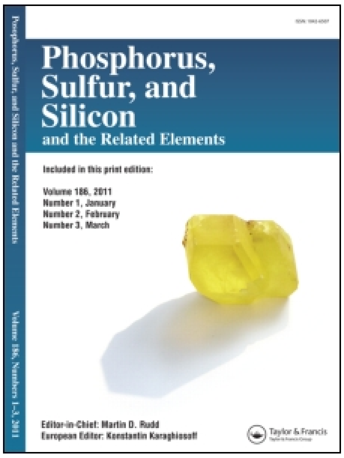

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GENERATION AND REACTIVITIES OF PHENYLSILYLENE

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GENERATION AND REACTIVITIES OF PHENYLSILYLENE

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2-Phenyl-1,1,1-trimethyldisilane(3) was synthesized from the acid-cleavage reaction, followed by the reduction of 1,1,1-trimethyltriphenyldisilane as a thermal precursor of phenylsilylene, PhHSi:. The phenylsilylene generated from the FVP of 2-phenyl-1,1,1-trimethyldisilane(3) at 600 °C was trapped by insertions into Si-H and O-H bonds as well as additions to dienes. The neat FVP of 2-phenyl-1,1,1-trimethyldisilane(3) at 600 °C led to the formation of phenylsilane, $PhSiH_3$ and diphenylsilane, Ph_2SiH_2 as major products.

Keywords: Phenylsilyene; flow vacuum pyrolysis; Si-H insertion; O-H insertion; C-H insertion; π-addition

INTRODUCTION

Despite intense investigation of phenylmethylene during the past 20 years,[1–5] the study of phenylsilylene, PhHSi: has been limited to a few reports on the generation as a byproduct in the photodissociation of phenylsilane at 193nm and to theoretical studies.[6] Our intention in studying phenylsilylene was to investigate how the mechanistic idea of phenylmethylene chemistry could be modified to deal with the reaction of silylenes.

Phenylmethylene has been studied actively since Jones reported its existence.[7] (Scheme 1) It has now been demonstrated that phenylmethylene undergoes intramolecular π-addition,[7–10] dimerization,[11] and isomerization.[12,13] These reactivities of phenylmethylene aroused our interest to study its silicon analogue, phenylsilylene.

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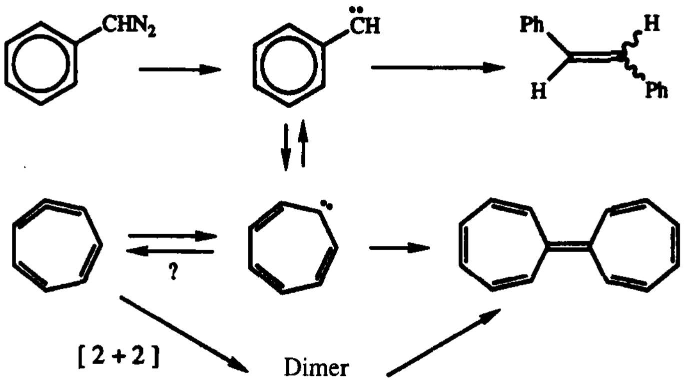
*Corresponding author.



SCHEME 1

2-Phenyl-1,1,1-trimethyldisilane(3) was chosen as a thermal precursor, pyrolysis of which was expected to extrude the species of PhHSi:.

$$\underset{\mathbf{3}}{PhH_2SiSiMe_3} \xrightarrow{\Delta} [\ PhHSi:\ ] + Me_3SiH$$

In this contribution, the results of recent studies on the synthesis of the phenylsilylene-precursor and inter- and intra-molecular reactivities of phenylsilylene are presented.

RESULTS AND DISCUSSION

2-Phenyl-1,1,1-trimethyldisilane(3) was synthesized by the acid-cleavage of 1,1,1-trimethyltriphenyldisilane(1) and the reduction of dichlorodisilane (2) with LiAlH$_4$ in yield of 48%.

