

# Synthetic Pathways to Disilylmethane, $\text{H}_3\text{SiCH}_2\text{SiH}_3$ , and Methylidisilane, $\text{CH}_3\text{SiH}_2\text{SiH}_3$ <sup>1)</sup>

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Disilylmethane is available in a four-step synthesis starting with phenylsilane. This is converted into chlorophenylsilane by  $\text{HCl}/\text{AlCl}_3$ . The reaction of  $\text{PhSiH}_2\text{Cl}$  and dibromomethane with magnesium in tetrahydrofuran affords bis(phenylsilyl)methane, which yields bis(bromosilyl)methane by treatment with anhydrous hydrogen bromide.  $(\text{BrH}_2\text{Si})_2\text{CH}_2$  is converted into disilylmethane by reduction with  $\text{LiAlH}_4$  in a two-phase

system using a phase-transfer catalyst. – Methylidisilane is available by alkylation of a monohalodisilane,  $\text{XSi}_2\text{H}_5$  ( $\text{X} = \text{Cl}, \text{Br}$ ), with methyl lithium in a high-boiling ether or by silylation of bromomethylsilane with silylpotassium. Due to secondary silylation reactions the overall yields of methylidisilane are low in all cases.

Hydrogenated amorphous silicon carbide (a-SiC:H) has shown much promise as a material for thin-film device applications such as solar cells, photoreceptors, and many other photoelectric units. Layers of this kind are deposited in glow-discharge (plasma) chemical vapour deposition (CVD) processes using mixtures of silane gas, hydrogen and methane, acetylene, or other hydrocarbons<sup>2)</sup>.

The higher thermodynamical stability of C–H bonds as compared to Si–H bonds causes differences in the depositing rates of carbon and silicon from the plasma. As a consequence, even the number of the carbon atoms in the silicon framework and the nature of their incorporation are difficult to control. Currently, there is a growing interest in using volatile organosilanes with a high silicon content as carbon sources, where the desired Si–C linkages are already given in the substrate such that a more effective incorporation of carbon should be possible. The most promising feedstock gases of this kind are the polysilylmethanes  $(\text{H}_3\text{Si})_n\text{CH}_{4-n}$  with  $n = 1-4$ .

Recent investigations have shown a close relationship between the physical properties of the a-SiC:H layer – e. g. the band gap and the photoconductivity – and its structural features. The photoelectrical quality of the thin film decreases with an increasing number of methyl groups, the carbon atoms of which cannot participate in the building of the amorphous network. It is therefore not surprising that experiments using methylsilane,  $\text{CH}_3\text{SiH}_3$ , as a CVD feedstock gas instead of methane have shown only moderate success<sup>3,4)</sup>. However, more recent studies with disilylmethane,  $(\text{H}_3\text{Si})_2\text{CH}_2$ , gave a-SiC:H layers containing a reduced number of  $\text{CH}_3$  groups, as detected by infrared spectroscopy and effusion measurements, as well as by the enhanced photoconductivity<sup>5-7)</sup>.

Except for these results, only a few data are available about the dependence of the physical properties of the amor-

phous silicon carbide on the molecular structure of the feedstock gas. The knowledge of these relations is a prerequisite for manipulating the physical characteristics of photovoltaic films by changing the structure and stoichiometry of the substrate gas. A direct comparison of a-SiC:H layers deposited from organosilanes with isomeric structures appears to be a possible systematic approach to obtain such information.

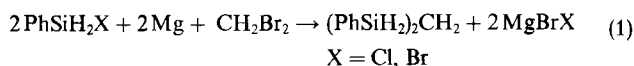
Prompted by the encouraging results with disilylmethane as a feedstock gas, we have developed a new synthesis for this compound. This study is part of our continuing efforts to explore new economical preparative pathways to polysilylmethanes and organosilanes for CVD application<sup>8-13)</sup>. Furthermore, we have probed synthetic routes to the only possible isomer of disilylmethane, i. e. methylidisilane,  $\text{CH}_3\text{SiH}_2\text{SiH}_3$ .

