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Generation and Trapping of Bis(dialkylamino)silylenes: Experimental Evidence for Bridged Structure of Diaminosilylene Dimers

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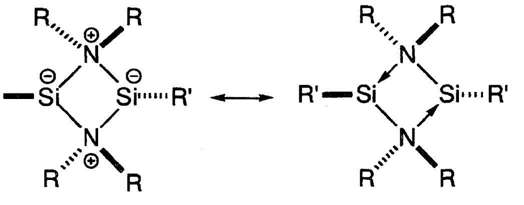
Reduction of dichlorobis(diisopropylamino)silane and dichlorobis(*cis*-2,6-dimethylpiperidino) silane by alkali metals gave the corresponding bis(diisopropylamino)silylene and bis(*cis*-2,6-dimethylpiperidino)silylene, respectively. These were successfully trapped by toluene and benzene as well as by hydrosilane, olefin, and acetylene. As the first evidence for the existence of the bridged-dimer of the diaminosilylenes, we have found scrambling of the amino-substituents on a silicon atom during the simultaneous generation of two different bis(dialkylamino)silylenes in benzene. Diaminosilyenes generated thermally from the other new precursors designed here gave no evidence for the bridged dimer, due to the high temperature required for the generation.

Divalent silicon species (silylenes) have attracted considerable interest of both experimental and theoretical chemists.[1] Among various substituted silylenes, amino- and alkoxy-substituted silylenes are unique; recent theoretical calculations[2] have shown that Y_2Si: as well as HYSi: ($Y = OH, NH_2$) form thermodynamically and kinetically stable heteroatom-bridged dimers, as shown in Scheme 1, instead of the conventional silicon–silicon double-bonded species, disilenes. Although a similar bridged-dimer structure has been found for bis(dimethylamino)stannylene as determined by X-ray crystallographic analysis,[3] no such silylene dimer has been known experimentally, even as a transient species, up to now.[4] Since the dissociation energy of the amino-bridged dimer of diaminosilylene to the corresponding silylene is calculated to be rather large (15.3 kcal mol^{-1}),[2] dimers of bis(dialkylamino)silylenes should be the best targets for synthesis.


Scheme 1.

Whereas cyclic diaminosilylenes **1a**, **1b**, and **2** have recently been synthesized as isolable silylenes by the reduction of the corresponding dichlorosilanes with potassium (Chart 1),[5] no evidence for the dimerization has been reported; they may not form the stable dimers because of the superior stability of the monomers as well as unfavorable geometrical arrangement for dimer formation.

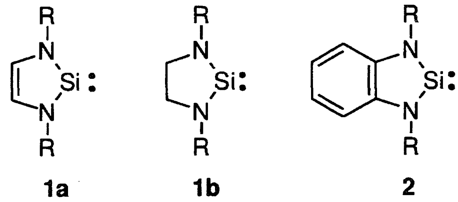

1a **1b** **2**

Chart 1.

Meller et al. have reported that reduction of acyclic dichlorobis(dialkylamino)silanes by Na–K alloy gives the corresponding silylenes, which are trapped by benzene and toluene to produce the corresponding hydrophenylsilane and benzylhydrosilane derivatives, respectively.[6] Since the reduction of dichlorobis(dialkylamino) silanes by alkali metals is the sole convenient method to generate the bis(dialkylamino)silylenes at present, we have investigated generation of various bis(dialkylamino)silylenes by this method and their possible amino-bridged dimer formation. As the first evidence for the bridged-dimer of the diaminosilylenes, we have found scrambling of the amino-substituents during the simultaneous generation of the two different bis(dialkylamino)silylenes in benzene. A diaminosilylene generated thermally from the corresponding silacyclopropane and 3-silacyclopropene gave no evidence for the bridged dimer, due to the high temperatures required for the generation.

Results and Discussion

Reduction of Dichlorobis(diisopropylamino)silane (3a) in the Presence of Various Silylene Trapping Reagents. Although Meller et al. have proposed the intermediacy of the bis(dialkylamino)silylenes during the reaction of the corresponding dichlorobis(dialkylamino)silanes with alkali metals,[6] the discussion is based on the rather exceptional

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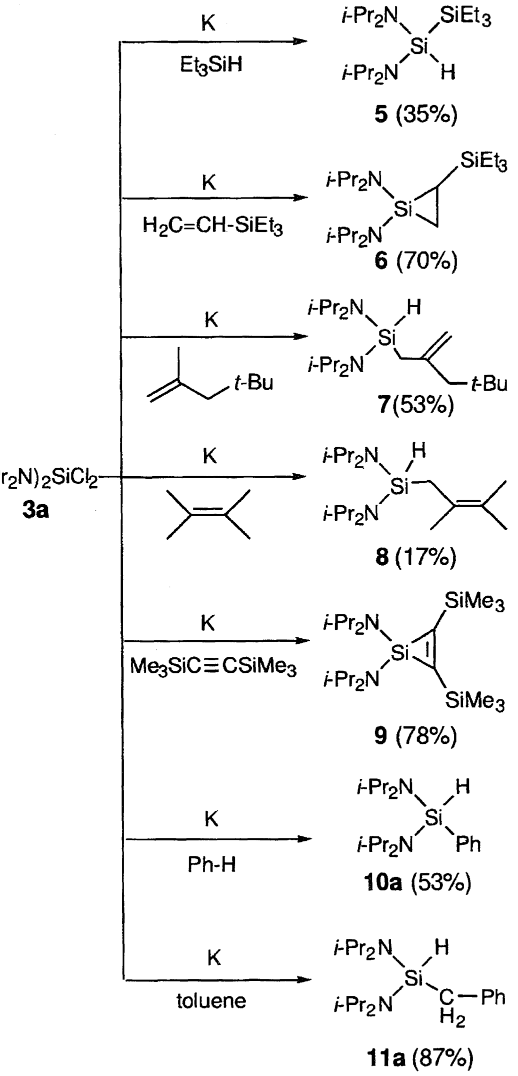
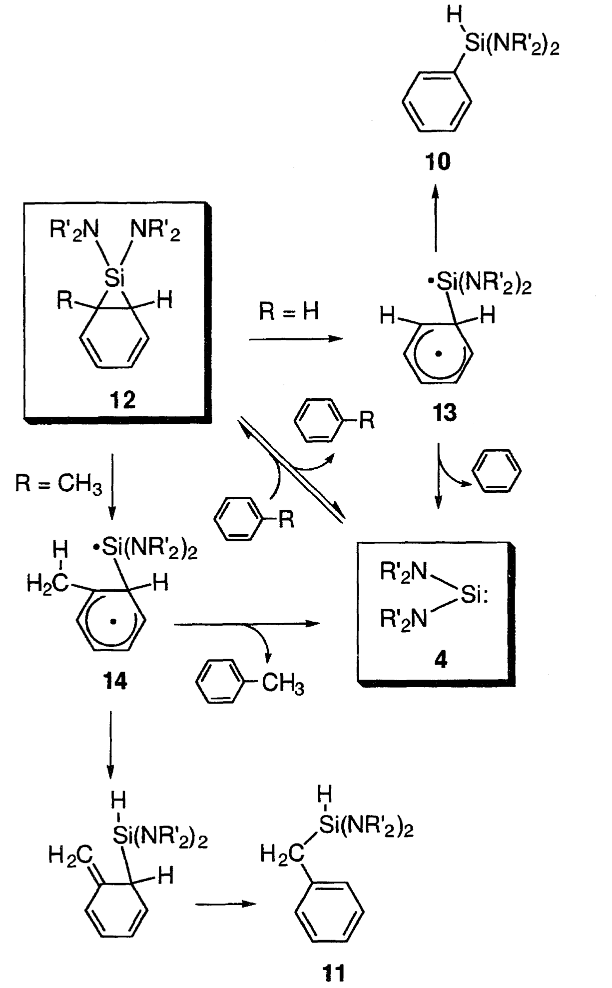
trapping reactions of the silylenes by benzene and toluene.[7] At the beginning of our study, the reduction of **3a** in the presence of various trapping reagents of silylene was investigated to confirm the formation of a diaminosilylene **4a** by this method. The results are summarized in Scheme 2. Thus, a reaction of **3a** with potassium in refluxing triethylsilane gave a disilane **5** in 35% yield. A similar reduction of **3a** in triethylvinylsilane afforded the corresponding silacyclopropane **6** in 70% yield. The reduction **3a** in 2,4,4-trimethyl-1-pentene and 2,3-dimethyl-2-butene gave the corresponding allylsilanes **7** and **8**, respectively, in accord with the reactions of photochemically generated methylphenylsilylene with cyclohexene.[11] The reaction of **3a** with potassium in bis(trimethylsilyl)acetylene gave a 3-silacyclopropene **9** in 78% yield. All these results establish the formation of the corresponding diaminosilylene **4a** as the major reactive intermediate.

