-Ge1-C7	114.9(2)	C14-C15-Cl15	120.2(5)
C2...Cl2	1.739(6)	C19-Ge1-C13	59.3(2)	C16-C15-Cl15	120.8(4)
C3...Cl3	1.725(6)	C24-Ge1-C1	122.3(2)	C16-C15-C14	118.9(5)
C4...Cl4	1.711(5)	C24-Ge1-C7	106.0(2)	C15-C16-Cl16	119.3(4)
C5...Cl5	1.717(7)	C24-Ge1-C13	87.9(2)	C17-C16-Cl16	120.1(5)
C6...Cl6	1.743(6)	C24-Ge1-C19	29.0(2)	C17-C16-C15	120.7(5)
C8...Cl8	1.731(5)	C2-C1-Ge1	119.9(4)	C16-C17-Cl17	117.7(4)
C9...Cl9	1.717(5)	C6-C1-Ge1	124.0(4)	C18-C17-Cl17	122.2(4)
C10...Cl10	1.719(6)	C6-C1-C2	116.1(4)	C18-C17-C16	119.7(6)
C11...Cl11	1.722(5)	C1-C2-Cl2	120.0(3)	C17-C18-C13	119.3(4)
C12...Cl12	1.738(5)	C3-C2-Cl2	117.9(5)	C19-C18-C13	114.4(4)
C14...Cl14	1.713(7)	C3-C2-C1	122.1(6)	C19-C18-C17	126.0(5)
C15...Cl15	1.725(6)	C2-C3-Cl3	120.3(5)	C18-C19-Ge1	74.5(3)
C16...Cl16	1.723(5)	C4-C3-Cl3	120.3(3)	C20-C19-Ge1	151.6(3)
C17...Cl17	1.721(7)	C4-C3-C2	119.4(5)	C20-C19-C18	126.5(4)
C20...Cl20	1.731(5)	C3-C4-Cl4	119.6(4)	C24-C19-Ge1	42.8(3)
C21...Cl21	1.726(6)	C5-C4-Cl4	120.9(5)	C24-C19-C18	115.0(5)
C22...Cl22	1.715(6)	C5-C4-C3	119.5(4)	C24-C19-C20	118.1(4)
C23...Cl23	1.722(5)	C4-C5-Cl5	119.6(4)	C19-C20-Cl20	120.7(4)
C2...C1	1.393(7)	C6-C5-Cl5	120.6(5)	C21-C20-Cl20	118.7(4)
C6...C1	1.368(9)	C6-C5-C4	119.8(6)	C21-C20-C19	120.1(4)
C3...C2	1.390(6)	C1-C6-Cl6	120.4(3)	C20-C21-Cl21	119.2(4)
C4...C3	1.384(9)	C5-C6-Cl6	116.7(5)	C22-C21-Cl21	120.0(4)
C5...C4	1.364(8)	C5-C6-C1	123.0(5)	C22-C21-C20	120.7(5)
C6...C5	1.385(6)	C8-C7-Ge1	122.5(3)	C21-C22-Cl22	120.5(5)
C8...C7	1.387(7)	C12-C7-Ge1	121.8(4)	C23-C22-Cl22	120.6(4)
C12...C7	1.392(6)	C12-C7-C8	115.7(5)	C23-C22-C21	118.6(5)
C9...C8	1.393(8)	C7-C8-Cl8	120.9(4)	C22-C23-Cl23	119.2(4)
C10...C9	1.385(7)	C9-C8-Cl8	116.7(4)	C24-C23-Cl23	119.8(4)
C11...C10	1.353(7)	C9-C8-C7	122.4(4)	C24-C23-C22	121.1(4)
C12...C11	1.376(8)	C8-C9-Cl9	120.5(4)	C19-C24-Ge1	108.2(4)
C14...C13	1.386(7)	C10-C9-Cl9	120.8(4)	C23-C24-Ge1	129.8(4)
C18...C13	1.393(8)	C10-C9-C8	118.7(5)	C23-C24-C19	120.0(5)
C15...C14	1.395(7)	C9-C10-Cl10	118.3(4)		
C16...C15	1.385(10)	C11-C10-Cl10	121.0(4)		
C17...C16	1.385(8)	C11-C10-C9	120.7(5)		
C18...C17	1.401(7)	C10-C11-Cl11	119.6(4)		
C19...C18	1.494(7)	C12-C11-Cl11	120.9(4)		
C20...C19	1.397(7)	C12-C11-C10	119.5(5)		
C24...C19	1.402(6)	C7-C12-Cl12	119.7(4)		
C21...C20	1.399(7)	C11-C12-Cl12	117.4(3)		
C22...C21	1.375(7)	C11-C12-C7	122.9(5)		
C23...C22	1.398(9)	C14-C13-Ge1	129.9(4)		
C24...C23	1.378(7)	C18-C13-Ge1	109.6(3)		