## Disilylmethane

Among the range of synthetic methods developed for disilylmethane to date, the  $\text{LiAlH}_4$  reduction of bis(trichlorosilyl)methane  $(\text{Cl}_3\text{Si})_2\text{CH}_2$  is most prominent<sup>8)</sup>. This hexachloro compound is available either by a direct synthesis using dichloromethane and a Si/Cu alloy as starting materials<sup>14)</sup> or by the Benkeser reaction of chloroform and trichlorosilane with a tertiary amine<sup>8,15)</sup>. Treatment of dichloro- or dibromomethane with silyl potassium,  $\text{KSiH}_3$ , yields only small amounts of disilylmethane<sup>16,17)</sup>.  $(\text{H}_3\text{Si})_2\text{CH}_2$  has now more recently become available as a by-product in the synthesis of tri- and tetrasilylmethane<sup>12,13)</sup> via phenylated precursors.

This observation has led to an investigation aiming at the construction of the Si–C–Si framework of disilylmethane by an in-situ Grignard reaction of a monohalophenylsilane with methylene bromide,  $\text{CH}_2\text{Br}_2$ , and magnesium under Merker-Scott conditions in boiling tetrahydrofuran<sup>18)</sup> lead-

ing to bis(phenylsilyl)methane as the primary product (Eq. 1).



Monohalophenylsilanes,  $\text{PhSiH}_2\text{X}$ , are stable compounds that can be prepared on a large scale. The phenyl group may be substituted by hydrogen in two high-yield steps as described later. Consequently,  $\text{PhSiH}_2\text{X}$  compounds may serve as synthons for the corresponding halosilanes,  $\text{H}_3\text{SiX}$ , which are difficult to handle owing to their low boiling points, their inflammability in air, and their tendency to undergo redistribution reactions. Bromophenylsilane,  $\text{PhSiH}_2\text{Br}$ , is obtained by partial Si–Ph cleavage in diphenylsilane with hydrogen bromide at  $-78^\circ\text{C}$  according to the method of Fritz and Kummer<sup>19</sup> (Eq. 2).



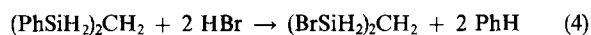
Chlorophenylsilane,  $\text{PhSiH}_2\text{Cl}$ , is prepared by treatment of phenylsilane with dry HCl gas in diethyl ether in the presence of solid  $\text{AlCl}_3$  (Eq. 3, 90% yield). Only traces of dichlorophenylsilane,  $\text{PhSiHCl}_2$ , and benzene, resulting from Si–phenyl cleavage, are detected by GC-MS analysis of the raw product.



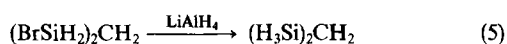
In the Merker-Scott reaction (1) the two halophenylsilanes (X = Cl, Br) give different yields of  $(\text{PhSiH}_2)_2\text{CH}_2$ : With chlorophenylsilane, 40% of the expected product is obtained, whereas bromophenylsilane yields only 25% of bis(phenylsilyl)methane. Under Merker-Scott conditions, the reaction of  $\text{PhSiH}_2\text{Br}$  leads to a cleavage of the THF solvent to yield high-boiling products resulting in a serious decrease of the yield.

Bis(phenylsilyl)methane thus obtained is a colourless, air-stable liquid with spectroscopic characteristics (see Experimental) in agreement with previously reported data<sup>12,20</sup>.

The reaction of  $(\text{PhSiH}_2)_2\text{CH}_2$  with an excess of dry hydrogen bromide at  $-78^\circ\text{C}$  yields bis(bromosilyl)methane in good yields (81%, Eq. 4)<sup>12</sup>.



Bis(bromosilyl)methane, also a liquid, is converted into disilylmethane in nearly quantitative yield by treatment with  $\text{LiAlH}_4$  (Eq. 5) using a two-phase system and a phase-transfer catalyst to suppress the cleavage of Si–C bonds in  $(\text{BrSiH}_2)_2\text{CH}_2$ <sup>12</sup>.



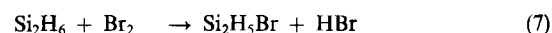
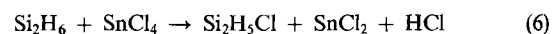
All intermediates in this new four-step synthesis of disilylmethane can be handled without difficulty and are available in large quantities using standard laboratory equipment. The individual reaction steps give good to quantita-

tive yields. Disilylmethane is obtained in high purity in an economical process from commercial chemicals such that this route can be regarded as superior to previous methods.