As reported by Meller et al.,[6] the reduction of **3a** in benzene and toluene gave the corresponding phenylsilane **10a** and benzylsilane **11a**, respectively, in good yields; deuterated benzene and toluene gave the corresponding deuteriosilanes. The production of **10a** and **11a** was suppressed in the presence of the other trapping reagents like bis(trimethylsilyl)acetylene. The production of **10a** and **11a** is indicative of the ability of benzene and toluene as silylene trapping reagents, while the reactivity of these aromatic compounds toward silylenes is much lower than the other trapping reagents used in the present study. The reduction of **3a** in a 1 : 1 mixture of benzene and toluene at 70 °C gave only **11a**, which means a lower reactivity of benzene than toluene as a silylene trapping reagent.



Scheme 2.

A plausible reaction mechanism for the addition of a diaminosilylene to aromatic hydrocarbons is shown in Scheme 3. The first step will be a [1+2] addition of the silylene to a double bond to form a 7-silanorcaradiene **12**. The final phenylsilane **10** and benzylsilane **11** will be produced by a ring carbon–silicon bond cleavage followed by 1,2- and 1,4-hydrogen shifts, respectively. The first step of our mechanism is similar to that proposed by Liu et al.[8] and Okazaki et al.,[9] whereas at present, it is difficult to explain the difference between the final products from the diaminosilylene and those from the Okazaki's silylene.



Scheme 3.

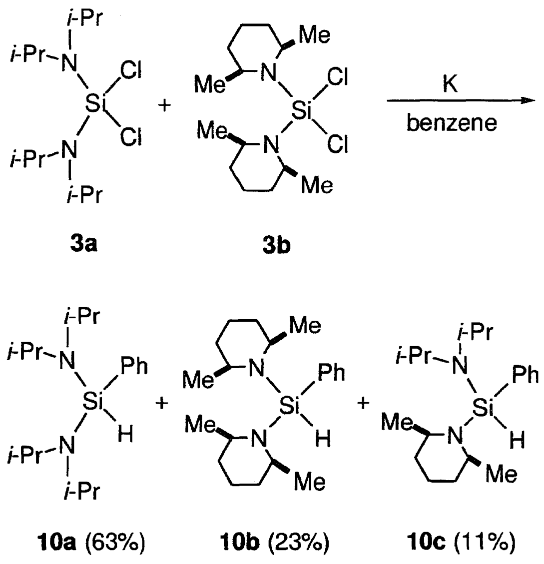
Evidence for the Existence of Amino-Bridged Dimer

of Diaminosilylenes. Reduction of a 1 : 1 mixture of **3a** and **3b** with potassium in benzene gave three products: bis(diisopropylamino)phenylsilane (**10a**), bis(*cis*-2,6-dimethylpiperidino) phenylsilane (**10b**), and (diisopropylamino)(*cis*-2,6-dimethylpiperidino)phenylsilane (**10c**) in 63, 23, and 11% yields, respectively (Scheme 4). The production of **10c** is indicative of the scrambling of the amino-substituents at a silicon. Neither the starting dichlorosilanes nor the final phenylsilanes are responsible for the scrambling. Thus, dichloro(diisopropylamino)(*cis*-2,6-dimethylpiperidino)silane (**3c**) was not detected during the reaction of **3a** and **3b** with potassium in benzene. Treatment of a mixture of the phenylsilanes **10a** and **10b** with 2 molar amounts of potassium in benzene did not give **10c**.

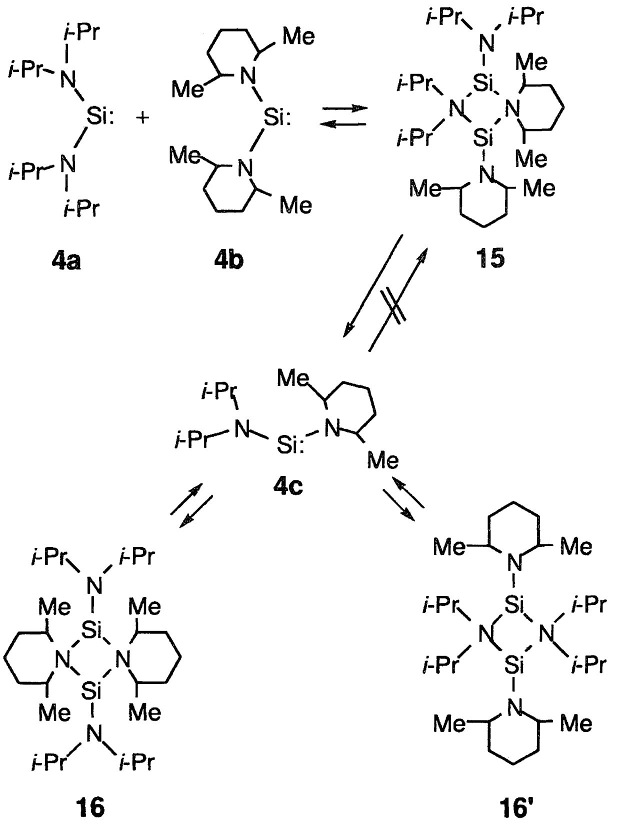
The scrambling is explained by reversible formation of the bridged dimers of silylenes, as shown in Scheme 5.[2] Two kinds of diaminosilylenes, **4a** and **4b**, will associate to form an asymmetrically amino-bridged cyclic dimer **15**. Dissociation of the dimer would give not only the starting silylenes but also silylene **4c** having different amino substituents. Although **4c** can also form two symmetric dimers, **16** and **16′**, dissociation of the dimers gave the same unsymmetrically substituted silylene again. Only **15** is responsible for the scrambling reaction.

The reduction of **3c** in benzene gave only **10c** (56%); no scrambling of the amino groups occurred (Scheme 6). The results suggest that only the symmetric dimers **16** and/or **16′** are formed from **4c**, probably due to steric and/or electronic reasons.

