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Generation of silanimines by photolysis of hindered azidosilanes *

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Abstract

Trimesitylazidosilane (**1**) and three new azidodisilanes, $Mes_2Si(N_3)SiPh_2$-t-Bu (**2**), $Me_2Si(N_3)SiMes_2$-t-Bu (**3**) and i-$Pr_2Si(N_3)SiMes_2$-t-Bu (**4**), were prepared and photolyzed at 254 nm. Compound **1** photolyzes in glassy 3-methylpentane (3-MP) at 77 K or in 3-MP solution at −140 °C to $Mes_2Si{=}NMes$ (**5**) and a C–H insertion product **6**. Compounds **2–4** photolyze in 3-MP at low temperatures to give stable solutions of silanimines, $R_2Si{=}NSiR_2R'$. Photolysis of **1–4** in the presence of alcohols yields alkoxyaminosilanes.

Introduction

Most molecules containing Si=N double bonds (silanimines) are thermodynamically unstable since two Si–N single bonds are lower in energy than one Si=N double bond. This, coupled with the low barrier to unhindered silanimine dimerization, for many years limited the scope of silanimine chemistry to the study of reactive intermediates [1]. Recent progress in this field includes the generation of two silanimines in hydrocarbon glasses at 77 K [2,3]. In addition, silanimines have also been isolated at room temperature and characterized by X-ray crystallography [4–6].

In this paper, we describe the preparation of several silanimines via the photolysis of hindered organosilyl azides. The photochemistry of each of these compounds **1–4** was investigated in a 3-methylpentane (3-MP) glass at 77 K and in solution at low temperatures.

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* Dedicated to Colin Eaborn, in recognition of his outstanding contributions to silicon chemistry over many years, with warm personal regards.

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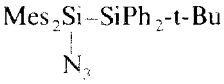
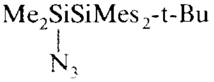
Mes_3SiN_3

(1)



$Mes_2Si(N_3)\text{-}SiPh_2\text{-}t\text{-}Bu$

(2)



$Me_2Si(N_3)SiMes_2\text{-}t\text{-}Bu$

(3)

$(i\text{-}Pr)_2Si(N_3)SiMes_2\text{-}t\text{-}Bu$

(4)

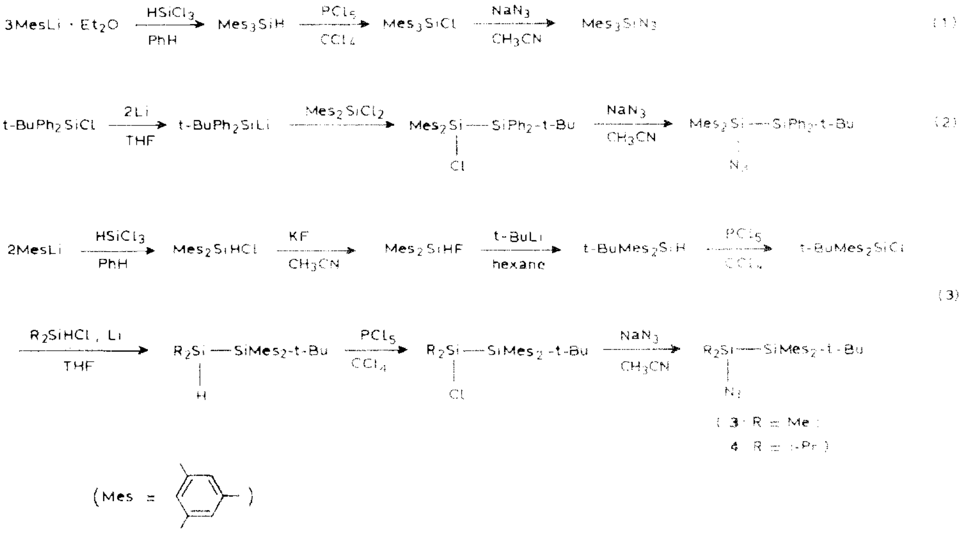
(Mes = 2,4,6-trimethylphenyl)

Results and discussion

The synthesis of each azide was straightforward and is illustrated in Scheme 1.

A. Photochemistry of trimesitylazidosilane (1). Irradiation of Mes_3SiN_3 (**1**) in a 3-methylpentane glass (ca. 1.5×10^{-3} *M*) at 77 K led to an intense yellow coloration of the glass, and analysis by UV-visible spectroscopy showed that three new absorptions were produced at 257, 296, and 444 nm (Fig. 1). The ratio of the intensity of the 296 nm band to the 444 nm band remained constant as a function of photolysis time, which is consistent with the assignment of both bands to one species. When the yellow glass was annealed, the 296 and 444 nm absorptions shifted to 278 and 429 nm, respectively (the 257 nm band was unaffected by annealing).

