A Synthetic Route to Poly(silyl)methanes via Poly(phenylsilyl)methanes and Poly(bromosilyl)methanes

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A three-step synthesis is presented for di- and tri(silyl)methane, two feedstock gases for the chemical vapour deposition of amorphous hydrogenated silicon/carbon alloys (a-SiC:H). Chloro(phenyl)silane and di- or trihalomethanes react with magnesium in tetrahydrofuran to give high yields of bis- and tris(phenylsilyl)methane, respectively. The two products can be converted into bis- and tris(bromosilyl)methane by treatment with anhydrous hydrogen bromide. Bromide/hydride substitution in these precursors is accomplished with lithium aluminum hydride in a two-phase system using a phase-transfer catalyst. The compounds $CH_2(SiH_2Ph)_2$, $CH(SiH_2Ph)_3$, $CH_2(SiH_2Br)_2$, $CH(SiH_2Br)_3$, $CH_2(SiH_3)_2$, and $CH(SiH_3)_3$ have been characterized by standard spectroscopic methods, and the crystal and molecular structure of $CH(SiH_2Ph)_3$ has been determined by single-crystal X-ray diffraction. The molecule adopts a conformation with crystallographic C_3 symmetry. This result is discussed with regard to the structure of related molecules with three substituents of potential C_s symmetry at a tetrahedral center.

Ein Syntheseweg zu Poly(silyl)methanen über Poly(phenylsilyl)methane und Poly(bromsilyl)methane

Für Di- und Tri(silyl)methan, aus denen durch Dampfphasenzersetzung (CVD) Kohlenstoff-haltiges amorphes Silicium (a-SiC:H) erhalten werden kann, wird eine ergiebige dreistufige Synthese beschrieben: Chlor(phenyl)silan und Di- oder Trihalogenmethane reagieren in guten Ausbeuten mit Magnesium in Tetrahydrofuran zu Bis- bzw. Tris(phenylsilyl)methan. Durch Behandlung mit wasserfreiem Bromwasserstoff können daraus fast quantitativ die Zwischenprodukte Bis- bzw. Tris(bromsilyl)methan erhalten werden, deren Hydrierung mit Lithiumaluminiumhydrid im Zweiphasensystem mit Phasentransferkatalysator die Zielverbindungen $CH_2(SiH_3)_2$ bzw. $CH(SiH_3)_3$ ergibt. Wie diese Verbindungen wurden auch $CH_2(SiH_2Ph)_2$, $CH(SiH_2Ph)_3$, $CH_2(SiH_2Br)_2$ und $CH(SiH_2Br)_3$ durch spektroskopische Standardmethoden charakterisiert. Die Kristall- und Molekülstruktur von $CH(SiH_2Ph)_3$ wurde durch Einkristallröntgenbeugung ermittelt. Die für das Molekül gefundene kristallographische C_3-Symmetrie wird unter Bezugnahme auf die Struktur anderer Spezies diskutiert, in denen drei Substituenten mit potentieller C_s-Symmetrie an ein tetraedrisches Zentrum gebunden sind.

Currently, there is growing interest in new and efficient methods of synthesis for volatile ternary compounds containing silicon, carbon, and hydrogen ($Si_xC_yH_z$). Species of this series rich in hydrogen and silicon are promising feedstock gases for chemical vapour deposition (CVD) of amorphous hydrogenated silicon/carbon alloys (a-SiC:H). Films of this type constitute the semiconductor basis for solar cells in small devices or large panels, but also for photosensors and many other photoelectric units.

Established technology for the production of a-SiC:H modules is based on glow-discharge CVD of silane gas and its mixures with methane, acetylene, or other carbon sources. Due to the very different bond energies in SiH_4 and CH_4, the nature of the incorporation of carbon into the silicon framework is difficult to control. As demonstrated by vibrational spectroscopy and by effusion experiments, most of the carbon is incorporated as carbon centers rich in high-energy carbon – hydrogen bonds, but not as quaternary carbon atoms (carbide centers). This is true even when a large excess of silane is employed[1,2]).