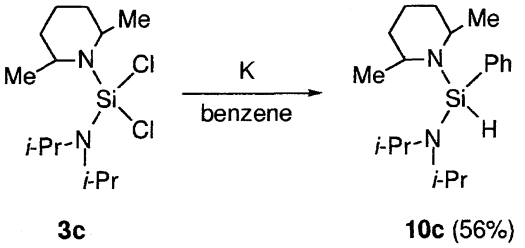
In the scrambling reaction shown in Scheme 4, the observed ratio of the products [**10a**] : [**10b**] : [**10c**] was 65 : 24 : 11, while the theoretical ratio should be $(1-\alpha/2):(1-\alpha/2):\alpha$, where α represents the degree of scrambling $(0\leq\alpha\leq1)$. The low yield of **10b** compared with **10a** would be caused by decomposition of **10b** during the reduction. Actually, **10b** decomposed during the treatment with 20 molar amounts of potassium in benzene, while **10a** was stable under the conditions. The lability of **10b** would arise from the less hindered substituents. Thus, the following experiments using deuterium-labeled **3a** were made for quantitative analysis of the scrambling.



Scheme 4.



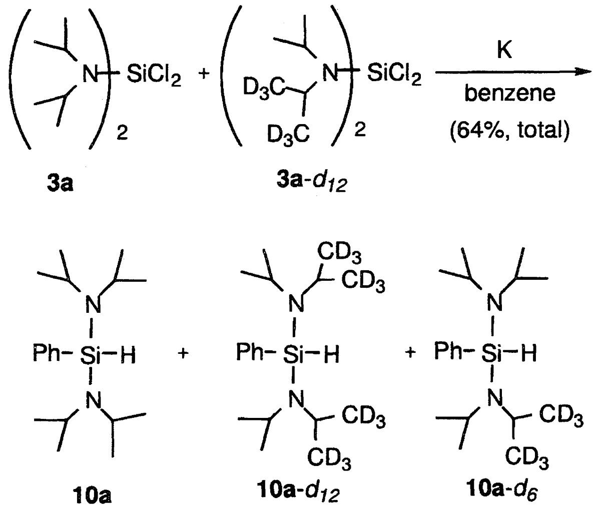
Scheme 5.



Scheme 6.

Reaction of a 1 : 1 mixture of **3a** and **3a**-d_{12} with potassium in benzene gave **10a**, **10a**-d_{12}, and **10a**-d_6 in 64% total yield (Scheme 7). The product ratio of [**10a**] : [**10a**-d_{12}] : [**10a**-d_6] was 4 : 4 : 1 as estimated by mass spectroscopy. If the reaction of diaminosilylenes with benzene takes place after an equilibrium between the diaminosilylenes and their dimers is achieved, the ratio should be 25 : 25 : 50 ($\alpha = 1$). The α value less than 1 ($\alpha = 0.22$) indicates that the equilibrium is not completed under the reaction conditions. The rate for the insertion of the diaminosilylene to a C–H bond of benzene would be comparative or even faster than the dimerization.

No such scrambling was observed when a more reactive silylene trapping reagent like toluene was used. Thus, the reduction of a 1 : 1 mixture of **3a** and **3b** with potassium in toluene gave only benzylbis(diisopropylamino)si-



Scheme 7.

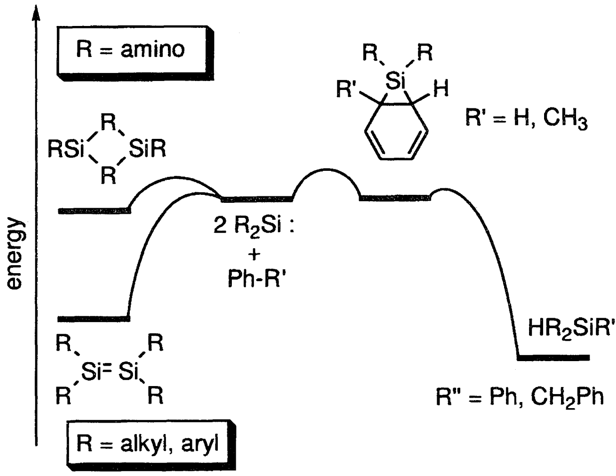


Fig. 1. Schematic energy diagram for reactions of silylenes.

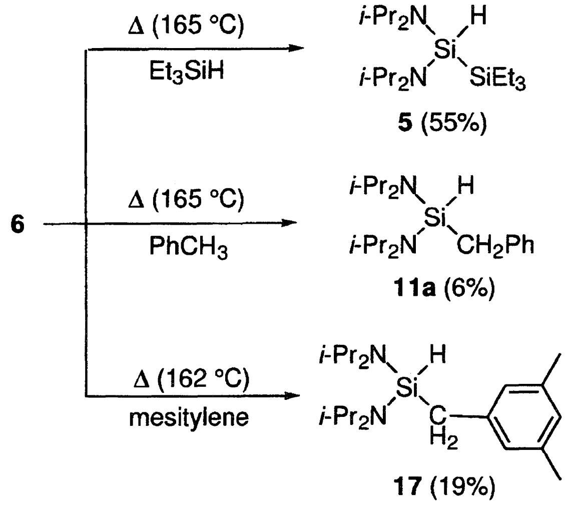
lane (**11a**) and benzylbis(*cis*-2,6-dimethylpiperidino)silane (**11b**), while dichloro(diisopropylamino)(*cis*-2,6-dimethylpiperidino)silane (**3c**) gave benzyl(diisopropylamino)(*cis*-2,6-dimethylpiperidino)silane (**11c**).

Although all the features of the scrambling experiments are in good accord with the mechanism involving formation and dissociation of the amino-bridged silylene dimer, the scrambling may also be explained if we assume the following sequence of reactions: the formation of the normal disilene from diaminosilylenes, the facile dyotropic 1,2-diamino rearrangement in the disilene, and then re-dissociation to silylenes. Recently, thermal 1,2-diaryl dyotropic rearrangement for bis(2,6-dimethylphenyl)bis(2,4,6-trimethylphenyl)disilenes through a bicyclobutane-like transition state has been reported.[12] As described above, Okazaki et al. have reported facile thermal dissociation of a disilene into silylene.[9] Combining these results, we cannot eliminate strictly the scrambling through the latter mechanism. However, the former mechanism is favorable because it is in good accord with the theoretical expectation for diaminosilylene.[2]

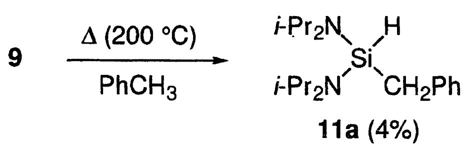
It is interesting to discuss the reason why benzene serves as a trapping reagent for diaminosilylenes, while dialkyl- and diarylsilylenes do not usually react with benzene. Energy profiles for the reactions of a diaminosilylene and dialkyl- and diarylsilylenes in the presence of benzene are compared schematically in Fig. 1. Dimers of dialkyl- and diarylsilylenes are usually much more stable than the corresponding two monomeric silylenes,[13] and hence the activation energy for the dimerization of silylenes is expected to be small. Therefore, in the absence of any effective trapping reagent, the dialkylsilylene dimerizes rapidly in an irreversible manner, which hampers a competitive reaction with benzene. On the other hand, the stabilization energy for the dimerization of diaminosilylene is small; the energy for diaminosilylene :Si$(NH_2)_2$ is calculated to be only 15.3 kcal mol^{-1}.[2] Therefore, the reaction of the diaminosilylene with benzene would compete with the reversible dimerization of the silylene, while a more effective silylene trapping reagent will react with the diaminosilylene before the dimerization. During the competitive dimerization–dissociation processes of the diaminosilylene in benzene, the scrambling of the amino-substituents on silicon will be achieved.

