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Flash Pyrolysis of 1,1,1-Trimethyltetrasilane – Evidence for the Formation of Dibridged Si_2H_2

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Pulsed flash pyrolysis of 1,1,1-trimethyltetrasilane (**5**) led to trimethylsilane, silane and a further species which is believed to be dibridged Si_2H_2 (**13**). Another route to **13** was found in the cocondensation of hydrogen and silicon atoms in an argon matrix at 12 K. The identification of matrix-isolated **13** is based on observed IR bands at 1475.6, 1092.8 and 890.3 cm^{-1}. These positions are in good agreement with the ab initio calculated wavenumbers for the strongest absorptions of **13**. The band shifts for the mono- and dideuterated isotopomers support this assignment.

The current growing interest in small unsaturated silicon compounds is due to the important role of such intermediates in chemical vapor deposition (CVD). Si_2H_2 has been proposed as one possible participant in the deposition of silicon starting from silanes[1]. Even following the report of Demuynck et al. concerning the submillimeter wave rotational spectra for mono- and dibridged Si_2H_2 isomers generated in a low-power SiH_4 plasma at −196°C[2–4], the formation of these compounds by more selective methods remained, for us, a challenging project within the scope of our investigations of silicon π systems. Apart from obtaining their IR and UV spectra, the matrix isolation of these compounds may also allow their photochemical interconversion into the elusive bent disilyne[5], which was not observed by Demuynck and coworkers.

Results and Discussion

Synthesis of 1,1,1-Trimethyltetrasilane

1,1,1-Trimethyltetrasilane (**5**) was synthesized for the first time, by our group, as outlined below. The tetrasilane moiety was built up by the reaction of chlorodisilane **1** and lithiodisilane **2**. Total dephenylation could be achieved by stirring tetraphenyltetrasilane **3** in liquid HBr at −72°C for one week, thus yielding tetrabromotetrasilane **4**. The reduction of crude **4** with $LiAlH_4$ in diethyl ether at 0°C resulted in a very small amount of the desired tetrasilane **5**. The pyrophoric compound was isolated by preparative gas chromatography.

$$\underset{\mathbf{1}}{PhH_2Si{-}SiHClPh} + \underset{\mathbf{2}}{Me_3Si{-}SiPh_2Li} \longrightarrow$$

$$\underset{\mathbf{3}}{Me_3Si{-}SiPh_2{-}SiHPh{-}SiH_2Ph} \xrightarrow{HBr}$$

$$\underset{\mathbf{4}}{Me_3Si{-}SiBr_2{-}SiHBr{-}SiH_2Br} \xrightarrow{LiAlH_4}$$

$$\underset{\mathbf{5}}{Me_3Si{-}SiH_2{-}SiH_2{-}SiH_3}$$

Chlorodisilane **1** could be synthesized by selective monochlorination of 1,2-diphenyldisilane (**9**) with PCl_5 under mild conditions. The synthesis of diphenyldisilane **9** started with commercially available trichlorophenylsilane **6**, which was reduced in nearly quantitative yield to phenylsilane (**7**). This compound was brominated with bromine in pentane. Coupling of bromophenylsilane (**8**) with lithium sand resulted in 1,2-diphenyldisilane (**9**). This sequence represents a shorter route, with a better overall yield, when compared with the synthesis of **9** as reported by Mawaziny[6].

$$\underset{\mathbf{6}}{PhSiCl_3} \xrightarrow{LiAlH_4} \underset{\mathbf{7}}{PhSiH_3} \xrightarrow{Br_2} \underset{\mathbf{8}}{PhSiH_2Br} \xrightarrow{Li} \underset{\mathbf{9}}{(PhH_2Si)_2}$$

Lithiodisilane **2** is available via a two-step synthesis. Dichlorodiphenylsilane (**10**) and chlorotrimethylsilane were coupled using magnesium as reducing agent. The resulting trisilane **11** was treated with one equivalent of methyllithium in tetrahydrofuran to give the compound **2** quantitatively.

$$\underset{\mathbf{10}}{Ph_2SiCl_2} \xrightarrow{2\ Me_3SiCl,\ Mg} \underset{\mathbf{11}}{Ph_2Si(SiMe_3)_2} \xrightarrow{MeLi} \underset{\mathbf{2}}{Ph_2Si(SiMe_3)Li}$$

Pulsed Flash Pyrolysis of 1,1,1-Trimethyltetrasilane

When gaseous mixtures of tetrasilane **5** and argon (1:1000) were subjected to *high-vacuum* flash pyrolysis, fol-

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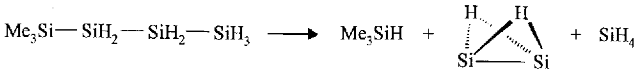
[◇] Part 22: Ref.[7].

lowed by the direct condensation of the reaction products onto a spectroscopic window at 12 K, only large amounts of silane (**14**) and trimethylsilane (**12**) were found. No Si_2H_2 isomers, which may have been formed, were sufficiently stable to be observed upon application of these routine pyrolysis conditions.