A new approach to a more direct influence on the structural characteristics of a-SiC:H suggests the application of organosilanes with little or no CH_3, CH_2, or CH functions in the molecules. The most attractive candidates for these new Si/C/H feedstock gases are the poly(silyl)methanes $(H_3Si)_xH_{4-x}C$ with $x = 1, 2, 3$, or 4. With a decreasing number of C – H bonds in the members of this series, the incorporation of hydrogen-free carbon into a-SiC:H films should become more prominent. Recent experiments have shown, that the physical properties of photovoltaic films, like e. g. the band gap and the photoconductivity, depend very strongly on structural features and can thus be influenced by changes in the feedstock gas stoichiometry and structure. Following a number of earlier studies[3,4]) with methylsilane, H_3SiCH_3, which showed only moderate success, more recent investigations with di(silyl)methane, $(H_3Si)_2CH_2$, proved much more encouraging[5-7]).

Due to the increasing evidence for potential usage of poly(silyl)methanes as CVD feedstock gases, existing methods of synthesis for these molecules have been revisited and new preparative routes have become the goal of several current studies[8,9]). As part of our own continuing efforts in this direction we have been exploring a synthetical pathway, which should be applicable not only for *di*- and *tri*(silyl)methane, for which other routes exist, but also for the elusive *tetra*(silyl)methane, $(H_3Si)_4C$. This report describes our latest pertinent results.

A New Synthesis for Di(silyl)methane and Tri(silyl)methane

Di(silyl)methane has been synthesized, in small quantities, by a number of synthetic routes, most of which involve the corresponding hexachloro derivative $(Cl_3Si)_2CH_2$. This precursor is available in the Direct Synthesis using Si/Cu alloys and CH_2Cl_2 or other halohydrocarbons[10]), but also in the Benkeser Reaction using silicochloroform, halohydro-

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carbons, and an auxiliary base[11], in the Merker/Scott procedure using magnesium reduction of halosilanes and halohydrocarbons in polar solvents[12], or in the pyrolysis of methylchlorosilanes[13]. Other methods employ potassium silyl as a reagent for dihalomethanes[14], but the yields are again in the lower region as observed also in most investigations with $Cl_3SiCH_2SiCl_3$, where the final step (the hydride/chloride substitution) is associated with an unacceptable loss of product[8,9].

Tri(silyl)methane has been obtained, in very low yields, via methods similar to those probed for di(silyl)methane. The hydride/chloride substitution in $HC(SiCl_3)_3$ is even more critical than with $H_2C(SiCl_3)_2$, since the process leads to considerable, sometimes complete Si–C cleavage to give also di(silyl)methane instead of tri(silyl)methane[8,14,15].

It is probably for that reason, that *tetra(silyl)methane* has not been prepared to date. Thus, for a successful synthesis of the three poly(silyl)methanes an approach was desirable, where the danger of Si–C cleavage by hydride in the final step is minimized. Such a method has now been developed.

The Merker/Scott reduction of SiX_4/CX_4 mixtures (X = Cl, Br) with magnesium is unsatisfactory for the generation of $C(SiX_3)_4$ molecules. But even if this step could be improved, the conversion into the target molecule $C(SiH_3)_4$ would be overruled by Si–C cleavage to give $CH(SiH_3)_3$ or even $CH_2(SiH_3)_2$, owing to the excellent leaving group properties of the Cl_3Si^- ion.

It therefore appeared that the magnesium reduction should be employed with almost fully hydrogenated silicon components, whose remaining substituents could be converted into hydride functions without complications. Halosilanes H_3SiX are unstable and difficult to handle in larger quantities and would thus be ruled out for practical reasons. Experiments with H_3SiCl and H_3SiBr confirmed these doubts even on the laboratory scale.

A more promising candidate was *chloro(phenyl)silane*, which is a readily available, stable compound[16], and for which a clean electrophilic cleavage of the phenyl group could be envisaged[17].

Experiments under Merker/Scott conditions, using magnesium turnings in tetrahydrofuran as a reducing medium for bromoform and chloro(phenyl)silane, gave the expected product in acceptable yield (Eq. 1, 2).

$$CH_2Br_2 + 2\,ClH_2SiPh + 2\,Mg \rightarrow 2\,MgClBr + CH_2(SiH_2Ph)_2 \quad (1)$$
$$CHBr_3 + 3\,ClH_2SiPh + 3\,Mg \rightarrow 3\,MgClBr + CH(SiH_2Ph)_3 \quad (2)$$

In the reaction with $CHBr_3$ not only expected $CH(SiH_2Ph)_3$ is formed (ca. 50% yield), but significant amounts of $CH_2(SiH_2Ph)_2$ can also be isolated (ca. 30%). It can be assumed that transmetallation reactions lead to a reduction of bromoform to dibromomethane, which gives then rise to the formation of $CH_2(SiH_2Ph)_2$, a compound previously synthesized by a different route[18,19].