When the 3-MP glass was melted and the solution was warmed, all three bands persisted up to −125 °C. Above this temperature the 278 nm and 429 nm maxima rapidly diminished. The 257 nm band remained unchanged even after warming to room temperature and recooling to 77 K. These results indicate that two products, one stable and one thermally unstable, are formed in the photolysis of **1** at 77 K.



Scheme 1. Synthetic routes to hindered azidosilanes **1**–**4**.

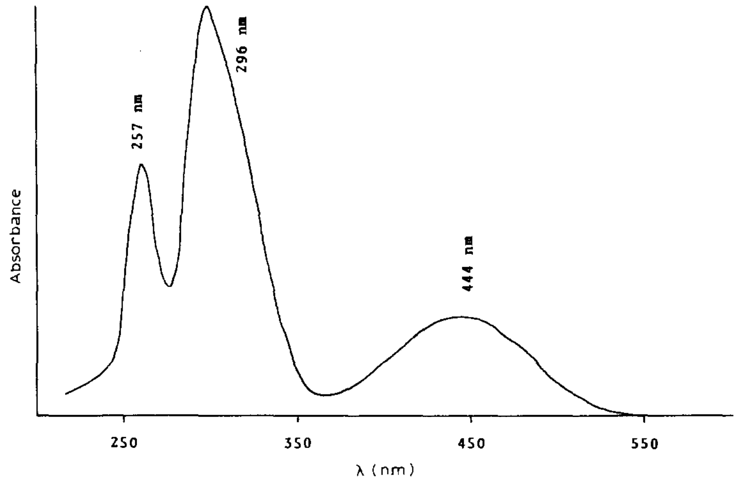
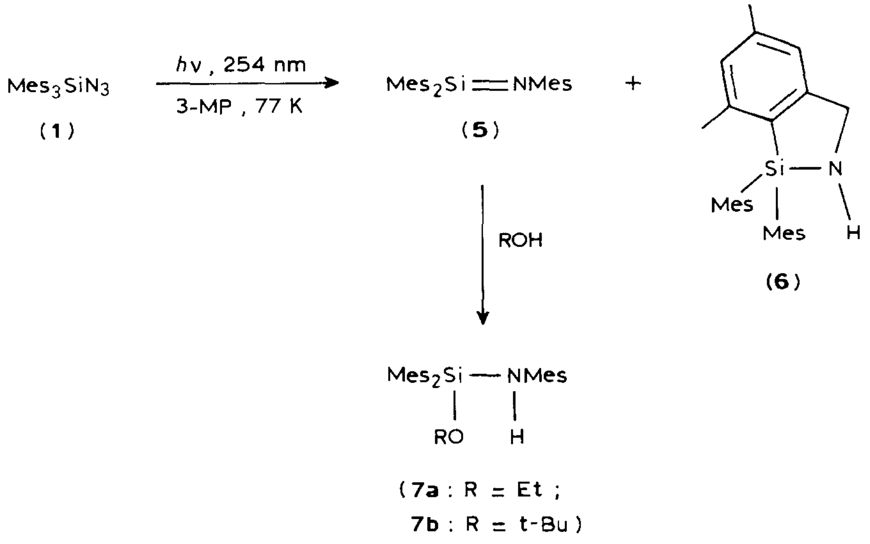


Fig. 1. The UV-visible spectrum that results on photolysis of trimesitylazidosilane (**1**) in 3-MP at 77 K.

To determine the structure of the photoproducts, **1** was irradiated in a glass containing 0.5% EtOH as a trapping agent. In these experiments, the same three UV bands were formed, but those at 296 and 444 nm immediately disappeared on annealing. Again, the 257 nm band was unaffected by increasing temperature. Analysis of the photolysate by GC-mass spectrometry and ^{1}H NMR showed that only two products were formed, the alkoxysilazane **7a** and the C–H insertion compound **6**, in a ratio of 1/2 (eq. 1). Analogous results were obtained when t-BuOH was used as a trapping agent.