### Methyldisilane

Small amounts of methyldisilane have been synthesized in a glow discharge experiment using a mixture of  $\text{SiH}_4$  and dimethyl ether<sup>21</sup>. This compound has also been observed in the pyrolysis of disilane,  $\text{Si}_2\text{H}_6$ , in the presence of an excess of methylsilane,  $\text{CH}_3\text{SiH}_3$ <sup>22</sup>. Small amounts of  $\text{CH}_3\text{Si}_2\text{H}_5$  have been prepared by direct alkylation of bromodisilane with MeLi in diethyl ether<sup>23</sup> and by direct methylation of  $\text{Si}_2\text{H}_6$  with methyllithium<sup>24</sup>. This reaction, however, gives extremely low yields, and the product is obtained in minute quantities as confirmed by our own studies.

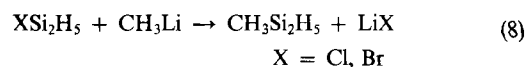
Monohalogenation of disilane and treatment of the obtained product with a methylating agent have appeared to be a more attractive route for the preparation of methyldisilane. A number of methods have been developed for the halogenation of  $\text{Si}_2\text{H}_6$  to date, using hydrogen halides, elemental halogen, or metal halides, but most of these are only useful for small-scale syntheses<sup>24,25</sup>. For reactions on a larger scale chlorination with  $\text{SnCl}_4$  in mesitylene<sup>26</sup> (Eq. 6) and bromination with elemental bromine in octane are more practical (Eq. 7).



Working in solution and efficient cooling are indispensable to control the exothermic reaction and to avoid the danger of explosions, especially in the bromination. In both methods, however, there is the possibility of 1,2-di- or polyhalogenation of disilane, which can be suppressed only ineffectively by using an excess of  $\text{Si}_2\text{H}_6$ . As a consequence of this poor selectivity of the halogenation, the yields of monosubstituted disilanes are below 20% even if the stoichiometric ratio of  $\text{Si}_2\text{H}_6$  to  $\text{SnCl}_4$  and of  $\text{Si}_2\text{H}_6$  to  $\text{Br}_2$  is 1:0.8 and 1:0.5, respectively. In each case considerable amounts of dihalodisilanes are detected.

Monochloro- and monobromodisilane are colourless liquids, which ignite in air and can only be handled in a closed system. The compounds are isolated by a low-temperature distillation under vacuum by using a cooled column as described by F  her<sup>26</sup>.

Both halodisilanes are converted into methyldisilane in good yield (ca. 50%, Eq. 8) by alkylation with methyllithium in a high-boiling ether. Traces of  $\text{CH}_3\text{SiH}_3$  and  $\text{Si}_2\text{H}_6$  (ca. 15%) resulting from a reduction of the halosilane are formed as by-products which can be separated by fractional condensation.



Methyldisilane is a colourless liquid, b. p.  $16^\circ\text{C}$ , and very sensitive to air. It is characterized by standard analytical methods (see Experimental).

Disilylmethane,  $\text{H}_3\text{SiCH}_2\text{SiH}_3$ , and Methylidisilane,  $\text{CH}_3\text{SiH}_2\text{SiH}_3$

Silylation of bromomethylsilane,  $\text{CH}_3\text{SiH}_2\text{Br}$ , by silylpotassium,  $\text{KSiH}_3$ , is an alternative to build up the C—Si—Si frame of methylidisilane. Bromomethylsilane has previously been synthesized by halogenation of methylsilane with elemental bromine<sup>27)</sup> or  $\text{HBr}/\text{AlBr}_3$ <sup>28)</sup> and by bromination of iodomethylsilane,  $\text{CH}_3\text{SiH}_2\text{I}$ , with  $\text{AgBr}$ <sup>29)</sup>. A superior method is the cleavage of a phenyl group of methylphenylsilane with an excess of pure  $\text{HBr}$  at  $-78^\circ\text{C}$  (Eq. 9) which yields 91% of bromomethylsilane as a colourless and moisture-sensitive liquid (b. p.  $36^\circ\text{C}$ ).



The nucleophilic substitution of the bromine atom of  $\text{CH}_3\text{SiH}_2\text{Br}$  by a silyl group (Eq. 10) in diglyme has been found to be a vigorous reaction. Potassium bromide and other products are formed instantaneously.