Bis(phenylsilyl)methane is a colourless, distillable liquid (b.p. 96°C at 0.2 Torr), while tris(phenylsilyl)methane is obtained after distillation (b.p. 190°C at 0.2 Torr) as a waxy solid of m.p. 47°C. Both compounds are easily identified by standard analytical and spectroscopic methods (see Experimental). In addition, the crystal and molecular structure of tris(phenylsilyl)methane has been determined by single-crystal X-ray diffraction (below).

Tetrakis(phenylsilyl)methane has been prepared following the same synthetic procedure. Its properties, structure and conversion into tetrakis(bromosilyl)methane and tetra(silyl)methane will be reported in due course.

The phenyl groups in bis- and tris(phenylsilyl)methane can by cleaved by treatment with anhydrous hydrogen bromide at −78°C in the absence of a solvent. Bis- and tris(bromosilyl)methane are thus obtained in 92 and 84% yield, respectively (Eq. 3, 4).

$$CH_2(SiH_2Ph)_2 + 2\,HBr \rightarrow 2\,C_6H_6 + CH_2(SiH_2Br)_2 \quad (3)$$
$$CH(SiH_2Ph)_3 + 3\,HBr \rightarrow 3\,C_6H_6 + CH(SiH_2Br)_3 \quad (4)$$

Both products are colourless liquids, fuming in air, which can be distilled in vacuo (b.p. 68°C at 20 Torr and 57°C at 0.2 Torr, respectively). Analytical and spectroscopic data are in accord with the proposed formulae (see Experimental).

The final conversion of these two precursors into di- and tri(silyl)methane has been accomplished through reduction with lithium aluminum hydride in a two-phase system employing a phase-transfer catalyst. It is under these carefully controlled conditions, that Si–C cleavage is minimized such that high yields of 91 and 83%, respectively, are secured (Eq. 5, 6).

$$CH_2(SiH_2Br)_2 + LiAlH_4 \rightarrow CH_2(SiH_3)_2 \quad (5)$$
$$CH(SiH_2Br)_3 + LiAlH_4 \rightarrow CH(SiH_3)_3 \quad (6)$$

Direct treatment of the (bromosilyl)methanes with $LiAlH_4$ in a standard solvent (ethers, e.g. di-*n*-butyl ether) gives very poor yields of $CH_2(SiH_3)_2$ and even less (sometimes none at all) in the case of $CH(SiH_3)_3$.

In summary, both di- and tri(silyl)methane have now become available by a three-step synthesis starting from chloro(phenyl)silane in good to moderate yields and in high purity. The individual steps present no experimental difficulties and can be carried out on a larger scale using conventional apparatus. The preparation are thus superior to methods previously applied and can supply the two gases in an economical way from commercial chemicals.

The Crystal and Molecular Structure of Tris(phenylsilyl)methane

Tris(phenylsilyl)methane is an interesting compound regarding its ground-state conformation. In this molecule three substituents – SiH_2Ph with potential mirror symmetry (C_s) are attached to the central tetrahedral carbon atom. Highest possible symmetry should thus correspond to point group C_{3v}, but reduction of symmetry to point group C_3, C_s or even C_1 could occur as a consequence of steric interactions, both intra- and intermolecular.

We have previously been interested in the ground-state conformations of species, where a tetrahedral center bears *four* substituents of threefold symmetry or mirror symmetry, as exemplified by the tetrakis(*tert*-butyl)- or -(isopropyl)-phosphonium cations and their silicon analogues[20–22].

$CH(SiH_2Ph)_3$ offered a chance to extend these studies into another series, where information from both theory and experiment was still limited. An example in case is tribenzylamine $N(CH_2Ph)_3$, an "azatricarba" analogue of the title compound[23].