1,1-Diamino-1-silacyclopropane (6) and 3,3-Diamino-3-silacyclopropene (9) as Thermal Precursors for Diaminosilylene. It is well known that silacyclopropanes and 3-silacyclopropenes serve as good thermal precursors of silylenes.[16] In order to confirm the reactivity of diaminosilylenes under anion-free conditions, pyrolysis of diaminosilacyclopropane **6** and diaminosilacyclopropene **9** was investigated in the presence of various trapping reagents. The behavior of the diaminosilylene **4a** generated by the thermal reactions of **6** and **9** is parallel with that of **4a** generated by reduction of the corresponding diaminodichlorosilane with potassium. The pyrolysis of **6** in benzene did not gave the expected adducts, probably due to the high-temperature conditions.[17]

When a triethylsilane solution of **6** was heated at 165 °C, 1,1-diamino-2,2,2-triethyldisilane **5** was obtained in 55% yield, together with triethylvinylsilane (20%), as shown in Scheme 8. Similarly, pyrolysis of **6** in toluene at 165 °C and in mesitylene at 162 °C gave diaminobenzylsilanes **11a**



Scheme 8.



Scheme 9.

(6%) and **17** (19%), respectively.

Pyrolysis of a toluene solution of **9** in a sealed tube at 200 °C for 60 h gave benzylbis(diisopropylamino)silane-(**11a**) and bis(trimethylsilyl)acetylene in 4 and 77% yields, respectively (Scheme 9).

Experimental

Apparatus. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker AC-300P FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. Mass spectra and high resolution mass spectra were obtained on a JEOL JMS D-300 mass spectrometer. Electric absorption spectra were recorded on a Milton Roy Spectronic 3000 Array spectrometer. Gas–liquid chromatography (GLC) analysis was conducted by use of Shimadzu GC-8A and GC-14A gas chromatographs; octadecane was used as an internal standard.

Materials. Isopropylamine, diisopropylamine, *cis*-2,6-dimethylpiperidine, triethylamine, tetrachlorosilane, triethylsilane, 2, 3-dimethyl-2-butene, 2,4,4-trimethyl-1-pentene, ethylene glycol, hydriodic acid (57 wt% in water), sodium borohydride, octadecane, acetone-d_6, benzene-d_6, toluene-d_8, sodium, and potassium were commercially available. Triethylvinylsilane[18] and bis(trimethylsilyl)acetylene[19] were synthesized by the reported procedure. THF, benzene, toluene, and mesitylene were dried over sodium benzophenone ketyl and distilled just before use.

1,1,1,3,3,3-Hexadeuterio-2-iodopropane (2-Iodopropane-d_6). Hydriodic acid (57% wt in water) (100 ml) was added dropwise to 2-propanol-d_6 (23.0 g, 347 mmol), prepared by the reaction of acetone-d_6 (Aldrich, isotopic purity of 99 atom % D) with sodium borohydride, at room temperature. The mixture was heated under reflux for 19 h. The organic layer was washed with water and aqueous sodium hydrogencarbonate. Drying over anhydrous calcium chloride and then filtration gave 2-iodopropane-d_6[20] as a brown oil (25.1 g, 143 mmol, 41.2%). ^{1}H NMR ($CDCl_3$) $\delta = 4.24$ (s, 1H); ^{13}C NMR ($CDCl_3$) $\delta = 21.0$, 30.5 (sept, $^1J_{C-D} = 22$ Hz). HRMS Found: *m/z* 175.9964. Calcd for C_3HD_6I: M, 175.9969. The deuterium content was 92% as determined by ^{1}H NMR.

(1,1,1,3,3,3-Hexadeuteriopropan-2-yl)(propan-2-yl)amine (Diisopropylamine-d_6). A mixture of 2-iodopropane-d_6 (24.8 g, 141 mmol), isopropylamine (25.4 g, 430 mmol), and ethylene glycol (8.88 g, 143 mmol) was gently heated under reflux (ca. 70 °C) for 23 h. The amine salt was dissolved in water, and the amine was extracted into ether. The ethereal solution was dried over potassium hydride. Distillation gave 8.72 g (81.3 mmol, 57.7 %) of diisopropylamine-d_6. A colorless oil; bp 75—81 °C; ^{1}H NMR ($CDCl_3$) $\delta = 0.94$ (d, $J = 6.2$ Hz, 6H), 2.7—2.8 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 22.7$ (sept, $^1J_{C-D} = 19$ Hz), 23.7, 44.9, 45.3. HRMS Found: *m/z* 107.1581. Calcd for $C_6H_9D_6N$: M, 107.1581.

Trichloro(diisopropylamino)silane. In a three-necked flask (1 dm^3) equipped with a dropping funnel and a magnetic stirring bar were placed tetrachlorosilane (25.3 g, 149 mmol) and THF (300 ml). A THF solution (450 ml) of diisopropylamine (62.5 g, 618 mmol) was added dropwise at room temperature. The solution was stirred for 11 h. After removal of the solvent in vacuo, the reaction mixture was dissolved in hexane. Filtration of the resulting white precipitates, evaporation of hexane from the filtrate, and distillation gave trichloro(diisopropylamino)silane[21] (21.2 g, 90.4 mmol, 60.7%). A colorless oil; bp 29—32 °C/0.06 mmHg (1 mmHg = 133.322 Pa); ^{1}H NMR ($CDCl_3$) $\delta = 1.23$ (d, $J = 6.7$ Hz, 12H), 3.56 (sept, $J = 6.7$ Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 23.1$, 46.3; ^{29}Si NMR ($CDCl_3$), $\delta = -30.7$; MS (70 eV) *m/z* (%) 235 ($M^+ + 2$; 3), 233 (M^+; 3), 220 (24), 218 (24), 168 (65), 166 (65), 43 (100).

Trichloro[(1,1,1,3,3,3-hexadeuteriopropan-2-yl)(propan-2-yl)amino]silane (Trichloro(diisopropylamino)silane-d_6). In a three necked flack (200 ml) equipped with a dropping funnel and a magnetic stirring bar were placed tetrachlorosilane (6.79 g, 40.0 mmol), triethylamine (4.08 g, 40.3 mmol), and THF (50 ml). A THF solution (50 ml) of diisopropylamine-d_6 (3.99 g, 37.2 mmol) was added dropwise at room temperature. The solution was stirred for 5.5 h. After removal of the solvent in vacuo, the reaction mixture was dissolved in hexane. The usual workup gave trichloro(diisopropylamino)silane-d_6 (6.61 g, 27.5 mmol, 73.9%). A colorless oil; bp 26—26.5 °C/0.8 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 1.23$ (d, $J = 6.8$ Hz, 6H), 3.5—3.7 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 22.1$ (sept, $^1J_{C-D} = 19$ Hz), 23.0, 45.9, 46.3; ^{29}Si NMR ($CDCl_3$) $\delta = -30.7$. HRMS Found: *m/z* 239.0331. Calcd for $C_6H_8Cl_3D_6NSi$: M, 239.0338.

Dichlorobis(diisopropylamino)silane (3a). In a stainless-steel autoclave tube (50 ml) were placed tetrachlorosilane (6.49 g, 38.2 mmol), diisopropylamine (22.5 g, 222 mmol), and benzene (15 ml). The mixture was heated for 18 h at 200 °C. A colorless solid was obtained by Kugelrohr distillation. After removal of the insoluble solid hexane by filtration and centrifugation, evaporation of hexane in vacuo gave **3a**[21] (7.33 g, 24.5 mmol, 64.1%). Colorless crystals; mp 47.5—48.0 °C; bp 80—100 °C/0.01 mmHg; ^{1}H NMR (C_6D_6) $\delta = 1.17$ (d, $J = 6.7$ Hz, 24H), 3.40 (sept, $J = 6.7$ Hz, 4H); ^{13}C NMR (C_6D_6) $\delta = 23.1$, 45.6; ^{29}Si NMR (C_6D_6) $\delta = -35.4$; MS (70 eV) *m/z* (%) 300 ($M^+ + 2$; 4.4), 298 (M^+; 6.9), 285 (45), 283 (65), 198 (50), 196 (74), 156 (42), 43 (100).