Elmer 682 spectrometer. The UV spectra were recorded on a Beckmann Acta M-VI spectrometer. Molecular weights were determined with a KNAUER vapour pressure osmometer for solutions in $CHCl_3$. HPLC analysis were performed with a Perkin

Table 3

Angles between the ring planes (°)[a]

Ring–ring	Angle	
	M = Si	M = Ge
1–2	56.43	56.1
3–4	33.8	33.26

[a] Ring 1: C(1)–C(6); ring 2: C(7)–C(12); ring 3: C(13)–C(18); ring 4: C(19)–C(24).

Elmer Series 3B Liquid Chromatograph using a SPHERISORB ODS-2 5 (15 × 0.4 cm) column, with elution with a 9/1 mixture of acetonitrile/water, and UV detection at 254 nm.

*Perchloro(2,2′-biphenylene)diphenylsilane (**2**)*

(a) Synthesis from $SiCl_4$. A THF solution of pentachlorophenylmagnesium chloride (made from hexachlorobenzene (28.5 g, 0.1 mol), Mg (3.6 g, 0.15 atg), and THF (140 ml), and filtered through glass wool) was added dropwise to a stirred

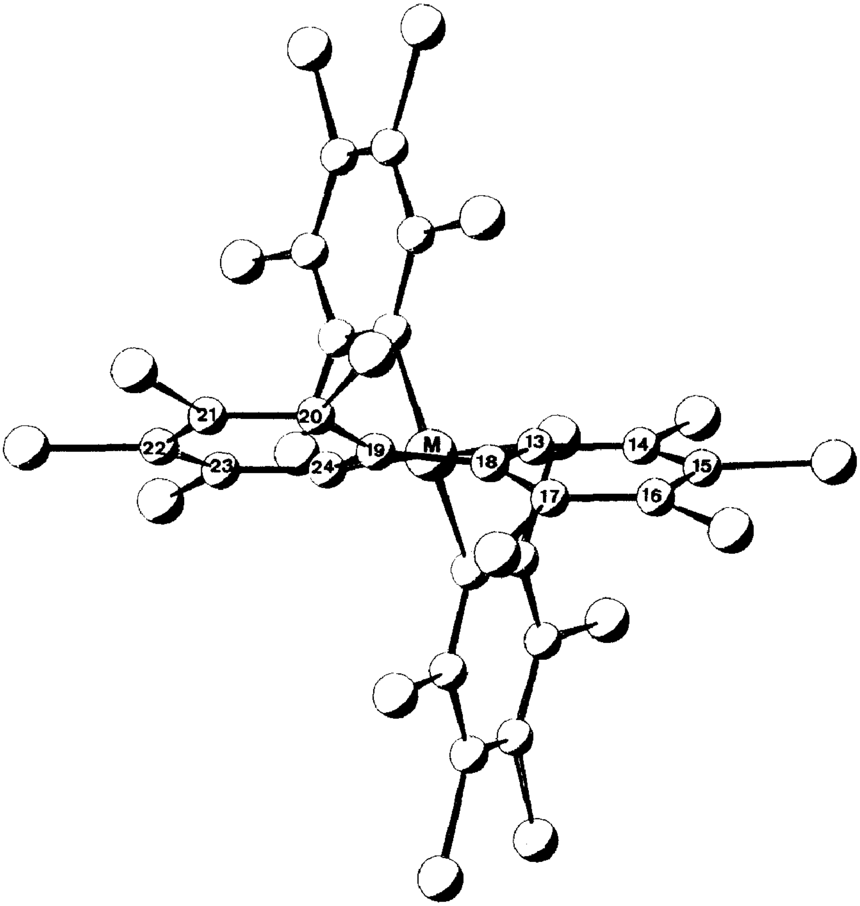


Fig. 2. The structures of **2** and **3** showing the twist angle between rings **3** and **4** of the octachlorobiphenyl group.

solution of $SiCl_4$ (4.25 g, 0.025 mol) in THF (20 ml) under argon. The mixture was stirred for 3 h at room temperature and then for 2 h under reflux. The solvent was distilled off, benzene (120 ml) was added to the residue, and the mixture was boiled for 1 h. The insoluble material was filtered off, the filtrate was evaporated to dryness, the residue was passed through a column of silica gel with hexane as eluant, and low molecular weight components (C_6Cl_6 and C_6HCl_5, 4.27 g) were sublimed off. The residue was recrystallized from benzene to give perchloro(2,2′-biphenylene)diphenylsilane (1.1 g; 5%), m.p. 390 °C (dec.; DSC * and TG). IR (KBr): 1510(m), 1492(w), 1380(w), 1355(w), 1338(m), 1325(s), 1315(s), 1308(s), 1296(s), 1272(m), 1250(w), 1220(w), 1200(w), 1162(m), 1148(m), 1115(s), 