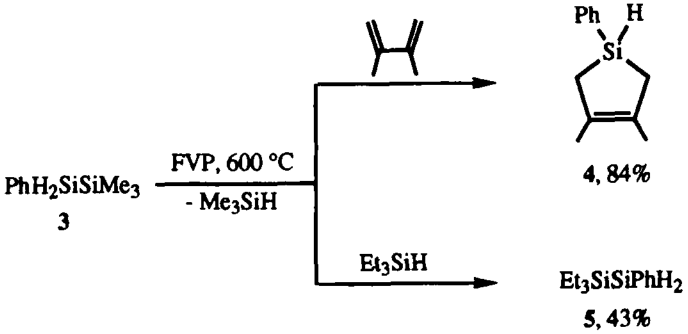
$$Ph_3SiCl + Me_3SiCl \xrightarrow[THF]{Li} \underset{\mathbf{1},\ 71\%}{Ph_3SiSiMe_3}$$

$$\underset{\mathbf{1}}{Ph_3SiSiMe_3} \xrightarrow[C_6H_6]{AlCl_3/HCl} \underset{\mathbf{2}}{PhCl_2SiSiMe_3}$$

$$\underset{\mathbf{2}}{PhCl_2SiSiMe_3} \xrightarrow[Et_2O]{LiAlH_4} \underset{\mathbf{3},\ 48\%}{PhH_2SiSiMe_3}$$

Direct generation of the free phenylsilylene was observed from the results of the pyrolysis of the precursor 3 in the presence of trapping agents such as 2,3-dimethyl-1,3-butadiene and triethylsilane as shown in Scheme 2. Flow vacuum pyrolysis (FVP) of 2-phenyl-1,1,1-trimethyldisilane(3) at 600 °C in the presence of a 27-fold excess of 2,3-dimethyl-1,3-butadiene gave 84% yield of 3,4-dimethyl-1-phenyl-1-silacyclopent-3-ene(4) derived from the addition of phenylsilylene to the diene.[14] In the presence of excess triethylsilane, 43% yield of 2-phenyl-1,1,1-triethyldisilane(5) formed through a Si-H insertion of PhHSi: was obtained.

To explore an addition mechanism of phenylsilylene to a diene, we carried out

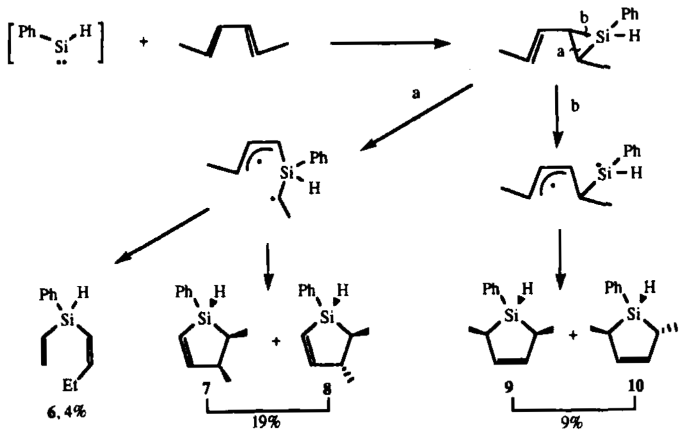


SCHEME 2

the pyrolysis of 3 in the presence of terminally methyl-substituted diene, trans, trans-2,4-hexadiene. The formation of nonstereospecific products was believed to proceed *via* an initial 1,2-addition of phenylsilylene to the diene to yield 2-vinylsilane followed by further reaction, that is, either cabon-silicon or carbon-carbon bond homolysis giving diradicals that cyclized to 1-silacyclopent-3- and -2-enes, respectively and a retro-homo-ene reaction giving an open-chain dialkenylsilane as shown in Scheme 3.[14–16]

In order to study the intramolecular reactivities of the phenylsilylene, FVP of 2-phenyl-1,1,1-trimethyldisilane(3) was carried out in the absence of a trapping agent. In this thermolysis, phenylsilane (27%), diphenysilane(19%), 1,1,1-trimethyl-2,3-diphenyltrisilane(7%) and 9,10-dihydro-9,10-disilaanthracene(2%) were formed as products in addition to low boiling components, like trimethylsilane, trimethyldisilane and benzene, as shown in the Scheme 4.