Dichlorobis[(1,1,1,3,3,3-hexadeuteriopropan-2-yl)(propan-2-yl)amino]silane (3a-d_{12}). In a stainless-steel autoclave tube (50 ml), trichloro(diisopropylamino)silane-d_6 (3.54 g, 14.7 mmol), diisopropylamine-d_6 (10.9 g, 102 mmol), and benzene (10 ml) were placed. The mixture was heated at 200 °C for 18 h. The usual workup gave **3a**-d_{12} (2.36 g, 7.56 mmol, 51.4%). Colorless crystals; mp 43.9—47.4 °C; bp 78—95 °C/0.7 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 1.19$ (d, $J = 6.7$ Hz, 12H), 3.4—3.6 (m, 4H); ^{13}C NMR ($CDCl_3$) $\delta = 22.4$ (sept, $^1J_{C-D} = 21$ Hz), 23.1, 44.9, 45.4. HRMS Found: *m/z* 310.2140. Calcd for $C_{12}H_{16}Cl_2D_{12}N_2Si$: M, 310.2152.

Dichlorobis(*cis*-2,6-dimethylpiperidino)silane (3b). In a stainless-steel autoclave tube (50 ml) were placed tetrachlorosilane (3.99 g, 23.5 mmol), *cis*-2,6-dimethylpiperidine (16.7 g, 148 mmol), and benzene (15 ml). The mixture was heated at 200 °C for 21 h. The usual workup gave **3b**[6] (3.92 g, 12.1 mmol, 51.5%). Colorless crystals; mp 39.6— 43.0 °C; bp 110—120 °C/0.13 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 1.24$ (d, $J = 7.1$ Hz, 12H), 1.4—1.7 (m, 10H), 1.7—1.9 (m, 2H), 3.6—3.8 (m, 4H); ^{13}C NMR ($CDCl_3$) $\delta = 14.0$, 23.3, 30.8, 45.3; ^{29}Si NMR ($CDCl_3$) $\delta = -33.6$. HRMS Found: *m/z* 322.1402. Calcd for $C_{14}H_{28}Cl_2N_2Si$: M, 322.1399.

Dichloro(diisopropylamino)(*cis*- 2, 6- dimethylpiperidino)silane (3c). In a stainless steel autoclave tube (50 ml), trichloro(diisopropylamino)silane (5.06 g, 21.6 mmol), *cis*-2,6-dimethylpiperidine (9.78 g, 86.4 mmol), and benzene (15 ml) were placed. The mixture was heated at 110 °C for 8 d. Kugelrohr distillation of the residue gave **3c** (4.43 g, 14.2 mmol, 65.7%). A yellow oil; bp 125—140 °C/0.09 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 1.20$ (d, $J = 7$ Hz, 12H), 1.25 (d, $J = 7$ Hz, 6H), 1.4—1.7 (m, 5H), 1.7—2.0 (m, 1H), 3.46 (sept, $J = 7$ Hz, 2H), 3.74 (tq, $J = 7$ and 7 Hz, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 14.0$, 23.2, 30.9, 45.1, 45.4; ^{29}Si NMR

(CDCl$_3$), $\delta = -34.9$. HRMS Found: *m*/*z* 310.1400. Calcd for $C_{13}H_{28}Cl_2N_2Si$: M, 310.1399.

Reduction of 3a in Triethylsilane. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.380 g, 9.72 mmol), **3a** (0.654 g, 2.18 mmol), and triethylsilane (7.11 g, 61.1 mmol). The mixture was heated at reflux for 3 h. After the filtration of the salt, the solvent was removed in vacuo. Kugelrohr distillation of the residue gave 1,1-bis(diisopropylamino)-2,2,2-triethyldisilane (**5**, 0.260 g, 7.54×10^{-4} mol, 34.6%). Colorless crystals; mp 56.8—60.8 °C; bp 95—115 °C/0.015 mmHg; ^{1}H NMR (CDCl$_3$) $\delta = 0.68$ (q, $J = 7.9$ Hz, 6H), 1.00 (t, $J = 7.9$ Hz, 9H), 1.09 (d, $J = 6.7$ Hz, 12H), 1.15 (d, $J = 6.7$ Hz, 12H), 3.21 (sept, $J = 6.7$ Hz, 4H), 5.03 (s, 1H); ^{13}C NMR (CDCl$_3$) $\delta = 4.6$, 8.5, 24.7, 25.1, 46.9; ^{29}Si NMR (CDCl$_3$) $\delta = -44.0$, -13.2. HRMS Found: *m*/*z* 344.3044. Calcd for $C_{18}H_{44}N_2Si_2$: M, 344.3043.

Reduction of 3a in Triethylvinylsilane. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (423 mg, 10.8 mmol), **3a** (653 mg, 2.18 mmol), and triethylvinylsilane (6.94 g, 48.7 mmol). The mixture was heated under reflux for 2 h. Filtration of the salt and then evaporation of the solvent in vacuo gave 1,1-bis(diisopropylamino)-2-triethylsilyl-1-silacyclopropane (**6**, 569 mg, 1.53 mmol, 70.4 %). A colorless oil; bp 110—120 °C/0.1 mmHg; ^{1}H NMR (CDCl$_3$) $\delta = -0.10$ (dd, $J = 10$ and 13 Hz, 1H), 0.4—0.5 (m, 1H), 0.5—0.6 (m, 6H), 0.71 (dd, $J = 10$ and 13 Hz, 1H), 0.95 (t, $J = 8$ Hz, 9H), 1.12 (d, $J = 7$ Hz, 6H), 1.13 (d, $J = 7$ Hz, 6H), 1.15 (d, $J = 7$ Hz, 6H), 1.20 (d, $J = 7$ Hz, 6H), 3.40 (sept, $J = 7$ Hz, 2H), 3.43 (sept, $J = 7$ Hz, 2H); ^{13}C NMR (CDCl$_3$) $\delta = -0.1$, 4.8, 5.2, 8.0, 24.0, 24.4, 24.4, 24.9, 46.2, 47.7; ^{29}Si NMR (CDCl$_3$) $\delta = -61.1$, 5.0; UV (hexane) λ_{max}/nm (ε) 211 (sh, 5330), 228 (sh, 2630), 250 (sh, 330). HRMS Found: *m*/*z* 370.3213. Calcd for $C_{20}H_{46}N_2Si_2$: M, 370.3200.

Reduction of 3a in 2,4,4-Trimethyl-1-pentene. In a two-necked flask (50 ml) equipped with magnetic stirring bar were placed sodium (0.467 g, 11.9 mmol), **3a** (0.745 g, 2.49 mmol), and 2,4,4-trimethyl-1-pentene (7.20 g, 64.2 mmol). The mixture was heated under reflux for 3 h. After the filtration of the salt, the solvent was removed in vacuo. Kugelrohr distillation of the residue gave allylsilane **7** (0.494 g, 1.45 mmol, 58.2%). A colorless oil; bp 88—95 °C/0.15 mmHg; ^{1}H NMR (CDCl$_3$) $\delta = 0.92$ (s, 9H), 1.05 (d, $J = 6.7$ Hz, 12H), 1.11 (d, $J = 6.7$ Hz, 12H), 1.77 (d, $J = 3.0$ Hz, 2H), 1.97 (s, 2H), 3.19 (sept, $J = 6.7$ Hz, 4H), 4.53 (t, $J = 2.3$ Hz, 1H), 4.70—4.75 (m, 1H), 4.79 (t, $J = 3.0$ Hz, 1H); ^{13}C NMR (CDCl$_3$) $\delta = 24.1$, 24.8, 28.2, 30.2, 31.5, 44.8, 50.9, 112.3, 145.0; ^{29}Si NMR (CDCl$_3$) $\delta = -34.9$. HRMS Found: *m*/*z* 340.3279. Calcd for $C_{20}H_{44}N_2Si$: M, 340.3274.