1092(s), 875(s), 868(s), 812(w), 720(w), 712(w), 700(w), 680(m), 645(m), 605(w), 575(w), 452(m), 432(s), 415(m), cm^{-1}. UV-vis ($CHCl_3$): 305 (sh) nm, 313 (ε 13600, 15000). Anal. Found: C, 30.4; Cl, 66.8. $C_{24}Cl_{18}Si$ calcd.: C, 30.2; Cl, 66.8%. Molecular weight (osmometer): Found 1008; calcd. 954.4.

The mother liquids were concentrated to give perchlorotriphenylsilane (2.83 g, 14%), m.p. 301–314 °C (lit. [1], 304 °C).

(a′) Synthesis from perchlorotriphenylsilane. A solution of perchlorotriphenylsilane (0.457 g, 0.57 mmol) in THF (20 ml) was added dropwise to a stirred THF solution of pentachlorophenylmagnesium chloride (prepared from hexachlorobenzene (0.750 g, 2.63 mmol) and magnesium (0.100 g; 0.004 atg) in THF (5 ml)) under argon, the mixture was refluxed for 16 h and the solvent then distilled off. Benzene (30 ml) was added to the residue and the mixture boiled for 1 h. The insoluble material was filtered off, the filtrate was evaporated to dryness, and the residue was passed through a column of silica gel with hexane as eluant. The low molecular weight components were sublimed off (0.688 g, C_6Cl_6 and C_6HCl_5) and the residue after recrystallization from benzene gave perchloro(2,2′-biphenylene)diphenylsilane (0.035 g, 6%). Perchlorotriphenylsilane (0.415 g, 91%) was recovered by evaporating the mother liquor to dryness.

(b) Hydrolysis

A mixture of the silane **2** (0.1 g, 0.1 mmol), THF (15 ml) and aqueous sodium hydroxide (10%) (15 ml) was heated under reflux (5 h) and then an excess of dilute hydrochloric acid was added. Extraction with chloroform followed by separation, drying (Na_2SO_4) and evaporation of the extract left a residue. Sublimation (90 °C, 0.5 mmHg) gave pentachlorobenzene (0.049 g, 94%) and left a residue of 2,3,4,5,2′,3′,4′,5′-octachlorobiphenyl (0.045 g, 100%), m.p. 155–156 °C (lit. [8] 156–157 °C).