Methylidisilane, however, is only obtained in 5% yield. Significant amounts of methylsilane and disilane have been detected by GC-MS and infrared analysis of the volatile products. Furthermore, dimethylidisilane and unsubstituted mono-, and dimethylated tri- and tetrasilanes are detected in the product mixture which is difficult to separate. It may be assumed that secondary silylation of initially formed methylidisilane leads to silanes with concomitant formation of  $\text{KH}$ , which gives rise to the reduction of  $\text{CH}_3\text{SiH}_2\text{Br}$  to  $\text{CH}_3\text{SiH}_3$ .

In summary, methylidisilane is available by two different two-step syntheses starting from disilane and methylphenylsilane, respectively. The silylation of  $\text{CH}_3\text{SiH}_2\text{Br}$  yields only small quantities of methylidisilane containing a number of other methylated (poly)silanes. Alkylation of a monohalodisilane gives methylidisilane in good yield and high purity. This method of preparation is superior, although it has to be accepted that the quality of halodisilanes produced is limited even with high experimental sophistication.

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## Experimental

All experiments were carried out under pure, dry nitrogen. Solvents were purified, dried, and kept under nitrogen. — NMR:  $\text{C}_6\text{D}_6$  as solvent, tetramethylsilane as internal standard, Bruker WP 100 SY, Jeol GX 270, Jeol GX 400 spectrometers. — IR: films between KBr plates, Nicolet FT 5 DX spectrophotometer. — Gas chromatography: columns SIL 5, Hewlett Packard GC 5890 A instrument with a mass-sensitive detector MSD 5970 (EI, 70 eV).

*Starting Materials:* Phenylsilane, diphenylsilane, and methylphenylsilane were obtained by  $\text{LiAlH}_4$  reduction of  $\text{PhSiCl}_3$ ,  $\text{Ph}_2\text{SiCl}_2$ , and  $\text{CH}_3\text{SiCl}_2\text{Ph}$ , respectively. Bromophenylsilane was

prepared from diphenylsilane according to the method of Fritz and Kummer<sup>19)</sup>. Chlorodisilane was synthesized by halogenation of disilane with  $\text{SnCl}_4$ <sup>26)</sup>. Silylpotassium was obtained by cleavage of disilane with K/Na alloy<sup>30)</sup>.

*Chlorophenylsilane:* A mechanically stirred solution of 184.0 g (1.7 mol) of phenylsilane in 150 ml of diethyl ether was saturated with dry HCl gas at room temperature. After the addition of 1 g  $\text{AlCl}_3$ , vigorous  $\text{H}_2$  evolution was observed. During the reaction a slow stream of HCl was passed through the solution, and occasionally more  $\text{AlCl}_3$  was added such that there was always some solid catalyst present in the reaction mixture. When the evolution of hydrogen had stopped (ca. 24 h), the solvent was removed under reduced pressure. Distillation of the remaining liquid yielded 216.0 g (89%) of  $\text{PhSiH}_2\text{Cl}$ , b. p.  $58^\circ\text{C}/14$  Torr. —  $^1\text{H}$  NMR:  $\delta = 5.05$  [s, SiH,  $J(\text{SiH}) = 236$  Hz], 7.3 (m, Ph). — MS:  $m/z = 144-141$  [ $\text{C}_6\text{ClSiX}_x$ ], 107–105 [ $\text{C}_6\text{SiH}_x$ ], 79–77 [ $\text{C}_4\text{SiH}_x$ ], 65/63 [ $\text{ClSi}$ ].

*Bis(phenylsilyl)methane, General Procedure:* A mechanically stirred solution of dibromomethane in tetrahydrofuran was added dropwise (ca. 5 h) to a mixture of a halophenylsilane  $\text{PhSiH}_2\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and magnesium turnings in refluxing tetrahydrofuran. External heating was reduced as the exothermic nature of the reaction enabled the refluxing to be maintained. After completion of the addition and a further reflux period of 4 h, the mixture was poured onto crushed ice, neutralised with sodium hydrogencarbonate and filtered. The organic layer was diluted with 200 ml of hexane, washed twice with water (200 ml each) and dried with magnesium sulfate. Solvents and low-boiling reaction products were removed in vacuo, and bis(phenylsilyl)methane was isolated as a colourless liquid from the remaining yellow oil by distillation, b. p.  $95^\circ\text{C}/0.2$  Torr.