Reduction of 3a in 2,3-Dimethyl-2-butene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed sodium (0.380 g, 9.72 mmol), **3a** (0.659 g, 2.20 mmol), and 2,3-dimethyl-2-butene (10 ml, 84.1 mmol). The mixture was heated under reflux for 73 h. The usual workup gave allylsilane **8** (0.118 g, 3.70×10^{-4} mol, 17.2%). A colorless oil; bp 80—95 °C/0.2 mmHg; ^{1}H NMR (CDCl$_3$) $\delta = 1.04$ (d, $J = 6.7$ Hz, 12H), 1.12 (d, $J = 6.7$ Hz, 12H), 1.59 (s, 3H), 1.64 (s, 3H), 1.69 (s, 3H), 1.70 (d, $J = 3.2$ Hz, 2H), 3.16 (sept, $J = 6.7$ Hz, 4H), 4.83 (t, $J = 3.2$ Hz, 1H); ^{13}C NMR (CDCl$_3$) $\delta = 20.3$, 20.4, 20.9, 24.2, 24.3, 24.5, 45.0, 120.7, 125.6. HRMS Found: *m*/*z* 312.2961. Calcd for $C_{18}H_{40}N_2Si$: M, 312.2961.

Reduction of 3a in Bis(trimethylsilyl)acetylene. In a two-necked flask (30 ml) equipped with a magnetic stirring bar were placed sodium (0.201 g, 5.14 mmol), **3a** (0.352 g, 1.18 mmol), and bis(trimethylsilyl)acetylene (6.10 g, 35.8 mmol). The mixture was heated at 100 °C for 2 h. The usual workup gave 3,3-bis(diisopropylamino)-1,2-bis(trimethylsilyl)-3-silacyclopropene **9** (0.367 g, 9.20×10^{-4} mol, 78.2%). **9** was slightly air sensitive, but stable thermally under an inert atmosphere. **9**: Yellow crystals; mp 40.5—43.5 °C; ^{1}H NMR (C$_6$D$_6$) $\delta = 0.33$ (s, 18H), 1.10 (d, $J = 6.7$ Hz, 24H), 3.33 (sept, $J = 6.7$ Hz, 4H); ^{13}C NMR (C$_6$D$_6$) $\delta = 0.5$, 24.4, 46.1, 207.1; ^{29}Si NMR (C$_6$D$_6$) $\delta = -100.2$, -15.43; UV (hexane) λ_{max}/nm (ε) 207 (15600), 273 (460), 386 (54). HRMS Found: *m*/*z* 398.2951. Calcd for $C_{20}H_{46}N_2Si_3$: M, 398.2969.

Reduction of 3a in a 1 : 1 Mixture of Bis(trimethylsilyl)acetylene and Toluene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed sodium (0.691 g, 30.1 mmol), **3a** (3.06 g, 10.2 mmol), bis(trimethylsilyl)acetylene (17.2 g, 101 mmol), and toluene (10 ml, 93.9 mmol). The mixture was heated under reflux for 19 h. The usual workup gave **9** (3.26 g, 8.18 mmol, 80.2%).

Reduction of 3a in Benzene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.560 g, 14.3 mmol), **3a** (1.00 g, 3.34 mmol), and benzene (10 ml, 112 mmol). The mixture was heated under reflux for 15 h. The usual workup gave bis(diisopropylamino)phenylsilane (**10a**, 0.540 g, 1.76 mmol, 52.7%). A colorless oil; bp 85—95 °C/0.02 mmHg; ^{1}H NMR (CDCl$_3$) $\delta = 1.11$ (d, $J = 6.7$ Hz, 12H), 1.21 (d, $J = 6.7$ Hz, 12H), 3.39 (sept, $J = 6.7$ Hz, 4H), 5.31 (s, 1H), 7.3—7.4 (m, 3H), 7.7—7.8 (m, 2H); ^{13}C NMR (CDCl$_3$) $\delta = 24.0$, 24.7, 44.9, 127.3, 128.6, 134.8, 140.3; ^{29}Si NMR (CDCl$_3$) $\delta = -36.4$. HRMS Found: *m*/*z* 306.2491. Calcd for $C_{18}H_{34}N_2Si$: M, 306.2491.

Reduction of 3a in Benzene-*d*$_6$. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.423 g, 10.8 mmol), **3a** (0.716 g, 2.39 mmol), and benzene-*d*$_6$ (10 ml, 113 mmol). The mixture was heated under reflux for 10 h. The usual workup gave deuteriobis(diisopropylamino)(pentadeuteriophenyl) silane (**10a**-*d*$_6$, 0.399 g, 1.28 mmol, 53.4%). A colorless oil; bp 105—110 °C/0.06 mmHg; ^{1}H NMR (CDCl$_3$) $\delta = 1.13$ (d, $J = 6.6$ Hz, 12H), 1.22 (d, $J = 6.6$ Hz, 12H), 3.40 (sept, $J = 6.6$ Hz, 4H); ^{13}C NMR (CDCl$_3$) $\delta = 24.0$, 24.7, 44.9, 126.8 (t, $^1J_{C-D} = 24$ Hz), 128.0 (t, $^1J_{C-D} = 24$ Hz), 134.4 (t, $^1J_{C-D} = 24$ Hz), 140.0; ^{29}Si NMR (CDCl$_3$) $\delta = -36.5$. HRMS Found: *m*/*z* 312.2860. Calcd for $C_{18}H_{28}D_6N_2Si$: M, 312.2868.

Reduction of 3a-*d*$_{12}$ in Benzene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.318 g, 8.13 mmol), **3a**-*d*$_{12}$ (0.483 g, 1.55 mmol), and benzene (10 ml, 112 mmol). The mixture was heated under reflux for 17 h. The usual workup gave bis[(1,1,1,3,3,3-hexadeuteriopropan-2-yl)(propan-2-yl)amino]phenylsilane (**10a**-*d*$_{12}$, 0.243 g, 7.62×10^{-4} mol, 49.2%). A colorless oil; bp 95—110 °C/0.5 mmHg; ^{1}H NMR (CDCl$_3$) $\delta = 1.09$ (d, $J = 6.8$ Hz, 6H), 1.19 (d, $J = 6.8$ Hz, 6H), 3.3—3.5 (m, 4H), 5.28 (s, 1H), 7.3—7.4 (m, 3H), 7.7—7.8 (m, 2H); ^{13}C NMR (CDCl$_3$) $\delta = 23.3$ (sept, $^1J_{C-D} = 21$ Hz), 24.0, 24.7, 44.5, 44.9, 127.3, 128.6, 134.8, 140.4; ^{29}Si NMR (CDCl$_3$) $\delta = -36.4$. HRMS Found: *m*/*z* 318.3247. Calcd for $C_{18}H_{22}D_{12}N_2Si$: M, 318.3245.