Tris(phenylsilyl)methane crystallizes from ethanol in large needles belonging to the trigonal space group $R\bar{3}$ with six molecules in the unit cell (hexagonal axes). Each molecule has crystallographic C_3 symmetry with the methylidyne hydrogen and carbon atoms on the threefold axis (Figure 1). The phenylsilyl substituents have approximate C_s symmetry (torsional angle C1–Si–C10–C15 = 90.9°). Should the plane through the atoms H1, C1, and Si1 be parallel or perpendicular to the phenyl planes, then the molecules in principle could approach C_{3v} symmetry. However, these planes form an angle of 73.51° (dihedral angle H1–C1–Si1–C10 = −47.53°), and thus the overall symmetry does not exceed the point group C_3.

The propeller-like molecules are chiral by symmetry and exist as two optical isomers in a single crystal (left- and right-handed propellers). Their structure is similar to the conformation found in crystals of tribenzylamine at low temperature[23], but also in the hexamethylated homologue tris(dimethylphenylsilyl)methane[24]. Molecular dimensions in $HC(SiH_2Ph)_3$ and $HC(SiMe_2Ph)_3$ are also very similar (for details of bond distances and angles see Table 1).

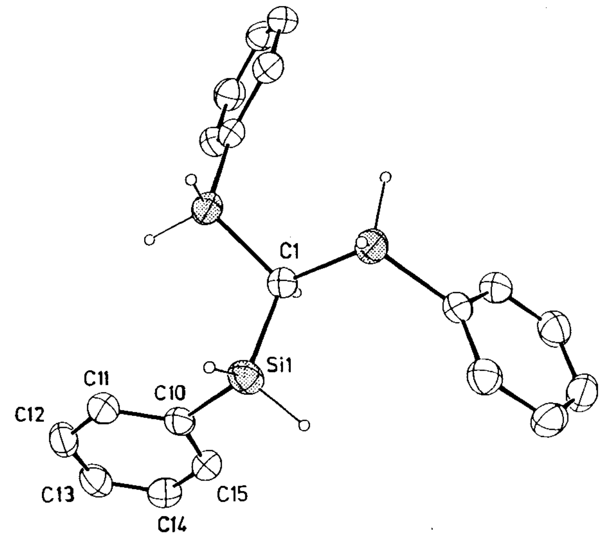

Figure 1. Molecular structure of tris(phenylsilyl)methane (ORTEP, 50% probability ellipsoids); the molecule has a crystallographic threefold axis through C1 and the hydrogen atom attached to it; phenyl hydrogen atoms are omitted for clarity

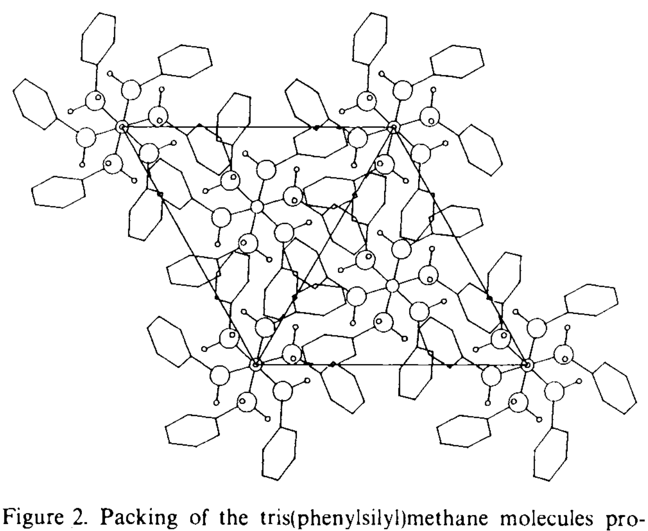

Figure 2. Packing of the tris(phenylsilyl)methane molecules projected onto the *xy* plane of the unit cell

Table 1. Selected interatomic distances [Å] and angles [°] in the tris(phenylsilyl)methane molecule