The formation of phenylsilane (15) and trimethyldisilane(12) may be attributed to the intramolecular C-H insertion of phenylsilylene to give the 2,3-benzosilirene (17) which undergoes silicon-carbon homolysis or the extrusion of silylene. (Scheme 5) And 1,1,1-trimethyl-2,3-diphenyltrisilane (16) is formed

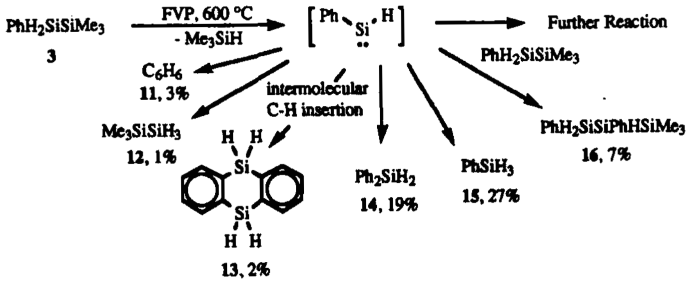


SCHEME 3

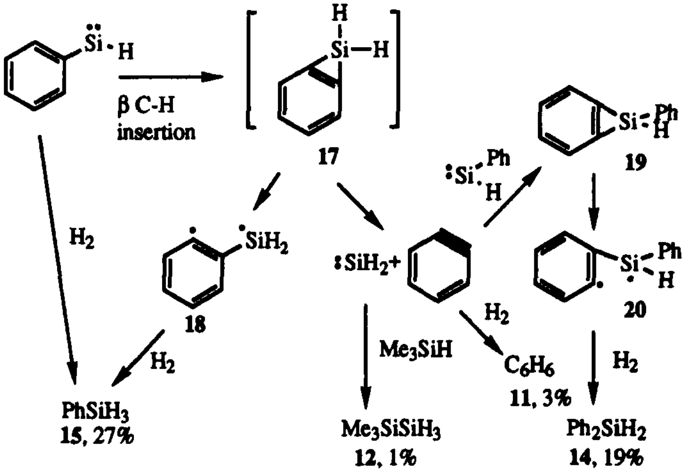
from the insertion of phenylsilylene into the Si-H bond of 2-phenyl-1,1,1-trimethyldisilane(3), the precursor. The formation of 9,10-dihydro-9,10-disilaanthracene(13) indicates that intermolecular C-H insertion between phenylsilylenes occurs.

Although possible mechanisms for the formation of diphenylsilane(14) are still not determined, the following three possible mechanisms may be suggested.

One is the mechanism in which diphenylsilane may be formed from the secondary addition of phenylsilylene to the π-bond of benzyne to give silylene and then hydrogen abstraction of diradical intermediate as shown in Scheme 5. To prove this mechanism, the pyrolyses of 2-phenyl-1,1,1-trimethyldisilane(3) in the presence of methanol and methanol-d_1 as a radical scavenger were carried out respectively. (Scheme 6) It was not possible to detect the addition product of the benzyne intermediate to the methanol(or methanol-d_1), anisol (24) and deu-



SCHEME 4



SCHEME 5

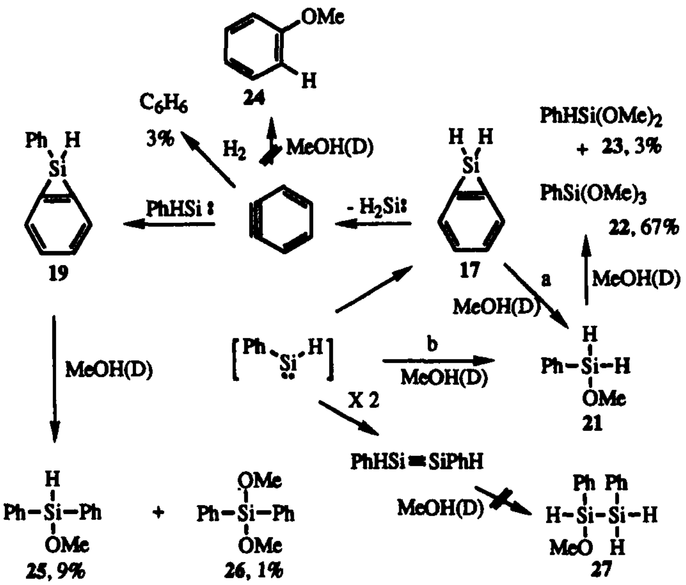
terated phenyl-substituted product, methoxydiphenylsilane (25). This allows us to eliminate the proposed mechanism.