As in the case of silacyclopropenylidene[7], the breakthrough was found in the *pulsed* flash pyrolysis of the gaseous mixture. When this method was applied to tetrasilane **5**, the IR spectrum of the products showed, in addition to the bands of silane and trimethylsilane, additional weak absorptions at 1475.6, 1092.8 and 890.3 cm^{-1}.



5 **12** **13** **14**

A comparison with the theoretical IR spectrum shows that these bands are close to the strongest, predicted, IR bands of **13**. The wavenumbers given in Table 1 were obtained from high level calculations [BD(TZ2P + *f*/DZP)] by Handy et al.[8], which include the anharmonic contributions to the fundamental frequencies.

Table 1. Experimentally observed (Ar matrix, 10 K) and calculated [BD(TZ2P + *f*/DZP)][8] IR absorptions [cm^{-1}] of dibridged Si_2H_2 (**13**). Experimental relative intensities (peak areas) and calculated [MP2(TZ2P + *f*)/SCF(DZP)][8] absolute intensities [km mol^{-1}] in parentheses. The geometry of **13** and the assignment of the vibrations are given in ref.[8]

Vibration		13, obsd.	13, calcd.
ν_1	a_1	-	1552 (9)
ν_5	b_1	1475.6 (1)	1479 (46)
ν_6	b_2	1092.8 (100)	1092 (438)
ν_4	a_2	-	1004 (0)
ν_2	a_1	890.3 (3)	902 (76)
ν_3	a_1	-	575 (2)

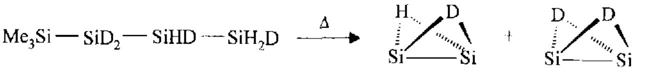
All other vibrations appear to be too weak for experimental observation. Futhermore, no characteristic UV/Vis bands between 200 and 800 nm were registered. It was therefore necessary to confirm the tentative assignment by other means. Suitable deuteration of the precursor **5** should provide such a possibility. For instance, fragmentation of the precursor **15** should result in the formation of the mono- and dideuterated isotopomers of Si_2H_2, which should exhibit characteristic isotopic shifts.

The preparation of tetrasilane **15** was straightforward. Upon reduction of tetrabromotetrasilane **4** with $LiAlD_4$, instead of $LiAlH_4$, 2,2,3,4-tetradeuteriotetrasilane **15** was formed and this was isolated by preparative GC.

Pulsed flash pyrolysis of tetradeuteriotetrasilane **15** resulted in two new bands, which were assigned to the monodeuterated isotopomer **16** and the dideuterated derivative **17**. The formation of these compounds can be explained by an α elimination of $(CH_3)_3SiD$ at Si-2 and of SiH_2D_2 or SiH_3D at Si-3. Both experimentally observed isotopic shifts for the most intense band are in satisfactory agreement with the ab initio (BLYP/6-31G**)[9] results (Table 2). In the case of the deuterated species the additional bands were too weak to be observed.

Table 2. Comparison of the experimentally observed and calculated (BLYP/6-31G**)[9] wavenumbers for the most intense IR band of **13**, **16**, and **17**. Calculated absolute intensities [km mol^{-1}] in parentheses

	13	16	17
exp.	1092.8	1060.8	818.2
calcd.	1102 (329)	1067 (191)	799 (173)



15 **16** **17**

Photochemistry of Dibridged Si_2H_2 (13)

Having elucidated the nature of the reactive intermediates formed in the pyrolysis of trimethyltetrasilane **5**, it was tempting to find out whether a photochemical interconversion of matrix-isolated **13** into other Si_2H_2 isomers could be initiated. The possible formation of acetylene-like, trans-bent disilyne was of particular interest.