*Reaction with Chlorophenylsilane:* The reaction of 15.8 g (111 mmol) of  $\text{PhSiH}_2\text{Cl}$  in 60 ml of THF with 3.0 g (123 mmol) of magnesium and 9.7 g (56 mmol) of dibromomethane in 200 ml of THF yielded 5.0 g (40%) of bis(phenylsilyl)methane.

*Reaction with Bromophenylsilane:* 26.0 g (130 mmol) of  $\text{PhSiH}_2\text{Br}$  in 100 ml of THF was treated with 3.6 g (146 mmol) of magnesium and 12.1 g (70 mmol) of dibromomethane in 250 ml of THF. Yield: 4.0 g (25%) of bis(phenylsilyl)methane. —  $^1\text{H}$  NMR:  $\delta = 0.18$  [quint,  $\text{CH}_2$ ,  $J(\text{HCSiH}) = 4.4$  Hz], 4.62 (t,  $\text{SiH}_2$ ), 7.3 (m, Ph). —  $^{13}\text{C}$  NMR:  $\delta = -11.1$  [t · quint,  $J(\text{CH}) = 116.7$ ,  $J(\text{CSiH}) = 6.4$ ,  $J(\text{SiC}) = 44.5$  Hz,  $\text{CH}_2$ ], 128.26 (dd, C-2/C-6), 129.89 (dt, C-4), 133.03 (m, C-1), 135.29 (dm, C-3/C-5),  $J(\text{CH}) = 159.5$ ,  $J(\text{CCCH}) = 7$  Hz. —  $^{29}\text{Si}$  NMR:  $\delta = -33.48$  [tm,  $J(\text{SiH}) = 196.3$  Hz]. — IR (film):  $\tilde{\nu} = 3070$   $\text{cm}^{-1}$  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:  $m/z = 229-223$  [ $\text{C}_{13}\text{Si}_2\text{H}_x$ ], 184–180 [ $\text{C}_{12}\text{SiH}_x$ ], 152–140 [ $\text{C}_7\text{Si}_2\text{H}_x$ ], 107–105 [ $\text{C}_6\text{SiH}_x$ ].

*Bis(bromosilyl)methane<sup>12)</sup>:* An excess of dry hydrogen bromide was condensed into a Schlenk tube containing 13.3 g (58 mmol) of bis(phenylsilyl)methane at  $-196^\circ\text{C}$ . The reaction mixture was stirred at  $-78^\circ\text{C}$  for 8 h and then warmed to room temp. to evaporate excess hydrogen bromide. The benzene formed in the reaction was removed under reduced pressure. Distillation of the remaining liquid yielded 11.0 g (81%) of bis(bromosilyl)methane, b. p.  $46^\circ\text{C}/8$  Torr. —  $^1\text{H}$  NMR:  $\delta = 0.21$  (quint,  $\text{CH}_2$ ), 4.28 [t,  $J(\text{HSiCH}) = 3.4$  Hz,  $\text{SiH}_2$ ]. —  $^{13}\text{C}$  NMR:  $\delta = -2.15$  [t · quint,  $J(\text{CH}) = 119.0$ ,  $J(\text{CSiH}) = 8.3$ ,  $J(\text{SiC}) = 46.9$  Hz]. —  $^{29}\text{Si}$  NMR:  $\delta = -22.2$  [ttt,  $J(\text{SiH}) = 241.1$ ,  $J(\text{SiCH}) = 9.4$ ,  $J(\text{SiCSiH}) = 4.4$  Hz]. — IR (film):  $\tilde{\nu} = 2931$   $\text{cm}^{-1}$  w, 2854 w ( $\nu\text{CH}_2$ ), 2179 s ( $\nu\text{SiH}_2$ ), 1054 m ( $\delta\text{CH}_2$ ), 941 m, 878 m ( $\delta\text{SiH}_2$ ), 843 s ( $\nu\text{CH}_2$ ), 765 m ( $\nu\text{SiC}$ ), 639 w ( $\nu\text{SiH}_2$ ).