The other mechanism is that diphenylsilane may be formed from the extrusion of trimethylsilylsilylene from $PhH_2SiSiPhHSiMe_3$ through the transition state in which phenyl bridges the Si-Si bond[17] as shown in Scheme 7.

Another mechanism is the C-H insertion of the phenylsilylene to the benzene directly, produced during the pyrolysis reactions.

From the above results, we have observed that the phenylsilylene generated from the pyrolysis of 2-phenyl-1,1,1-trimethyldisilane(3) underwent intermolecular π-addition, insertion into Si-H bond, intermolecular C-H insertion and O-H insertion.

Comparison of the reactivities of phenylsilylene to those of phenylmethylene indicates that except for the rearrangements *via* the ring expansion caused by intramolecular π-addition of phenylmethylene, other reactivities appeared to be similar in the both cases. Dewar and Landman performed MINDO/3 calculations on the rearrangement of phenylmethylene to cycloheptatrienylidene and found that in the singlet state there is a decreased order in energy from phenylmethylene (ΔH_f = 113.8 kcal/mol) to bicycloheptatriene (ΔH_f = 100.7 kcal/mol) to cycloheptatrienylidene (ΔH_f = 87.0 kcal/mol),[18] which allowed the intramolecular π-addition to form cycloheptatrienylidene. But, according to the AM1 calculation on our system, the heat of formation of intermediates are estimated to be about 89.6 kcal/mol for the intramolecular C-H insertion, 106.3 kcal/mol for the intramolecular π-addition of phenylsilylene and 91.0 kcal/mol for phenylsilylene itself. These values indicate that the ring expansion has about

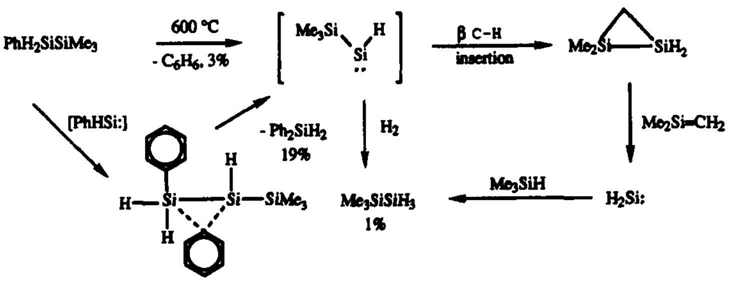


SCHEME 6

16.7 kcal/mol higher barrier than that in intramolecular C-H insertion. Therefore, it is thought that C-H insertion is a more favorable process than the π-addition in the rearrangement of phenylsilylene, which is different from the phenylmethylene case.

CONCLUSION

Direct generation of the free phenylsilylene was observed from the pyrolyses of 2-phenyl-1,1,1-trimethyldisilane(3) in the presence of trapping agents. We could



SCHEME 7

also observe that phenylsilylene shows the reactivities such as addition to dienes, insertion into the O-H bond of MeOH, insertion into the Si-H bond of Et_3SiH and intermolecular C-H insertion. But we have not observed any rearrangement products *via* the ring expansion by the intramolecular π-addition of phenylsilylene in our work.