Reduction of 3b in Benzene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.376 g, 9.62 mmol), **3b** (0.688 g, 2.13 mmol), and benzene (10 ml, 112 mmol). The mixture was heated under reflux for 3.5 h. The usual workup gave bis(*cis*-2,6-dimethylpiperidino)phenylsilane[13a] (**10b**, 0.348 g, 1.05 mmol, 49.3%). A colorless oil; bp 100—120 °C/0.15 mmHg; ^{1}H NMR (CDCl$_3$) $\delta = 1.11$ (d, $J = 7.0$ Hz, 6H), 1.25 (d, $J = 7.0$ Hz, 6H), 1.35—1.75 (m, 10H), 1.75—2.00 (m, 2H), 3.2—3.6 (m, 4H), 4.83 (s, 1H), 7.2—7.5 (m, 3H), 7.6—7.8 (m, 2H); ^{13}C NMR (CDCl$_3$) $\delta = 14.8$, 23.9, 24.3, 31.4, 31.5, 45.2, 45.8, 127.5, 129.0, 134.3, 138.2; ^{29}Si NMR (CDCl$_3$) $\delta = -20.1$. HRMS Found: *m*/*z* 330.2494. Calcd for $C_{20}H_{34}N_2Si$: M, 330.2491.

Reduction of 3c in Benzene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.428 g, 10.9 mmol), **3c** (0.730 g, 2.34 mmol), and benzene (10 ml, 112 mmol). The mixture was heated under reflux for 5 h. The usual workup gave (diisopropylamino)(*cis*-2,6-dimethylpiperidino)phenylsilane (**10c**, 0.419 g, 1.32 mmol, 56.4%). A colorless solid; mp 31.2—39.1 °C; bp 125—145 °C/0.15 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 1.02$ (d, $J = 6.6$ Hz, 6H), 1.18 (d, $J = 7.0$ Hz, 3H), 1.20 (d, $J = 6.6$ Hz, 6H), 1.26 (d, $J = 7.0$ Hz, 3H), 1.4—1.5 (m, 6H), 1.5—1.7 (m, 4H), 1.8—2.0 (m, 2H), 3.37 (sept, $J = 6.6$ Hz, 2H), 3.47 (tq, $J = 7.0$ and 7.0 Hz, 2H), 5.11 (s, 1H), 7.3—7.5 (m, 3H), 7.6—7.8 (m, 2H); ^{13}C NMR ($CDCl_3$) $\delta = 14.6$, 23.7, 24.0, 24.1, 24.5, 31.2, 31.3, 44.5, 44.8, 127.5, 128.8, 134.3, 138.7; ^{29}Si NMR ($CDCl_3$) $\delta = -29.6$. HRMS Found: *m*/*z* 318.2489. Calcd for $C_{19}H_{34}N_2Si$: M, 318.2491.

Reduction of a 1 : 1 Mixture of 3a and 3b in Benzene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.392 g, 10.0 mmol), **3a** (0.347 g, 1.16 mmol), **3b** (0.375 g, 1.16 mol), and benzene (10 ml, 112 mmol). The mixture was heated under reflux for 39 h. The usual workup gave 0.353 g of a mixture of **10a**, **10b**, and **10c**. The products ratio of [**10a**] : [**10b**] : [**10c**] is 65 : 24 : 11, estimated by ^{1}H NMR.

Reduction of a 1 : 1 mixture of 3a and 3a-*d*$_{12}$ in Benzene. In a two-necked flask (50 ml) equipped with a magnetic strring bar were placed potassium (0.291 g, 7.44 mmol), **3a** (0.181 g, 6.04×10^{-4} mol), **3a**-*d*$_{12}$ (0.188 g, 6.04×10^{-4} mol), and benzene (10 ml, 112 mmol). The mixture was heated under reflux for 3.5 h. The usual workup gave 0.240 g of a mixture of **10a**, **10a**-*d*$_{12}$, and **10a**-*d*$_6$. The product ratio of [**10a**] : [**10a**-*d*$_{12}$] : [**10a**-*d*$_6$] was estimated to be 4 : 4 : 1 by mass spectrometry of the mixture. The spectral pattern of the mixture was complicated because of the incomplete deuteration in the starting **3a**-*d*$_{12}$ (about 90% purity as a *d*$_{12}$ isomer). By analyzing the molecular–ion pattern observed as partially overlapped three series of peaks due to **10a**, **10a**-*d*$_{12}$, and **10a**-*d*$_6$, the product ratio was determined quantitatively. In this calculation, isotopic effects on the efficiency of the ionization and fragmentation for the molecular ions were neglected.

Reduction of 3a in Toluene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.426 g, 10.9 mmol), **3a** (0.714 g, 2.38 mmol), and toluene (10 ml, 93.9 mmol). The mixture was heated under reflux for 3 h. The usual workup gave **11a** (0.666 g, 2.08 mmol, 87.1%). A colorless oil; bp 80—100 °C/0.015 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 0.94$ (d, $J = 6.7$ Hz, 12H), 1.34 (d, $J = 6.7$ Hz, 12H), 2.29 (d, $J = 3.2$ Hz, 2H), 3.23 (sept, $J = 6.7$ Hz, 4H), 4.87 (t, $J = 3.2$ Hz, 1H), 7.0—7.1 (m, 1H), 7.1—7.3 (m, 4H); ^{13}C NMR ($CDCl_3$) $\delta = 24.0$, 24.5, 25.4, 44.8, 124. 0, 127.9, 129.0, 140.3; ^{29}Si NMR ($CDCl_3$) $\delta = -32.2$. HRMS Found: *m*/*z* 320.2634. Calcd for $C_{19}H_{36}N_2Si$: M, 320.2648.

Reduction of 3a in Toluene-*d*$_8$. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.728 g, 10.5 mmol), **3a** (0.728 g, 2.43 mmol), and toluene-*d*$_8$ (10 ml, 94.1 mmol). The mixture was heated under reflux for 3.5 h. The usual workup gave (benzyl-*d*$_7$)deuteriobis(diisopropylamino)silane **11a**-*d*$_8$ (0.649 g, 1.97 mmol, 81.1%). A colorless oil; bp 95—105 °C/0.05 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 1.04$ (d, $J = 6.7$ Hz, 12H), 1.23 (d, $J = 6.7$ Hz, 12H), 3.32 (sept, $J = 6.7$ Hz, 4H,); ^{13}C NMR ($CDCl_3$) $\delta = 24.1$, 24.5, 25.3 (quint, $^1J_{C\text{–}D} = 13$ Hz), 44.8, 123.5 (t, $^1J_{C\text{–}D} = 25$ Hz), 127.4 (t, $^1J_{C\text{–}D} = 24$ Hz), 128.5 (t, $^1J_{C\text{–}D} = 24$ Hz), 140.0; ^{29}Si NMR ($CDCl_3$) $\delta = -31.9$. HRMS Found: *m*/*z* 328.3150. Calcd for $C_{19}H_{28}D_8N_2Si$: M, 328.3150.

Reduction of 3a-*d*$_{12}$ in Toluene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.286 g, 7.31 mmol), **3a**-*d*$_{12}$ (0.507 g, 1.63 mmol), and toluene (10 ml, 93.9 mmol). The mixture was heated was under reflux for 3 h. The usual workup gave benzylbis[(1,1,1,3,3,3-hexadeuteriopropan-2-yl)(propan-2-yl)amino]silane (**11a**-*d*$_{12}$) (0.459 g, 1.38 mmol, 61.3%). A colorless oil; bp 80—100 °C/0.015 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 0.96$ (d, $J = 6.7$ Hz, 6H), 1.15 (d, $J = 6.7$ Hz, 6H), 2.30 (d, $J = 3.2$ Hz, 2H), 3.2—3.3 (m, 4H), 4.88 (t, $J = 3.2$ Hz, 1H), 7.0—7.1 (m, 1H), 7.1—7.3 (m, 4H); ^{13}C NMR ($CDCl_3$) $\delta = 23.4$ (sept, $^1J_{C\text{–}D} = 21$ Hz), 24.0, 24.5, 25.4, 44.4, 44.8, 124.0, 127.9, 129.0, 140.4; ^{29}Si NMR ($CDCl_3$) $\delta = -32.0$. HRMS Found: *m*/*z* 332.3408. Calcd for $C_{19}H_{24}D_{12}N_2Si$: M, 332.3401.