Si1-C1	1.879(1)	Si1-C10	1.864(2)
C10-C11	1.406(3)	C10-C15	1.407(3)
C11-C12	1.380(3)	C12-C13	1.378(3)
C13-C14	1.385(3)	C14-C15	1.382(3)
Si1-C1-Si1'	110.4(1)	C1-Si1-C10	113.5(1)
Si1-C10-C15	120.2(1)		
C11-C10-C15	117.4(2)	C10-C11-C12	120.8(1)
C11-C12-C13	120.7(2)	C12-C13-C14	119.9(2)
C13-C14-C15	120.0(2)	C10-C15-C14	121.2(2)

The phenyl rings show a noteworthy distortion from an ideal hexagon. The bond angle C11–C10–C15 at the *ipso* carbon atom C1 is significantly smaller than the 120° standard, and this angle contraction is accompanied by an elongation of the bonds C10–C11 and C10–C15 (average 1.403 Å) as compared to the remaining C–C bonds in the same ring (average 1.381 Å). This feature is in agreement with simple VSEPR rules, which predict such structural consequences for aryl groups attached to electropositive (electron-donating) substituents. In other words: the new structural results confirm the electropositive nature of silicon as a substituent for sp^2 carbon.

In the unit cell, the $HC(SiH_2Ph)_3$ molecules are stacked parallel to the *c* axis of the crystal in pairs of optical isomers related by centers of inversion. Shortest intermolecular contacts are between the methylidyne hydrogen atoms on the threefold axis (2.391 Å). Surrounding pairs of molecules are shifted along the *c* axis by 1/3 above and below the given level to form triplets in a staggered arrangement relative to each other. The atomic coordinates and displacement parameters are listed in Table 2, supplementary data have been deposited[25].

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters for tris(phenylsilyl)methane ($U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$)

ATOM	X/A	Y/B	Z/C	U(eq.)
SI1	-0.04529(5)	0.10936(5)	0.14337(3)	0.082
C1	0.00000	0.00000	0.1131(2)	0.063
C10	0.0353(2)	0.2570(2)	0.1000(1)	0.075
C11	0.1444(2)	0.3509(2)	0.1240(1)	0.079
C12	0.2016(2)	0.4591(2)	0.0907(1)	0.079
C13	0.1530(2)	0.4775(2)	0.0331(1)	0.091
C14	0.0459(2)	0.3865(2)	0.0080(1)	0.103
C15	-0.0124(2)	0.2779(2)	0.0411(1)	0.085

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Experimental

General: All experiments were carried out under pure dry nitrogen. Glassware and solvents were purified, dried and kept under nitrogen accordingly. C_6D_6 was used as solvent for NMR spectroscopy with tetramethylsilane as reference compound (Jeol GX 270 and GX 400 spectrometers). Infrared spectra were registered from films between KBr plates (Nicolet FT 5 DX spectrometer), mass spectra with electron impact sources (Varian MAT CH 7, 70 eV). For gas chromatography, columns SIL 5 were applied in a Hewlett-Packard GC 5890 A with a mass-sensitive detector MSD 5970.

Chloro(phenyl)silane: Tin tetrachloride (349.1 g, 1.34 mol) was added dropwise at 0°C and under reduced pressure (400 Torr) to a stirred solution of phenylsilane (145.2 g, 1.34 mol) in 1.8 l of *n*-hexane contained in a three-necked flask, which was connected to a cooling trap kept at −196°C to recieve the hydrogen chloride evolved in the reaction. After all the tin tetrachloride had been added (3 h), the tin dichloride precipitate was filtered off, and from the filtrate most of the *n*-hexane was removed by distillation. Finally, distillation of the residual liquid under reduced pressure yielded 166.3 g (87%) of $PhSiH_2Cl$ as colorless liquid, b.p. 77.5°C at 45 Torr. – ^1H NMR: δ = 5.1 [s, SiH, J(SiH) = 240.0 Hz], 7.3 (m, Ph). – ^{13}C NMR: δ = 128.6 (dd, C-2/C-6), 130.2 (m, C-1), 131.5 (dt, C-4), 134.6 (dm, C-3/C-5); J(CH) ≈ 160 Hz, J(CCH) ≈ 7 Hz. – ^{29}Si NMR: δ = −17.7 [t, J(SiH) = 240 Hz].