Compound **13** proved to be photostable at all wavelengths $\lambda > 254$ nm. Irradiation with 254 nm light resulted in a slow decrease of the 1092.8 cm^{-1} absorption. After 20 hours the band had nearly vanished but we were not able to find any experimental hint for new products formed in this photochemical process. Eventually this failure may be due to the fact that all calculated IR absorptions of the possible Si_2H_2 isomers should show much weaker intensities than **13**, the global minimum of the Si_2H_2 hyper surface[10].

Cocondensation of Hydrogen and Silicon Atoms

As an additional method for the matrix-isolation of reactive silicon species we examined a number of cocondensation reactions of atomic silicon with low molecular weight reactants. In these experiments silicon was vaporized from a boron nitride crucible, which was surrounded by an aluminum oxide tube. The oven was resistively heated to temperatures of 1490–1550°C by means of a tungsten wire wound around the alumina tube. The silicon atoms were codeposited with gaseous mixtures of the substrate and argon onto a CsI window at 12 K. The substrate/argon ratio was usually of the order of 1:100.

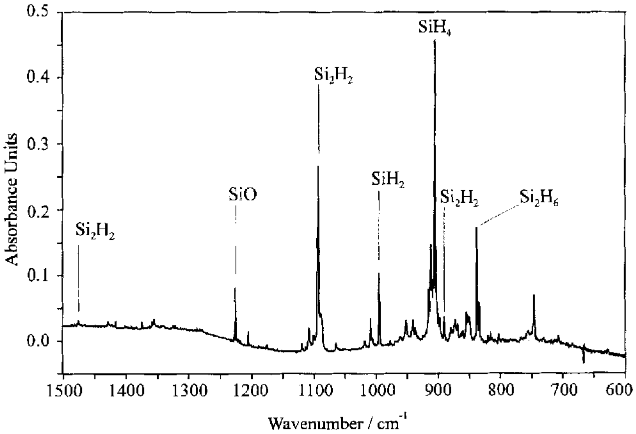
By chance, this method turned out to be a source for considerably larger amounts of **13**, and enabled us to confirm the assignments of the IR absorptions given above. After cocondensation of atomic silicon with acetylene, ethylene, and hydrogen cyanide, respectively, we were able to observe **13** as a byproduct in each experiment (the main results of these experiments are reported elsewhere[11]), in spite of the fact that no hydrogen was added. This is in accordance with results of Margrave and co-workers[12–14], who observed the 1093 cm^{-1} absorption after codeposition of silicon atoms with HF, but were only able to assign it to a silicon-hydrogen compound of undefined composition (Si_xH_y)[14].

In addition, we carried out experiments in which silicon atoms were cocondensed with "pure" argon; even then **13** as well as other silicon hydrides, such as SiH_2, SiH_4, and Si_2H_6, are obtained in considerable amounts. The formation of these compounds is probably due to hydrogen impurities in the metal surfaces of the cryostat (other observable products, such as SiO, SiCO, and SiNN, may also result from reactions of the silicon atoms with residual gases in the apparatus). The 1093 cm^{-1} band could not be detected in control experiments in which the empty BN crucible was heated up to 1500°C.

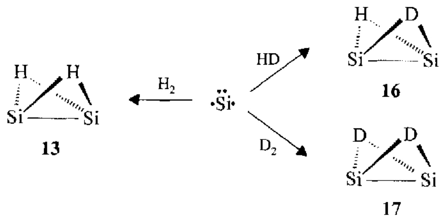
Hence, it was obvious that the isolated amounts of **13** should increase if molecular hydrogen is used as reactant. This is indeed the case for hydrogen/argon mixtures in a ratio up to 1:1000. If the hydrogen concentration is such that the ratio of the mixture exceeds a value of about 1:500, virtually only *saturated* silicon hydrides can be observed. This fact also supports the assignment of the three IR bands at 1475.6, 1092.8 and 890.3 (Figure 1) to an *unsaturated* silicon-hydrogen compound.

In the IR spectrum there is one rather strong signal at 746 cm^{-1} left, which could not be identified. It is tempting to assume that this absorption originates from a species Si_2H_4. However, the accordance with frequency calculations at the BLYP/6-31G** level of theory is rather poor for *trans*-bent disilene and silylsilylene, respectively.