Reduction of 3b in Toluene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.346 g, 8.85 mmol), **3b** (0.657 g, 2.03 mmol), and toluene (15 ml, 141 mmol). The mixture was heated under reflux for 2.5 h. The usual workup gave benzylbis(*cis*-2,6-dimethylpiperidino)silane (**11b**) (0.545 g, 1.58 mmol, 77.8%). A colorless oil; bp 145—160 °C/0.15 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 1.15$ (d, $J = 6.9$ Hz, 6H), 1.16 (d, $J = 6.9$ Hz, 6H), 1.35—1.55 (m, 10H), 1.75—1.90 (m, 2H), 2.26 (d, $J = 2.9$ Hz, 2H), 3.30—3.45 (m, 4H), 4.42 (t, $J = 2.9$ Hz, 1H), 7.05—7.15 (m, 1H), 7.15—7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) $\delta = 14.7$, 23.4, 24.1, 24.4, 31.46, 31.53, 45.6, 45.9, 124.0, 128.0, 129.0, 139.9, ^{29}Si NMR ($CDCl_3$) $\delta = -15.0$. HRMS Found: *m*/*z* 344.2645. Calcd for $C_{21}H_{36}N_2Si$: M, 344.2648.

Reduction of 3c in Toluene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.430 g, 11.0 mmol), **3c** (0.702 g, 2.25 mmol), and toluene (15 ml, 141 mmol). The mixture was heated under reflux for 10.5 h. The usual workup gave benzyl(diisopropylamino)(*cis*-2,6-dimethylpiperidino)silane (**11c**) (0.472 g, 1.42 mmol, 63.1%). A pale yellow oil; bp 125—140 °C/0.1 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 0.91$ (d, $J = 6.7$ Hz, 6H), 1.106 (d, $J = 6.7$ Hz, 3H), 1.108 (d, $J = 6.7$ Hz, 6H), 1.17 (d, $J = 6.7$ Hz, 3H), 1.3—1.6 (m, 5H), 1.7—1.9 (m, 1H), 2.22 (dd, $J = 14.1$ and 3.0 Hz, 1H), 2.31 (dd, $J = 14.1$ and 3.0 Hz, 1H), 3.20 (sept, $J = 6.7$ Hz, 2H), 3.3—3.5 (m, 2H), 4.64 (t, $J = 3.0$ Hz, 1H), 6.9—7.3 (m, 5H); ^{13}C NMR ($CDCl_3$) $\delta = 14.4$, 23.78, 23.81, 24.2, 24.3, 24.7, 31.1, 31.5, 44.3, 45.3, 45.6, 124.0, 128.0, 129.0, 140.1; ^{29}Si NMR ($CDCl_3$) $\delta = -34.3$. HRMS Found: *m*/*z* 332.2642. Calcd for $C_{20}H_{36}N_2Si$: M, 332.2648.

Reduction of 1 : 1 Mixture of 3a and 3b in Toluene. In a two-necked flask (50 ml) equipped with a magnetic stirring bar were placed potassium (0.412 g, 10.5 mmol), **3a** (0.360 g, 1.20 mmol), **3b** (0.389 g, 1.20 mmol), and toluene (10 ml, 93.9 mmol). The mixture was heated under reflux for 4.5 h. The usual workup gave 0.621 g of a mixture of **11a** and **11b**. The yields of **11a** and **11b** determined by ^{1}H NMR were 93 and 64%, respectively.

Pyrolysis of 6 in Triethylsilane. Pyrolysis of a mixture of **6** (206 mg, 5.55×10^{-4} mol) and triethylsilane (1.31 g, 11.3 mmol) in a sealed tube at 165 °C for 42 h gave **5** (54.7%) and triethylvinylsilane (19.8%). The yields were determined by GLC.

Pyrolysis of 6 in Toluene. Pyrolysis of a mixture of **6** (103 mg, 2.28×10^{-4} mol) and toluene (1.30 g, 14.1 mmol) in a sealed tube at 165 °C for 36 h gave **11a** (5.9%) and triethylvinylsilane (23.6%). The yields were determined by GLC.

Pyrolysis of 6 in Mesitylene. Thermal reaction of a mixture of **6** (153 mg, 4.13×10^{-4} mol) and mesitylene (10 ml, 71.9 mmol) under reflux (ca. 162 °C) for 51 h gave **17** (18.5%) and triethylvinylsilane (22.0%). The yields were determined by GLC. The authentic sample of **17** was prepared by the reduction of **3a** with potassium in mesitylene (77%). **17**: Colorless crystals; mp 54.3—57.6 °C; bp 115—120 °C/0.05 mmHg; ^{1}H NMR ($CDCl_3$) $\delta = 0.93$ (d, $J = 6.7$ Hz, 12H), 1.12 (d, $J = 6.7$ Hz, 12H), 2.19 (d, $J = 3.1$ Hz, 2H), 2.23 (s, 6H), 3.20 (sept, $J=6.7$ Hz, 4H), 4.82 (t, $J=3.1$ Hz, 1H), 6.68 (s, 1H), 6.74 (s, 2H); ^{13}C NMR ($CDCl_3$) $\delta=21.2$, 24.1, 24.5, 25.0, 44.8, 125.5, 126.9, 137.1, 140.0; ^{29}Si NMR ($CDCl_3$) $\delta=-32.3$. HRMS Found: m/z 348.2959. Calcd for $C_{21}H_{40}N_2Si$: M, 348.2961.

Pyrolysis of 9 in Toluene. Thermal reaction of a mixture of **9** (51.5 mg, 5.55×10^{-4} mol) and toluene (2 ml, 18.8 mmol) in a sealed tube at 200 °C for 60 h gave **11a** (4.0%) and bis(trimethylsilyl)acetylene (77.2%). The yields were determined by GLC.

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7) It has been reported that difluorosilylene is trapped by hexafluorobenzene to give pentafluoro(trifluorosilyl)benzene at 77 K.[8] Recently, Okazaki et al. have reported an interesting reaction of silylene with benzene; the silylene produced by the thermal dissociation of a disilene, Tbt(Mes)Si=Si(Mes)Tbt [Tbt = 2,4,6-tris(bis(trimethylsilyl)methyl]phenyl), gives adduct to benzene.[9] Reactions of silylene with the intramolecular aromatic groups are known, where benzylic C–H insertion products of the silylene are obtained.[9b,10]

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13) Disilene ($H_2Si=SiH_2$) was calculated to be more stable than the two isolated silylenes by 50—60 kcal mol^{-1}.[14] Experimentally, tetramethyldisilene generated by pyrolysis of 7,8-disilabicyclo[2.2.2]octa-2,5-diene derivatives was successfully trapped by dienes without dissociation to silylene even at 500 °C.[15a] Moreover, *cis*- and *trans*-1,2-dimethyl-1,2-diphenyldisilenes generated by pyrolysis of the corresponding 2,3-benzo-7,8-disilabicyclo[2.2.2]octa-2,5-diene derivatives at 300°C has been shown to maintain the configuration until trapped by anthracene.[15b] The results show that the dissociation of usual alkyl- and aryldisilenes to the corresponding silylenes did not take place under the conditions. For a recent discussion on the disilene-silylene equilibrium, see: R. Okazaki and R. West, *Adv. Organomet. Chem.*, **39**, 231 (1996).

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