Perchloro(2,2′-biphenylene)diphenylgermane (3)

(a) Synthesis from $GeCl_4$. A THF solution of pentachlorophenylmagnesium chloride (prepared from hexachlorobenzene (28.5 g, 0.1 mol) and magnesium (3.6 g, 0.15 atg) and THF (120 ml), and filtered through glass wool to remove unchanged magnesium) was added dropwise to a stirred solution of $GeCl_4$ (5.36 g, 0.025 mol) in THF (25 ml) at room temperature, and the mixture was then refluxed for 18 h under argon. Work-up was as before (see preparation of **2** from $SiCl_4$). The

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* DSC-differential scanning calorimetry.

sublimed fraction was a mixture (4.89 g) of C_6Cl_6 and C_6HCl_5 and the residue was perchloro(2,2′-biphenylene)diphenylgermane (4.21 g, 17%), m.p. 380 °C (dec.; DSC and TG) (from hexane–benzene). IR (KBr): 1510(m), 1495(w), 1380(w), 1355(w), 1340(s), 1330(s), 1315(s), 1300(s), 1200(w), 1170(w), 1150(m), 1110(m), 1070(m), 855(s), 805(m), 720(w), 710(w), 695(m), 680(s), 650(w), 640(m), 630(m), 570(w), 540(w), 410(w) cm^{-1}. UV-vis ($CHCl_3$): 299 (sh) nm, 309 (ε 15400, 18200). Anal. Found: C, 28.8; Cl, 63.3. $C_{24}Cl_{18}Ge$ calcd.: C, 28.9; Cl, 63.9%. Molecular weight (osmometer): Found 990; calcd. 998.9.

When the reaction was repeated at room temperature, similar results were obtained and perchloro(2,2′-biphenylene)diphenylgermane isolated in 20% yield.

(a′) Synthesis from perchlorotriphenylgermane. A filtered THF solution of pentachlorophenylmagnesium chloride (prepared from hexachlorobenzene (1.833 g, 6.44 mmol), magnesium (0.253 g, 0.010 atg) and THF (5 ml); HPLC analysis of an small hydrolyzed aliquot gave 98% of pentachlorobenzene) was added dropwise to a stirred refluxing solution of perchlorotriphenylgermane (1.52 g, 1.79 mmol) in THF (20 ml) under argon.

The mixture was refluxed for a further 20 h and the solvent then distilled off. Benzene (20 ml) was added and the mixture was boiled for 1 h. The benzene solution was washed with aqueous HCl and then water, then evaporated to dryness. The residue was passed through a column of silica gel with hexane as eluent. The low molecular weight components were sublimed off (1.069 g, molar proportion (HPLC) C_6Cl_6/C_6HCl_5, 5/1) to leave perchloro(2,2′-biphenylene)diphenylgermane (1.29 g, 73%).

(b) Reaction with chlorine. A slow stream of dry Cl_2 was passed (4 h) through a refluxing solution of perchloro(2,2′-biphenylene)diphenylgermane (0.098 g) in purified CCl_4 (25 ml) with illumination from a 500 W incandescent lamp situated underneath the Pyrex container, thus also providing heat. Evaporation of volatile fraction left a residue, that upon sublimation (120 °C, 0.5 mmHg) gave hexachlorobenzene (0.055 g, 98%) and left a residue of perchlorobiphenyl (0.046 g, 94%), m.p. 309–311 °C (lit. [9] 309 °C).

(c) Hydrolysis. A mixture of the germane **3** (0.070 g), THF (10 ml) and aqueous sodium hydroxide (10%) (10 ml) was heated and the products worked-up as described for the hydrolysis of silane **2** (see above). The residue was recrystallized from methanol to give 2,3,4,5,2′,3′,4′,5′-octachlorobiphenyl (0.028 g, 93%). Evaporation of the mother liquors left pentachlorobenzene (0.033 g, 94%).