Bis- and Tris(phenylsilyl)methane: A solution of tribromomethane (22.1 g, 0.087 mol) in 300 ml of tetrahydrofuran was added dropwise to a mixture of chlorophenylsilane (37.4 g, 0.262 mol) and magnesium (7.0 g, 0.288 mol) in 200 ml of boiling tetrahydrofuran at a rate to maintain reflux when the external heating was removed. After the addition (5 h) and a further reflux period of 4 h, the mixture was poured on crushed ice, neutralized with sodium hydrogen carbonate, and the organic layer washed twice with water (2 × 250 ml). After addition of 200 ml of *n*-hexane, the organic phase was stirred with dry magnesium sulfate for 2 h and filtered. The *n*-hexane was removed in vacuo and the remaining yellow oily liquid distilled at 0.5 Torr to yield fractions boiling at 120 and 210°C, respectively. The second fraction solidified in the receiver. Further distillation of the liquid fraction gave 6.6 g (33% based on $CHBr_3$) of $CH_2(SiH_2Ph)_2$, b.p. 96°C at 0.2 Torr (ref.[18] 93–95°C at 1 Torr, ref.[19] 98°C at 0.15 Torr). Diphenyldisiloxane is an impurity in the product as detected by GC/MS analysis. The solidified second fraction was recrystallized from anhydrous ethanol to give 13.1 g (45%) of $CH(SiH_2Ph)_3$ as a colourless solid, m.p. 47°C, b.p. 190°C at 0.2 Torr.

Bis(phenylsilyl)methane: ^1H NMR: δ = 0.19 (quint, CH_2), 4.62 [t, J(HCSiH) = 4.4 Hz, SiH_2), 7.3 (m, Ph). – ^{13}C NMR: δ = −11.08 [t quint, J(CH) = 116.7, J(CSiH) = 6.4, J(SiC) = 44.5 Hz, CH_2], 128.26 (dd, C-2, -6), 129.89 (dt, C-4), 133.03 (m, C-1), 135.29 (dm, C-3, -5); J(CH) ≈ 159.5, J(CCH) = 7 Hz. – ^{29}Si NMR: δ = −33.48 [tm, J(SiH) = 196.3 Hz]. – IR (film): $\tilde{\nu}$ = 3070 cm^{-1} m, 3048 w, 3017 sh, 2925 m, 2858 m, 2137 s, 1429 m, 1114 s, 1047 s, 944 s, 884 m, 860 sh, 843 s, 811 m, 764 m, 739 m, 696 s, 654 m. – MS: m/z = 228–223 [$C_{13}Si_2H_x$], 187–180 [$C_{12}SiH_x$], 152–147 [$C_7Si_2H_x$], 108–105 [C_6SiH_x].

Tris(phenylsilyl)methane: ^1H NMR: δ = −0.03 (sept, CH), 4.71 [d, J(HCSiH) = 4.0 Hz, SiH_2), 7.20 (m, Ph). – ^{13}C NMR: δ = −14.99 [dsept, J(CH) = 110.4, J(CSiH) = 6.7, J(SiC) = 38.1 Hz, CH], 128.22 (dd, C-2, -6), 130.04 (dt, C-4), 132.30 (m, C-1), 135.67 (dm, C-3, -5); J(CH) ≈ 159, J(CCH) ≈ 7 Hz. – ^{29}Si NMR: δ = −30.78 [tm, J(SiH) = 199.3 Hz]. – IR (Nujol): $\tilde{\nu}$ = 3080 cm^{-1} w, 3062 m, 3040 m, 3008 m, 2930 m, 2135 s, 1587 m, 1482 m, 1334 m, 1319 sh, 1303 m, 1265 m, 1115 s, 1002 s, 930 s, 855 s, 776 m, 730 s, 719 s, 690 s, 643 s, 541 w, 460 m, 385 m. – MS: m/z = 334–327 [$C_{19}Si_3H_x$], 257–251 [$C_{13}Si_3H_x$], 185–178 [$C_7Si_3H_x$], 150–145 [$C_7Si_2H_x$], 108–105 [C_6SiH_x].

Experiments with *dibromomethane*/chloro(phenyl)silane and magnesium in tetrahydrofuran gave high yields of $CH_2(SiH_2Ph)_2$ following the same procedure.