EXPERIMENTAL

General Comments

All preparative reactions were carried out in flame-dried glassware under an atmosphere of nitrogen as most of the organosilicon compound used are sensitive toward oxygen and (or) moisture. All solvents were dried according to standard methods. ^1H NMR and ^{13}C NMR spectra were recorded on Brucker AM-80MHz NMR or Brucker AM-500 NMR spectrometers with C_6D_6 or $CDCl_3$ as a lock solvent. Mass spectra were measured on a Hewlett-Packard 5890B mass-selective analyzer coupled to a Hewlett-Packard 5890 gas chromatography. Analytical gas chromatography was carried out on a Hitachi-163 gas chromatography instrument with a flame ionization detector employing 3mm × 1m stainless steel column (10% SE-30 on 80–100 mesh chromosomb W/AW). Isolation of products was done by Hitachi-063 gas chromatography with a thermal conductivity detector employing 1/4in. × 13ft stainless steel column with 15% SE-30 on 80–100 mesh chromosomb P/AW-DMCS. Vacuum was estimated with the Hastings Vacuum Guage (thermocouple type). All chemicals were used as recieved from Merck, Petrach, and Aldrich without further purification.

1,1,1-Trimethyl-2,2,2-Triphenyldisilane(1)

To a stirred solution of 200 mL of dry THF and 1.2 g(0.17 mol, 26% excess) of lithium was added 20 g(68 mmol) of chlorotriphenylsilane dissolved in 100 mL of THF. After stirring for 46h, unreacted lithium was removed by filtration and 7.34 g (68 mmol) of chlorotrimethylsilane was added to the remaining solution and was stirred overnight. The reaction mixture was poured into saturated ammonium chloride solution and the organic layer was separated and dried with anhydrous sodium sulfate. Solvent was evaporated and the solid residue was crystallized in ethanol (m.p. 108–109 °C, 71% yield). ^1H NMR($CDCl_3$, 80 MHz): 0.27ppm(s, $SiMe_3$, 9H), 7.11–7.70ppm(m, $SiPh_3$, 15H). MS *m/z*, (relative intensity): 332(18, M^+), 259(100), 239(3), 181(19), 135(7), 105(14), 73(5).

2-Phenyl-1,1,1-Trimethyldisilane(3)

To a mixture of 60 mL of benzene and 2.75 g(20.6mmol) of aluminum chloride was added 20.5 g(62 mmol) of compound 1 and the resultant was stirred well. Dry HCl gas was bubbled through the reaction mixture and the reaction was monitored by gas chromatography. Nitrogen gas was bubbled through the solution to remove the dissolved HCl gas. Aluminum chloride was filtered and benzene was removed under vacuum. The remaining dichlorodisilane(2) was added dropwise to the suspension of 20 mL of THF and 0.88 g(23.1 mmol, 50% excess) of lithium aluminum hydride (LAH). After refluxing for 1h, the solution was stirred at the room temperature overnight. Excess LAH was destroyed by adding 20 mL of saturated ammonium chloride solution to the reaction mixture, which was cooled in an ice bath and then, the organic layer was separated and dried. The reaction mixture was fractionally distilled to give 5.4 g(48% yield) of compound 3(b.p. 81–82 °C/15 torr). ^{1}H NMR($CDCl_3$, 80 MHz): 0.09 ppm (s, $SiMe_3$, 9H), 4.30 ppm(s, SiH_2, 2H), 7.03–7.65 ppm(m, SiPh, 5H). MS *m/z* (relative intensity): 180(17, M^+), 178(5), 163(6), 135(40), 105(28), 79(5), 73(100), 45(8).

Gas-Phase Pyrolyses

The pyrolyses were carried out in a vacuum flow system with hot zone of 10 mm i.d. × 200 mm quartz tube wrapped with heating wire. The temperature of the hot zone was measured with chromel-alumel thermocouple placed between the outer surface of the quartz tube and the inner layer of asbestos. The flow system is controlled with a constriction disc. The pyrolyzates were trapped in a U-trap immersed in liquid nitrogen. After pyrolysis, the reaction mixture was subject to a preliminary fractionation by trap-to-trap distillation in the vacuum line. The isolation of products was done by preparative GC.