(d) Reaction with bromine. A mixture of the germane **3** (1.01 g) and bromine (0.4 g) in CCl_4 (150 ml) was refluxed (13 h) with illumination from a 500 W incandescent lamp situated underneath the pyrex container and providing heat. The mixture was evaporated to dryness under vacuum and the residue, treated two or three times with CCl_4 with evaporating to dryness each time under vacuum to remove the bromine. Digestion with boiling benzene and then chloroform left bromo(2-(2′-bromooctachlorobiphenyl))bis(pentachlorophenyl)germane (**4**) (0.970 g, 83%), m.p. 415 °C (dec.; DSC and TG). IR (KBr): 1510(m), 1400(w), 1345(m), 1335(s), 1325(s), 1310(s), 1300(s), 1170(w), 1160(m), 1110(m), 1085(m), 1075(w), 855(s), 805(m), 750(w), 710(w), 695(w), 680(s), 640(w), 625(w), 550(w) cm^{-1}. UV-vis ($CHCl_3$): 288 (sh) nm, 298, 307 (ε 2020, 3407, 3630). Anal. Found: C, 24.9; Cl, 55.6; Br, 13.7. $C_{24}Br_2Cl_{18}Ge$ calcd.: C, 24.9; Cl, 55.1; Br, 13.8%.

*(e) Reaction of **4** with chlorine.* A slow stream of Cl_2 was passed (5 h) through a

Table 4

Summary of X-ray analysis

$C_{24}Cl_{18}M$	$C_{24}Cl_{18}M\cdot 2C_6H_6$	
	M = Si	M = Ge
a (Å)	9.751(3)	9.708(2)
b (Å)	14.191(4)	14.259(3)
c (Å)	17.809(9)	17.841(8)
α (°)	68.31(6)	67.72(5)
β (°)	76.28(5)	76.711(4)
γ (°)	70.98(3)	71.05(2)
V (Å)	2145	2145
Space group:	$P\bar{1}$	$P\bar{1}$
Z	2	2
D_x	1.72	1.79 g/cm^3
μ(calod)	12.1	17.8 cm^{-1}
F(000)	1096	1132
No. of collected reflections	7836	7809
No. of unique reflections	7570	7540
No. of observed reflections with ($I > 2.5\sigma(I)$)	4553	5495
Data collection range	$1 < \theta < 25°$	$1 < \theta < 25°$
Scan method	ω-2θ	ω-2θ
Range of hkl	-11-11; -16-16; 0-21	-11-11; -16-16; 0-21
No. of refined parameters	389	389
R factor	0.064	0.043
R_w	0.070	0.051
$w = 1/(\sigma^2(F) + nF^2)$	$n = 0.000222$	$n = 0.000556$
Max. diff. Fourier peak (eλ^{-3})	0.5	1.2
Min. diff. Fourier peak (eλ^{-3})	-0.5	-0.5

mixture of germane **4** (0.238 g, 0.21 mmol) and CCl_4 (75 ml) as in the case of **3** (see above). When the reaction was complete, work-up was as in (b), and perchlorobenzene (0.119 g, 100%) and perchlorobiphenyl (0.105 g, 100%) were isolated.

*X-ray crystallography of **2** and **3** as their benzene solvates*

Data collection was carried out on an Enraf–Nonius CAD4 diffractometer at room temperature operating in the ω–2θ scan mode, with graphite monochromated Mo-K_α radiation (λ 0.71069 Å). Intensities were corrected for Lorentz and polarization effects. The Ge atom in **3** was located by direct methods using MULTAN 11/84 [10]. The remaining non-H atoms were found by successive weighted Fourier synthesis *. The structure of the silicon compound **2** was refined directly from the refined atom positions for the germanium compound **3**. The structure of **3** shows small positive difference Fourier peaks at the centre of the benzene C–C bonds, suggesting a little rotational disorder of these solvent molecules. The relevant experimental details are summarized in Table 4. Atom coordinates are listed in Tables 5 and 6. Tables of anisotropic thermal parameters and observed and calculated structure factors are available from the authors.