Figure 1. IR spectrum after cocondensation of silicon atoms with a hydrogen/argon (1:2000) mixture



Cocondensation experiments have also been carried out with the hydrogen isotopomers HD and D_2, and these have led to the observation of the same IR absorptions at 1060 and 818 cm^{-1}, respectively, that were observed after pulsed flash pyrolysis of the deuterated tetrasilane **15**. The amounts of the unlabeled silicon hydrides Si_2H_2, and SiH_2 and SiH_4, concomitantly formed, could be minimized when the apparatus was exposed to a HD- or D_2-atmosphere (5–10 mbar), respectively, for several hours prior to deposition, in order to exchange the amount of hydrogen dissolved in the metal surfaces for the corresponding hydrogen isotopomer.



However, the intensities of the IR bands of **16** and **17** are calculated to be relatively weak compared with those of **13**. Thus, it was not possible to definitely assign further IR absorptions of **16** and **17**, with the exception of the most intense band in each respective system, although comparable amounts of all three isotopomers have probably been present in the corresponding experiments.

Conclusion

We were able to generate dibridged Si_2H_2 by two completely different pathways and to register the IR spectra of the parent compound as well as of its mono- and dideuterated isotopomers.

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Experimental Section

Equipment Used for Matrix Isolation, Photolyses and Pyrolyses: Cryostat for Matrix Isolation: Displex Closed Cycle Refrigeration System CSA 202 (Air Products). – Light Sources: Low-pressure mercury spiral lamp (Gräntzel, Karlsruhe) with Vycor filter. Excimer laser LPX 105 (Lambda Physics). – Spectrometers: FTIR spectrometer IFS 55 (Bruker), 4000–400 cm^{-1}, all spectra were recorded with 1 cm^{-1} resolution; UV/Vis: Diode array spectrometer HP 8452A (Hewlett-Packard), 190–820 nm, resolution 2 nm.

Pulsed Flash Pyrolyses: For a description see ref.[7]. The thermolysis products were deposited together with a large excess of Ar on a CsI window cooled to 12 K.

General: All reactions were carried out under dry argon. Solvents were dried using standard techniques. All glassware was thoroughly dried in an oven at 130°C prior to use. – NMR: Bruker AM-400 or AC-200 spectrometers. – IR: Bruker IFS 25 spectrometer. – Mass spectra: Varian Mat 111 or Varian Mat 311 A spectrometer. – Analytical gas chromatography: Carlo-Erba Fractovap 2900 gas chromatograph with a flame ionization detector, and a 10 m × 0.3 mm column coated with silicon phase OV 101. – Preparative gas chromatography: Carlo-Erba Fractovap 2450 using a thermal conductivity detector, and helium as the carrier gas (4 m × 6 mm, OV 101). – Trichlorophenylsilane (**6**) was obtained from Aldrich, dichlorodiphenylsilane (**10**) from Fluka.

Chloro-1,2-diphenyldisilane (**1**): This compound was prepared by successive addition of PCl_5 (13 g, 64 mmol) to a solution of redistilled 1,2-diphenyldisilane (**9**) (14 g, 64 mmol) in CCl_4 (50 ml) at 0°C. The use of impure diphenyldisilane samples resulted in the nearly complete failure of the reaction. After the completion of HCl formation distillation yielded pure chloro-1,2-diphenyl-disilane (**1**) (16 g, 60 mmol, 94%) as a colorless liquid of boiling point 105°C/0.001 Torr. – IR (neat): $\tilde{\nu}$ = 3071 cm^{-1} (CH), 2143 (SiH). – UV (cyclohexane): λ_{max} (lg ε) = 206 nm (4.43), 222 (4.20), 268 (3.08). – ^1H NMR (C_6D_6): δ = 4.27 (2 d × d, 2H, SiH_2), 5.33 (t, 1H, SiHCl), 7.03 (m, 10H, aromatic H). – ^{13}C NMR (C_6D_6): δ = 128.58, 128.63, 130.18, 131.00, 131.38, 131.40, 134.73, 136.40. – ^{29}Si NMR (C_6D_6): δ = –59.92 (SiH_2), –13.70 (SiHCl). – MS (70 eV); *m/z* (%): 248 (8) [M^+], 219 (37), 217 (100), 183 (70), 105 (41).

Lithio-1,1-diphenyl-2,2,2-trimethyldisilane (**2**): A solution of hexamethyl-2,2-diphenyltrisilane (**11**) (65.6 g, 200 mmol) in THF (250 ml) was stirred for one hour with an equimolar amount of methyllithium at room temperature.