(1)

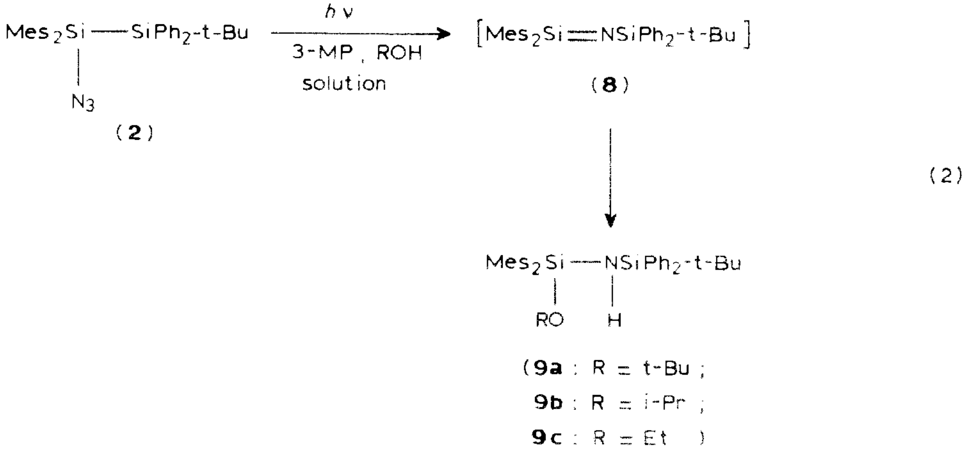
Based on this evidence, we assign the silanimine **5** as the species responsible for the 296 and 444 nm absorptions. The hypsochromic shift observed in each band on annealing the glass is tentatively attributed to a matrix effect. The silanimine could be generated in a twisted or other high energy conformation that does not relax to its ground state geometry until the constraints of the glass are removed. The 257 nm band is due to the stable C–H insertion compound **6** [7*,8*].

A yellow solution of **5**, admixed with **6**, was prepared by the photolysis of **1** in 3-MP at −140 °C. The UV-visible spectrum of this solution was identical to that obtained upon warming a mixture of **5** and **6**, which had been generated at 77–133 K. Addition of EtOH rapidly discharged the yellow color and resulted in the formation of a 1/2 mixture of **7a** and **6**. Warming the yellow solution above −125 °C led to loss of coloration and addition of EtOH at this point did not produce **7a**. Thus, the silanimine appears to be stable at low temperatures in solution, as well as in a 3-MP glass at 77 K.

Mixtures of **6** and **7a** or **7b** were also made by photolysis of **1** in 3-MP containing EtOH or t-BuOH at room temperature. Analysis of each product mixture by ^{1}H NMR, after addition of internal standard, revealed that **7a** and **7b** were each produced in ca. 30% yield. The C–H insertion compound was formed in 55% yield, showing that regardless of temperature, **6** is the major product in the photolysis of **1** [9*].

B. Photochemistry of $Mes_2Si(N_3)SiPh_2$*-t-Bu (2).* The photolysis of **2** in the presence of alcohols at temperatures ranging from −140 °C to room temperature gave only one product, the alkoxydisilazanes resulting from alcohol addition to silanimine (**8**) (eq. 2). The products **9a–9c** were formed in 80 to 85% yield and, from the ^{1}H NMR spectrum of each compound, it is clear that (a) only the silyl substituent undergoes migration to nitrogen and (b) no C–H insertion occurs.

Photolysis of **2** in 3-MP solution at temperatures ranging from −140 to −125 °C resulted in the formation of a faintly orange solution of **8** that immediately



(2)

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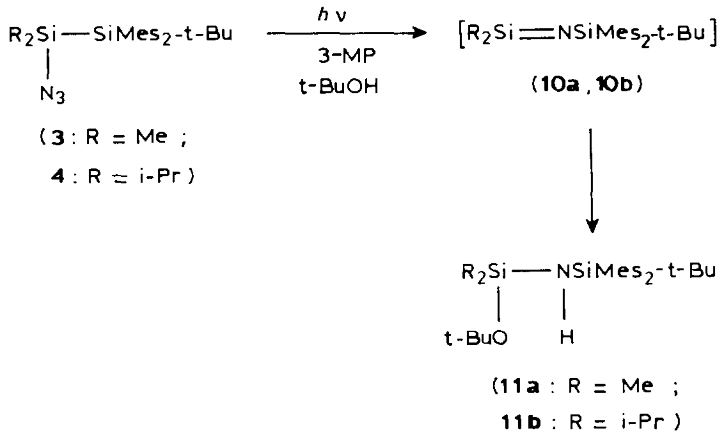
* Reference numbers with asterisks indicate notes in the list of references.