Pyrolysis of 3 in the Presence of 2,3-Dimethyl-1,3-Butadiene

A mixture of 61 mg(0.34 mmol) of compound 3 and 726 mg(8.84 mmol, 27-fold excess) of 2,3-dimethyl-1,3-butadiene was placed in a mixing chamber and was degassed with the repeated freeze-pump-thaw cycles. The reaction mixture was evaporated and passed through the hot zone at 600 °C and the pyrolyzates were trapped in a U-trap immersed in liquid nitrogen. 2,3-Dimethyl-1,3-butadiene in excess was separated from the reaction mixture by trap-to-trap distillation. The isolation of products was done by preparative GC on SE-30 column. 4 was obtained in yield of 84%. 3,4-Dimethyl-1-phenyl-1-silacyclopent-3-ene(4). ^{1}H

NMR(C_6D_6, 80 MHz): 1.62–1.72 ppm(m, H_2CSiCH_2 and MeC=CMe, 10H), 4.87 ppm(q, ^3J = 3.2 Hz, SiH, 1H), 7.17–7.64 ppm(m, SiPh, 5H). MS *m/z* (relative intensity): 188(70, M^+), 145(30), 111(18), 110(100), 78(32), 53(35), 32(41).

Pyrolysis of 3 in the Presence of Trans,Trans-2,4-Hexadiene

A mixture of 110 mg(0.61 mmol) of compound 3 and 1.45 g(18 mmol, 30-fold excess) of trans, trans-2,4-hexadiene was pyrolyzed at 600 °C in the same manner as above experiment. Five isomers were obtained.[14] (1-Butenyl)-vinylphenylsilane(6; 4%) and 4,5-dimethyl-1-phenyl-1-silacyclopent-2-ene isomers(7, 8; 19%). ^{1}H NMR(C_6D_6, 80 MHz): 0.93–2.19 ppm(m, SiCHMeCHMe, 8H), 4.24–4.78 ppm(m, SiH, 1H), 5.59–5.67 ppm(m, CH=CH, 2H), 7.25–7.70 ppm(m, SiPh, 5H). MS *m/z* (relative intensity): 188(30, M^+), 159(58), 145(18), 131(30), 105(100), 95(16), 82(28), 53(51). 2,5-Dimethyl-1-phenyl-1-silacyclopent-3-ene isomers(9, 10; 9%). ^{1}H NMR(C_6D_6, 80 MHz): 0.70–1.97 ppm(m, MeHCSiCHMe, 8H), 4.52–4.77 ppm(m, SiH, 1H), 5.92–5.99 ppm(m, CH=CH, 2H), 7.25–7.54 ppm(m, SiPh, 5H). MS *m/z* (relative intensity): 188(34, M^+), 173(55), 159(79), 145(38), 131(29), 105(100), 95(47), 79(20), 53(46).

Pyrolysis of 3 in the Presence of Triethylsilane

A mixture of 103 mg(0.57 mmol) of compound 3 and 1.62 g(14 mmol, 24-fold excess) of triethylsilane and 70 mg of decane as an internal standard was pyrolyzed at 600 °C in the same manner as above experiment. Mass recovery was 1.58 g(88%). 1,1,1-Triethyl-2-phenyldisilane(5) was obtained(43% yield). ^{1}H NMR($CDCl_3$, 80 MHz): 0.69–1.12 ppm(m, $SiEt_3$, 15H), 4.18 ppm(s, SiH_2, 2H), 7.29–7.57 ppm(m, SiPh, 5H). MS *m/z* (relative intensity): 222(19, M^+), 165(11), 137(22), 115(100), 87(95), 59(41).