1,1,1-Trimethyl-2,2,3,4-tetraphenyltetrasilane (**3**): Lithio-1,1-diphenyl-2,2,2-trimethyldisilane (**2**) (200 mmol) in THF was added dropwise to a solution of chloro-1,2-diphenyldisilane (**1**) (200 mmol, 49.7 g) at 0°C. After completion of the addition, the reaction mixture was poured into 2 N HCl at 0°C. After extraction of the aqueous phase with ether, the combined organic phases were dried with $MgSO_4$. After removal of volatiles in vacuo, compound **3** was used without further purification for the next step (to avoid loss ot the valuable tetrasilane **3**).

2,2,3,4-Tetrabromo-1,1,1-trimethyltetrasilane (**4**): The crude tetraphenyltetrasilane **3** was stirred for 7 days with a large excess of liquid HBr at –72°C. After this the excess of HBr and benzene were removed carefully in vacuo. For the same reason as above tetrabromotetrasilane **4** was also used without further purification.

1,1,1-Trimethyltetrasilane (**5**): 25 g of crude 2,2,3,4-tetrabromo-1,1,1-trimethyltetrasilane (**4**) were dissolved in 50 ml diethyl ether and added dropwise to a suspension of 2.0 g lithium aluminum hydride (52 mmol) in 250 ml diethyl ether at 0°C. Fifteen minutes after completion of the addition all volatiles, including the product, were removed in vacuo. After distillative removal of the solvent, the remaining colorless liquid (0.30 ml) was fractionated by preparative GC yielding a few μl of pyrophoric 1,1,1-trimethyltetrasilane (**5**) as a colorless liquid. – IR (gas): $\tilde{\nu}$ = 2962 (CH), 2155 (SiH), 2128 (SiH), 1255 ($SiMe_3$). – ^{1}H NMR (C_6D_6, capillary): δ = 0.18 (s, 9H, $SiMe_3$), 3.20 (t, J = 4.1 Hz, 2H, SiH_2), 3.27 (m, 2H, SiH_2), 3.44 (t, J = 3.7 Hz, 3H, SiH_3). – ^{13}C NMR (C_6D_6, capillary): δ = –0.14. – ^{29}Si NMR (C_6D_6, capillary): δ = –115.70, –115.60, –107.04 (SiH), –13.82 ($SiMe_3$). – MS (70 eV); *m/z* (%): 164 (49) [M^+], 149 (23), 130 (8), 115 (17), 73 (100).

Phenylsilane (**7**): Phenylsilane was prepared by reduction of phenyltrichlorosilane (**6**) with the stoichiometric amount of lithium aluminum hydride in ether according to a literature procedure[15].

Bromophenylsilane (**8**): Bromophenylsilane was prepared by dropwise addition of one equivalent of bromine to phenylsilane (**7**) in pentane at 0°C.

1,2-Diphenyldisilane (**9**): A mixture of 196 g bromophenylsilane (**8**) (1.06 mol), 7.28 g lithium sand (1.06 mol), 122 ml diethyl ether and 490 ml petroleum ether (30/50) was vigorously stirred until the complete conversion of bromophenylsilane was indicated by GC. After the filtration of the salts distillation of the remaining liquid yielded 51.4 g 1,2-diphenyldisilane (**9**) (0.24 mol; 45%) of boiling point 105°C/0.01 Torr.

Hexamethyl-2,2-diphenyltrisilane (**11**): This trisilane could be synthesized by the coupling of dichlorodiphenylsilane and chlorotrimethylsilane with magnesium according to a procedure developed in our laboratory[16]. As a substitute for the highly carcinogenic HMPA used as a solvent in earlier preparations, *N,N*-dimethylpropylene urea (DMPU) gave identical results.

2,2,3,4-Tetradeuterio-1,1,1-trimethyltetrasilane (**15**): This compound was accessible analogously to unlabeled tetrasilane **5** by reduction of tetrabromotetrasilane **4** with $LiAlD_4$ instead of $LiAlH_4$. – IR (argon marix): $\tilde{\nu}$ = 2969 cm^{-1} (CH), 2214 (SiH), 2176 (SiH), 1532 (SiD), 1252 ($SiMe_3$). – ^{1}H NMR (C_6D_6): δ = 0.72 (s, 9H, $SiMe_3$), 3.63 (t, J = 3.3 Hz, 1H, SiH), 3.82 (d, J = 3.3 Hz, 2H, SiH_2). – ^{2}H NMR (C_6D_6): δ = 3.71 (s, 2 D, SiD_2), 3.85 (s, 1 D), 4.04 (s, 1 D). – ^{13}C NMR (C_6D_6): δ = –1.22.

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