Bis- and Tris(bromosilyl)methane. – General Procedure: An excess of dry hydrogen bromide gas was condensed into a Schlenk tube containing bis- or tris(phenylsilyl)methane at liquid nitrogen temperature. The mixture was warmed to −78°C for a few hours, when the contents of the reaction vessel became homogeneous. Hydrogen bromide not consumed in the process was evaporated by warming the mixture to room temp., the benzene formed in the reaction was removed under reduced pressure, and the product isolated by distillation.

Bis(bromosilyl)methane: 6.0 g (0.026 mol) of $CH_2(SiH_2Ph)_2$ gave 5.3 g (92%) of product after 3 h, b.p. 67–69°C at 20 Torr. – ^1H NMR: δ = 0.23 (quint, CH_2), 4.29 [t, J(HSiCH) = 3.4 Hz, SiH_2]. – ^{13}C NMR: δ = −2.15 [tquint, J(CH) = 119.0, J(CCH) = 8.3, J(SiC) = 46.9 Hz]. – ^{29}Si NMR: δ = −22.18 [ttt, J(SiH) = 241.2, J(SiCH) = 9.4, J(SiCSiH) = 4.4 Hz]. – IR (film): $\tilde{\nu}$ = 2931 cm^{-1} w, 2854 w (νCH_2); 2179 s (νSiH_2); 1054 m (δCH_2); 941 m, 878 m (δSiH_2); 843 s (ϱCH_2); 765 m (νSiC); 639 w (ϱSiH_2); 390 m (νSiBr). – MS: m/z = 236–230 [$CBr_2Si_2H_x$], 156–150 [$CBrSi_2H_x$], 111–107 [$BrSiH_x$], 74–68 [CSi_2H_x], 45–41 [$CSiH_x$].

Tris(bromosilyl)methane: 11.7 g (0.035 mol) of $CH(SiH_2Ph)_3$ gave 9.8 g (84%) of product after 10 h, b.p. 56–58°C at 0.2 Torr. – ^1H NMR: δ = −0.01 (sept, CH), 4.40 [d, J(HSiCH) = 3.7 Hz, SiH_2]. – ^{13}C NMR: δ = −3.98 [dsept, J(CH) = 112.6, J(CCH) = 8.4, J(SiC) = 39.3 Hz]. – ^{29}Si NMR: δ = −23.04 [tdquint, J(SiH) = 249.5, J(SiCH) = 10.0, J(SiCSiH) = 4.3 Hz]. – IR (film): $\tilde{\nu}$ = 2907 cm^{-1} w, 2839 w (νCH); 2165 s (νSiH_2); 1085 m, 1000 s (δCH); 924 m, 846 w (δSiH_2); 832 s (ϱCH); 790 m (νSiC); 670 w (ϱSiH_2); 411 m (νSiBr). – MS: m/z = 347–338 [$CBr_3Si_3H_x$], 267–260 [$CBr_2Si_3H_x$], 235–228 [$CBr_2Si_2H_x$], 155–148 [$CBrSi_2H_x$], 111–107 [$BrSiH_x$], 73–68 [CSi_2H_x], 45–41 [$CSiH_x$].

Di(silyl)methane: A solution of bis(bromosilyl)methane (5.2 g, 0.023 mol) in 50 ml of tetrahydronaphthalene was added at room temp. to a suspension of lithium aluminum hydride (3.5 g, 0.092 mol) and benzyltriethylammonium chloride (0.52 g, 2.3 mmol) in 150 ml of tetrahydronaphthalene. The reaction mixture was stirred for 24 h at ambient temp. and finally for 4 h at 80°C. Under reduced pressure the product was removed, passed through a condenser cooled to −25°C, and received in a Schlenk tube kept at liquid nitrogen temp. The yield was 1.6 g (91%), b.p. 15°C. Impurities detected by GC/MS analysis (traces of triethylamine and of the solvent) were removed by fractional distillation. – ^1H NMR: δ = −0.53 (sept, CH_2), 3.63 [t, J(HSiCH) = 4.7 Hz, SiH_3]. – ^{13}C NMR: δ = −21.04 [tsept, J(CH) = 118.8, J(CSiH) = 4.9, J(SiC) = 43.9 Hz]. – ^{29}Si NMR: δ = −59.97 [qtq, J(SiH) = 197.7, J(SiCH) = 9.5, J(SiCSiH) = 4.5 Hz]. – IR (film): $\tilde{\nu}$ = 2959 cm^{-1} w, 2930 w, 2862 w (νCH_2); 2158 s (νSiH_3); 1054 m (δCH_2); 951 s, 912 s (δSiH_3); 806 s (ϱCH_2); 764 s (νSiC).. – MS: m/z = 76–68 [CSi_2H_x], 46–41 [$CSiH_x$], 31–28 [SiH_x].