390 m (νSiBr). — MS:  $m/z = 236-230$  [CBr<sub>2</sub>Si<sub>2</sub>H<sub>x</sub>], 158–150 [CBrSi<sub>2</sub>H<sub>x</sub>], 111–107 [BrSiH<sub>x</sub>], 72–68 [CSi<sub>2</sub>H<sub>x</sub>], 45–41 [CSiH<sub>x</sub>].

**Disilylmethane**<sup>12</sup>: A solution of 9.0 g (38.5 mmol) of bis(bromosilyl)methane in 20 ml of 1,2,3,4-tetrahydronaphthalene was added to a suspension of 5.9 g (155 mmol) of LiAlH<sub>4</sub> and 0.88 g (3.85 mmol) of benzyltriethylammonium chloride in 100 ml of tetrahydronaphthalene. The reaction mixture was stirred at room temp. for 12 h. The product was condensed in vacuo through a condenser cooled to –30 °C into a Schlenk tube cooled in liquid nitrogen, the temperature of the reaction flask being slowly increased from room temp. to 40 °C. The yield was 2.6 g (89%) of disilylmethane, b.p. 15 °C. — <sup>1</sup>H NMR: δ = –0.60 (sept, CH<sub>2</sub>), 3.63 [t, J(HSiCH) = 4.6 Hz, SiH<sub>3</sub>]. — <sup>13</sup>C NMR: δ = –21.05 [t, sept, J(CH) = 118.8, J(CSiH) = 4.9, J(SiC) = 43.9 Hz]. — <sup>29</sup>Si NMR: δ = –59.9 [qtq, J(SiH) = 197.8, J(SiCH) = 9.5, J(SiCSiH) = 4.5 Hz]. — IR (film):  $\tilde{\nu} = 2959$  cm<sup>–1</sup> w, 2930 w, 2862 w (νCH<sub>2</sub>), 2158 s (νSiH<sub>3</sub>), 1054 m (δCH<sub>2</sub>), 951 s, 912 s (δSiH<sub>3</sub>), 806 s (νCH<sub>2</sub>), 764 s (νSiC). — MS:  $m/z = 76-68$  [CSi<sub>2</sub>H<sub>x</sub>], 46–41 [CSiH<sub>x</sub>], 31–28 [SiH<sub>x</sub>].

**Bromodisilane**: A solution of 4.4 g (28 mmol) of bromine in 25 ml of octane was added to a solution of 3.3 g (53 mmol) of disilane in 140 ml of octane at –50 °C in the course of 2.5 h. The volatile components were condensed into a cooling trap (–196 °C) under reduced pressure. The condensation was repeated to remove traces of solvent and higher boiling compounds. The hydrogen bromide formed in the reaction was removed in vacuo by condensing it into a Schlenk tube at –196 °C through a condenser kept at –80 °C by warming the flask containing the product mixture from liquid nitrogen temperature to –80 °C. Disilane, not consumed in the reaction, was evaporated by warming the remaining liquid to room temp. under normal pressure leaving 0.40 g (10%) of bromodisilane in the flask. — <sup>1</sup>H NMR: δ = 3.38 [t, J(SiH) = 204 Hz, SiH<sub>3</sub>], 4.09 [q, J(SiH) = 225, J(HSiSiH) = 2.9 Hz, SiH<sub>2</sub>].

**Methylidisilane, General Procedure**: A stoichiometric amount of a monohalodisilane, XSi<sub>2</sub>H<sub>3</sub> (X = Cl, Br), was condensed into a flask containing a solution of methylolithium in 10 ml of di-*n*-butyl ether at –196 °C. The mixture was warmed to –20 °C and stirred for 15 min. After removing the cooling bath, the volatile compounds were removed under reduced pressure and collected in a Schlenk tube kept at liquid nitrogen temperature, leaving a white precipitate of lithium halide. Methylidisilane was isolated by fractional condensation as a colourless liquid boiling at 16 °C.

**Reaction with Chlorodisilane**: 0.90 g (9.5 mmol) of ClSi<sub>2</sub>H<sub>3</sub> yielded 0.35 g (46%) of CH<sub>3</sub>Si<sub>2</sub>H<sub>3</sub>.