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* The structure was refined by full-matrix least-squares methods using SHELX76 program [11].

(*continued on p. 332*)

Table 5. Fractional atomic coordinates ($\times 10^4$) with their e.s.d.'s and their equivalent isotropic temperature factors for perchloro(2,2′-biphenylen)diphenylsilane (**2**)

	x	y	z	B_{eq}
Si1	3153(2)	2739(2)	2568(1)	3.51
Cl2	727(3)	3573(2)	1336(2)	6.04
Cl3	−1547(3)	5712(2)	1037(2)	7.08
Cl4	−1535(3)	7289(2)	1862(2)	7.51
Cl5	980(3)	6798(2)	2844(2)	6.28
Cl6	3202(2)	4662(2)	3221(2)	5.09
Cl8	875(2)	3135(2)	4215(2)	5.57
Cl9	1813(3)	2296(3)	5905(2)	6.91
Cl10	4989(4)	1033(3)	6185(2)	8.00
Cl11	7249(3)	478(2)	4771(2)	6.62
Cl12	6391(2)	1276(2)	3051(2)	6.10
Cl14	5641(3)	4300(2)	1696(2)	6.68
Cl15	7250(3)	4401(2)	−40(2)	7.02
Cl16	6757(4)	3034(2)	−922(2)	7.44
Cl17	4687(3)	1609(2)	−86(2)	6.21
Cl20	5740(3)	−355(2)	1376(2)	5.79
Cl21	3596(3)	−1698(2)	2390(2)	6.64
Cl22	855(3)	−799(2)	3474(2)	7.38
Cl23	387(3)	1421(2)	3591(2)	6.88
C1	1830(8)	4111(6)	2330(5)	3.79
C2	759(8)	4421(6)	1819(5)	4.01
C3	−258(8)	5383(7)	1665(6)	4.61
C4	−218(9)	6109(7)	2003(7)	5.54
C5	876(9)	5866(6)	2473(6)	4.43
C6	1887(8)	4896(6)	2624(5)	3.82
C7	3661(8)	2223(6)	3642(5)	3.93
C8	2660(8)	2399(6)	4325(5)	4.14
C9	3053(9)	2054(6)	5079(5)	4.47
C10	4478(10)	1467(7)	5222(6)	5.43
C11	5496(9)	1227(6)	4591(6)	4.67
C12	5071(9)	1601(7)	3827(6)	4.61
C13	4615(8)	2765(6)	1674(5)	3.83
C14	5456(9)	3478(6)	1233(5)	4.25
C15	6167(9)	3537(7)	456(6)	4.68
C16	5957(9)	2931(7)	66(6)	4.89
C17	5120(9)	2196(6)	490(5)	4.36
C18	4564(8)	2073(6)	1290(5)	3.85
C19	3791(8)	1265(6)	1841(4)	3.28
C20	4091(8)	224(6)	1856(5)	4.12
C21	3186(10)	−411(6)	2363(6)	4.81
C22	1984(9)	−28(7)	2866(6)	4.94
C23	1803(8)	978(6)	2916(6)	4.33
C24	2703(8)	1621(6)	2438(5)	3.90
C30	6852(14)	4787(11)	3423(10)	10.62
C31	6976(12)	3746(10)	3855(8)	8.23
C32	7099(13)	3362(10)	4665(9)	9.52
C33	7158(13)	3962(11)	5072(9)	9.68
C34	7119(14)	5008(11)	4643(9)	9.91
C35	6849(13)	5413(10)	3866(9)	9.58
C40	−847(15)	1352(11)	1274(9)	11.14
C41	180(16)	1698(10)	668(10)	10.47
C42	1216(14)	1010(12)	371(10)	11.34
C43	1214(15)	5(11)	673(9)	11.13
C44	204(17)	−357(11)	1262(10)	11.56
C45	−830(14)	320(12)	1550(9)	11.33