Tri(silyl)methane: To a suspension of lithium aluminum hydride (6.6 g, 0.174 mol) and benzyltriethylammonium chloride (0.98 g, 4.35 mmol) in 200 ml of tetrahydronaphthalene was added with stirring a solution of tris(bromosilyl)methane (9.8 g, 0.029 mol) in 50 ml of tetrahydronaphthalene. The mixture was treated as described above for di(silyl)methane. Distillation yielded 2.5 g (83%) of the product as a colourless liquid, b. p. 61°C. GC/MS analysis indicated traces of tetrahydronaphthalene, which can be removed by fractional condensation. − ^{1}H NMR: δ = −1.17 (dec, CH), 3.71 [d, J(HSiCH) = 4.4 Hz, SiH_3]. − ^{13}C NMR: δ = −30.61 [ddec, J(CH) = 113.6, J(CSiH) = 5.5, J(SiC) = 37.8 Hz]. − ^{29}Si NMR: δ = −53.30 [qdsept, J(SiH) = 202.2, J(SiCH) = 9.2, J(SiCSiH) = 4.6 Hz]. − IR (film): ṽ = 2957 cm^{-1} w, 2925 w, 2855 w (νCH); 2153 s (νSiH_3); 1024 m (δCH); 969 m, 939 s, 908 s (δSiH_3); 826 s (ϱCH); 783 m (νSiC). − MS: m/z = 107−96 [CSi_3H_x], 76−68 [CSi_2H_x], 60−56 [Si_2H_x], 45−41 [$CSiH_x$], 32−28 [SiH_x].

Crystal Structure Determination of Tris(phenylsilyl)methane[26]: Syntex P2$_1$ diffractometer, Mo-K_α radiation, λ = 0.71069 Å, graphite monochromator, T = 23°C. − Crystal size: 0.30 × 0.30 × 0.35 mm. − Crystal data: $C_{19}H_{22}Si_3$, M = 334.65, space group $R\bar{3}$ with $a = b = 12.932(2)$, $c = 19.765(3)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 2862.6$ Å^3, $Z = 6$, $d_{calcd.} = 1.165$ gcm^{-3}, μ(Mo-K_α) = 2.4 cm^{-1}, $F(000) = 1068$. The intensities of 3364 reflexions were collected up to (sin Θ/λ) = 0.595 Å^{-1} (hkl range: ±15, ±15, +23) and averaged to 1123 unique data (R_{int} = 0.02), 1048 of which with $F_o \geq 4.0\sigma(F_o)$ were considered "observed" and used for all further calculations. Lp and empirical absorption corrections were applied (relative transmission: 0.87 − 1.00). The structure was solved by direct methods (SHELXS-86)[27] and refined with anisotropic displacement parameters. All hydrogen atoms were located but not refined. R (R_w) = 0.039 (0.046), $w = 1/\sigma^2(F_o)$, 67 refined parameters. The residual electron density was featureless: +0.29/−0.30 eÅ^{-3}.

CAS Registry Numbers

$CH_2(SiH_2Ph)_2$: 26799-07-5 / $CH(SiH_2Ph)_3$: 121232-83-5 / $CH_2(SiH_2Br)_2$: 58962-77-9 / $CH(SiH_2Br)_3$: 121232-84-6 / $CH_2(SiH_3)_2$: 1759-88-2 / $CH(SiH_3)_3$: 4335-85-7 / ClH_2SiPh: 4206-75-1 / H_3SiPh: 694-53-1 / $SnCl_4$: 7646-78-8 / $CHBr_3$: 75-25-2 / CH_2Br_2: 74-95-3

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[25] See Experimental.

[26] Further crystal structure data including complete tables of atomic parameters and observed and calculated structure factors have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2. Inquiries should be accompanied by quoting the depository number CSD-53782, the names of the authors, and the full literature citation.

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