**Reaction with Bromodisilane**: 0.30 g (2.3 mmol) of BrSi<sub>2</sub>H<sub>3</sub> gave 0.10 g (57%) of CH<sub>3</sub>Si<sub>2</sub>H<sub>3</sub>. — <sup>1</sup>H NMR: δ = –0.03 [t, J(HCSiH) = 4.9 Hz, CH<sub>3</sub>], 3.21 [t, J(HSiSiH) = 3.1 Hz, SiH<sub>3</sub>], 3.65 (16 lines of an A<sub>3</sub>M<sub>2</sub>X<sub>3</sub> spin system resolved, SiH<sub>2</sub>). — <sup>13</sup>C NMR: δ = –10.77 [qm, J(CH) = 123.2 Hz, CH<sub>3</sub>]. — <sup>29</sup>Si NMR: δ = –69.4 [tm, J(SiH) = 190.7 Hz, SiH<sub>2</sub>], –101.8 [qm, J(SiH) = 191.2 Hz, SiH<sub>3</sub>]. — MS:  $m/z = 78-69$  [CSi<sub>2</sub>H<sub>x</sub>], 61–56 [Si<sub>2</sub>H<sub>x</sub>], 45–42 [CSiH<sub>x</sub>], 31–28 [SiH<sub>x</sub>].

**Bromomethylsilane**: An excess of pure hydrogen bromide (ca. 30 ml) was condensed into a cooling trap containing 18.2 g (0.15 mol) of methylphenylsilane at liquid nitrogen temperature. The mixture was warmed to –80 °C and stirred for 5 h. The cooling trap was warmed to room temp. to evaporate hydrogen bromide not consumed in the reaction. The HBr gas was passed through a condenser (–45 °C) to hold back the product. Fractional distillation of the trapped liquid yielded 17.0 g (91%) of bromomethylsilane as

a colourless liquid fuming in air, b.p. 36 °C. — <sup>1</sup>H NMR: δ = 0.63 [t, J(HCSiH) = 4.0 Hz, CH<sub>3</sub>], 4.45 (q, SiH<sub>2</sub>). — <sup>13</sup>C NMR: δ = –2.24 [qt, J(CH) = 123.7, J(CSiH) = 8.3, J(SiC) = 55.8 Hz]. — <sup>29</sup>Si NMR: δ = –20.7 (see ref.<sup>27</sup>); δ = –7.4 [tq, J(SiH) = 231.3, J(SiCH) = 7.8 Hz].

**Reaction of Bromomethylsilane with Silylpotassium**: A solution of 0.21 mol of silyl potassium in 560 ml of diglyme was added dropwise to a solution of a stoichiometric amount of bromomethylsilane in 420 ml of diglyme until the colour of the mixture turned orange due to a small excess of silyl potassium. The volatile products were removed under reduced pressure from the solvent and the white precipitate formed in the reaction was collected in a Schlenk tube at liquid nitrogen temperature. Cooling-trap distillation of the raw product (–65, –115, –196 °C) yielded in the –115 °C-trap 0.8 g (5%) of methylidisilane containing traces of dimethylidisilane, trisilane, and methyltrisilane, as detected by GC-MS analysis.

#### CAS Registry Numbers

PhSiH<sub>3</sub>: 694-53-1 / PhSiH<sub>2</sub>Cl: 4206-75-1 / PhSiH<sub>2</sub>Br: 1631-90-9 / CH<sub>3</sub>Br: 74-95-3 / (PhSiH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>: 26799-07-5 / (BrSiH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>: 58962-77-9 / (H<sub>3</sub>Si)<sub>2</sub>CH<sub>2</sub>: 1759-88-2 / Si<sub>2</sub>H<sub>6</sub>: 1590-87-0 / ClSi<sub>2</sub>H<sub>5</sub>: 14565-98-1 / BrSi<sub>2</sub>H<sub>5</sub>: 13819-07-3 / CH<sub>3</sub>Si<sub>2</sub>H<sub>5</sub>: 13498-43-6 / CH<sub>3</sub>SiH<sub>2</sub>Ph: 766-08-5 / CH<sub>3</sub>SiH<sub>2</sub>Br: 1631-88-5

- <sup>1</sup> Dedicated to o. Univ.-Prof. *Edwin Hengge*, Technische Universität Graz, on the occasion of his 60th birthday.
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Disilylmethane,  $\text{H}_3\text{SiCH}_2\text{SiH}_3$ , and Methylidisilane,  $\text{CH}_3\text{SiH}_2\text{SiH}_3$

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