Pyrolysis of 3 in the Presence of Methanol

A mixture of 113 mg(0.63 mmmol) of compound 3 and 0.61 g(19 mmol, 30-fold excess) of methanol was pyrolyzed at 600 °C in the same manner as above experiment. Methanol in excess was separated from the reaction mixture by trap-to-trap distillation and the products obtained were identified as follow. Trimethoxyphenylsilane(22; 67%). ^{1}H NMR(C_6D_6, 80 MHz): 3.48 ppm(s, Si-$(OMe)_3$, 9H), 7.20–7.85 ppm(m, SiPh, 5H). MS *m/z* (relative intensity): 198(24,

M^+), 167(18), 137(11), 120(100), 107(33), 91(47), 59(18), 51(5). Dimethoxyphenylsilane(23; 3%). ^1H NMR(C_6D_6, 80MHz): 2.88 ppm(s, $Si(OMe)_2$, 6H), 4.78 ppm(s, SiH, 1H), 6.60–7.18 ppm(m, SiPh, 5H). MS *m/z* (relative intensity): 168(43, M^+), 167(100), 137(27), 107(11), 90(27), 59(10), Methoxydiphenylsilane(25; 9%). ^1H NMR(C_6D_6, 80 MHz): 3.36 ppm(s, SiOMe, 3H), 5.85 ppm(s, SiH, 1H), 6.85–7.66 ppm(m, $SiPh_2$, 10H). MS *m/z* (relative intensity): 213(9, $[M - 1]^+$), 183(16), 136(100), 105(17), 91(12), 71(7), 59(64). Dimethoxydiphenylsilane(26; 1%). ^1H NMR(C_6D_6, 80 MHz): 3.39 ppm(s, $Si(OMe)_2$, 6H), 6.85–7.76 ppm(m, $SiPh_2$, 10H). MS *m/z* (relative intensity): 244(59, M^+), 213(11), 181(14), 167(100), 137(30), 107(14), 78(19), 59(24).

Pyrolysis of 3 in the Presence of Methanol-d_1

A mixture of 86 mg(0.48 mmol) of compound 3 and 0.79 g(24 mmol, 50-fold excess) of methanol-d_1 was placed in a reaction vessel and was degassed with the repeated freeze-pump-thaw cycles. Pyrolysis was carried out in the same manner as above methanol experiment. The undeuteriated products such as dimethoxyphenylsilane, trimethoxyphenylsilane and methoxydiphenyl-silane were identified.

Pyrolysis of 3 without Trapping Agent

A sample of 110 mg(0.61 mmol) of 3 was passed through the hot zone at 600 °C. The products were isolated by preparative gas chromatography and identified from GC/MS and ^1H NMR data. 9,10-Dihydro-9,10-disilaanthracene(13; 2%). ^1H NMR(C_6D_6, 500 MHz): 5.02 ppm (s, SiH_2, 4H), 7.11 ppm(t, ^3J = 4.2 Hz, SiCCH, 4H), 7.56 ppm(t, ^3J = 4.2 Hz, SiCCCH, 4H). MS *m/z* (relative intensity): 212(98, M^+), 210(100), 181(43), 155(9), 134(25), 105(85), 81(12), 53(22). Diphenylsilane(14; 19%). ^1H NMR($CDCl_3$, 80 MHz): 4.77 ppm(s, SiH_2 2H), 6.74–7.27 ppm(m, $SiPh_2$, 10H). MS *m/z* (relative intensity): 184(46, M^+), 155(3), 152(1), 129(2), 106(100), 79(9), 53(11). Phenylsilane(15; 27%). ^1H NMR(C_6D_6, 80 MHz): 4.24 ppm(s, SiH_3, 3H), 7.00–7.39 ppm(m, SiPh, 5H). MS *m/z* (relative intensity): 107(100), 93(8), 77(32), 74(5), 66(8), 53(65). 1,1,1-Trimethyl-2,3-diphenyltrisilane(16; 7%). ^1H NMR(C_6D_6, 500MHz): 0.13ppm(s, $SiMe_3$, 9H), 4.39 ppm(t, ^3J = 3.4Hz, SiHPhSi, 1H), 4.66 ppm(d, ^3J = 3.1 Hz, PhH_2Si, 1H), 4.69 ppm(d, ^3J = 3.5 Hz, PhH_2Si, 1H), 7.05–7.61 ppm(m, PhSiSiPh, 10H). MS *m/z* (relative intensity): 286(10, M^+), 255(16), 212(93), 163(56), 135(51), 105(100), 73(53), 45(11).

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