Table 6. Fractional atomic coordinates ($\times 10^4$) with their e.s.d.'s and their equivalent isotropic temperature factors for perchloro(2,2'-biphenylene)diphenylgermane (**3**)

	x	*y*	*z*	B_{eq}
Ge1	3119.1(0.5)	2750.3(0.4)	2569.3(0.3)	3.24
Cl2	625(2)	3627(1)	1340(1)	5.69
Cl3	−1655(2)	5773(1)	1029(1)	6.58
Cl4	−1610(2)	7323(1)	1855(1)	7.31
Cl5	943(2)	6814(1)	2832(1)	5.94
Cl6	3169(1)	4675(1)	3205(1)	4.86
Cl8	879(1)	3100(1)	4228(1)	5.25
Cl9	1820(2)	2277(2)	5924(1)	6.69
Cl10	5004(2)	1012(2)	6220(1)	7.86
Cl11	7253(2)	463(1)	4814(1)	6.32
Cl12	6392(1)	1288(1)	3086(1)	5.84
Cl14	5621(2)	4301(1)	1666(1)	5.99
Cl15	7280(2)	4387(1)	−60(1)	6.42
Cl16	6789(2)	3025(10	−935(1)	6.82
Cl17	4695(2)	1614(1)	−102(1)	5.51
Cl20	5735(2)	−345(1)	1370(1)	5.22
Cl21	3578(2)	−1683(1)	2360(1)	6.12
Cl22	837(2)	−804(1)	3440(1)	6.76
Cl23	371(2)	1399(1)	3564(1)	6.17
C1	1763(5)	4179(3)	2320(3)	3.45
C2	686(5)	4474(4)	1816(3)	3.68
C3	−347(5)	5443(4)	1662(3)	4.36
C4	−295(6)	6151(4)	2006(3)	4.43
C5	806(5)	5904(4)	2461(3)	4.09
C6	1813(5)	4928(4)	2609(3)	3.70
C7	3670(5)	2201(4)	3688(3)	3.56
C8	2685(5)	2390(4)	4347(3)	3.97
C9	3078(6)	2011(4)	5132(3)	4.52
C10	4511(6)	1435(4)	5256(3)	4.60
C11	5491(6)	1206(4)	4634(3)	4.48
C12	5076(5)	1590(4)	3863(3)	4.02
C13	4627(5)	2772(4)	1628(3)	3.35
C14	5463(5)	3482(4)	1212(3)	4.03
C15	6190(5)	3532(4)	432(3)	4.40
C16	5976(6)	2916(4)	50(3)	4.45
C17	5147(5)	2200(4)	458(3)	3.95
C18	4579(5)	2062(3)	1278(3)	3.41
C19	3768(5)	1269(4)	1817(3)	3.53
C20	4085(5)	230(4)	1841(3)	3.88
C21	3164(6)	−403(4)	2341(3)	4.21
C22	1976(6)	−30(4)	2839(3)	4.47
C23	1781(5)	959(4)	2891(3)	4.07
C24	2689(5)	1588(3)	2409(3)	3.44
C30	6827(6)	4797(5)	3420(3)	10.09
C31	6949(6)	3731(5)	3838(3)	10.20
C32	7122(6)	3312(5)	4666(3)	9.84
C33	7173(6)	3959(5)	5075(3)	10.77
C34	7051(6)	5026(5)	4657(3)	11.23
C35	6878(6)	5444(5)	3829(3)	11.63
C40	−821(6)	1492(4)	1246(4)	9.60
C41	362(6)	1695(4)	654(4)	10.05
C42	1350(6)	887(4)	394(4)	10.69
C43	1156(6)	−125(4)	728(4)	10.67
C44	−27(6)	−329(4)	1321(4)	11.31
C45	−1015(6)	480(4)	1580(4)	10.30

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