(3)

decolorized upon addition of i-PrOH or EtOH. Analysis of the crude reaction mixture by ^1H NMR confirmed that, in addition to unphotolyzed **2**, the only compound present was the alkoxydisilazane **9b** or **9c**, respectively. Warming an orange solution of **8** to −78 °C for 20 minutes, followed by addition of i-PrOH, gave unphotolyzed **2**, a small amount of **9b**, and unidentified decomposition products. Thus, it appears that the silanimine **8** is modestly stable for brief periods of time at temperatures up to −78 °C.

The photochemistry of the azidodisilane was also investigated in 3-MP at 77 K. Under these conditions, no new bands appeared in the UV-visible spectrum, and when the glass was doped with EtOH, **9c** was not formed.

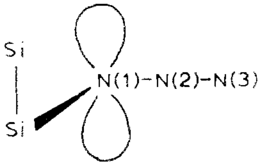
C. Photochemistry of azidodisilanes 3 and 4. The photochemistry of both **3** and **4** paralleled that of **2**. Photolysis in the presence of t-BuOH at various temperatures gave **11a** or **11b**, respectively (80–83%, eq. 3).

Photolysis of **3** in 3-MP solution at −140 °C resulted in the formation of a yellow solution of the silanimine (**10a**) [10]. Addition of t-BuOH at this point immediately discharged the yellow color and ^1H NMR and GC analysis of the crude photolysate showed that the only product formed was **11a**. A yellow solution of **10a** rapidly decolorized upon warming to temperatures above −100 °C; addition of t-BuOH at this point did not give **11a**. Similar results were obtained in the photolysis of the di-i-propyl derivative **4**. Neither silanimine (**10a** or **10b**) survives temperatures above −100 °C.

Irradiation of **3** in a 3-MP glass at 77 K produced no new bands in the UV, nor was **11a** produced when the glass contained t-BuOH. The azide did indeed undergo decomposition, as witnessed by the formation of a new compound detected by GC-mass spectrometry (M^+ m/z 395). The structure of this compound is not known, but is probably an intramolecular C–H insertion compound analogous to **6**.

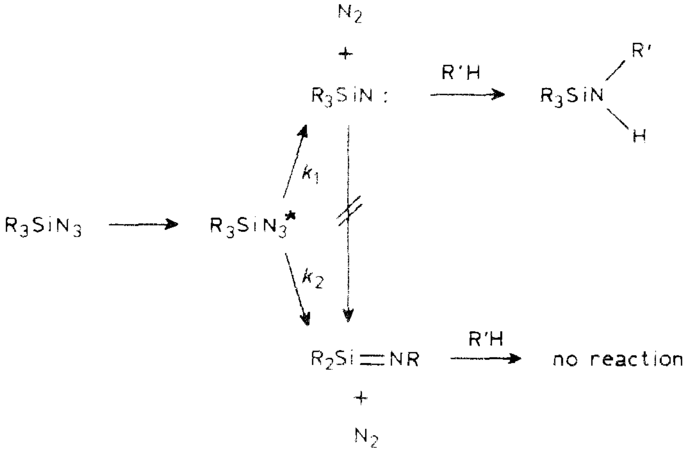
When photolyzed in solution, each of the azidodisilanes undergoes a clean migration of the silyl substituent from silicon to nitrogen, forming *N*-silylsilanimines **8**, **10a**, and **10b**. The following explanation, based on the photochemistry of alkyl azides, is offered to account for these observations.

In 1971, Abramovich and Kyba [11] published evidence implicating that the photochemical decomposition of alkyl azides to give imines does not proceed via a nitrene intermediate, i.e. migration of an R group from carbon to nitrogen occurs simultaneously with loss of N_2. Further, these authors postulated that the migrating R group is perpendicular to the departing N_2 molecule. If a similar mechanism is operative in the decomposition of our azidodisilanes, then the silicon–silicon bond would have to be perpendicular to the N(2)–N(3) bond. This would align the Si–Si bond with the *p* orbital on N(1).



An X-ray structural analysis of **2** [12] reveals that the Si–Si–N(1)–N(2) torsion angle is 103.0°, a value quite close to the perpendicular arrangement required for migration to occur [13*]. We therefore propose that *N*-silylsilanimines result from a migration (with simultaneous loss of N_2) in the excited state of the azidodisilane and not from an intermediate nitrene.

Bertrand and coworkers have recently proposed [16] that the excited state of azidosilanes gives rise to both silyl nitrene and silanimine intermediates, and that the former does not undergo rearrangement to silanimine (eq. 4). Our hypothesis is consistent with this scenario if replacement of an R group in eq. 4 with a silyl substituent results in the more rapid formation of silanimine relative to nitrene (i.e., $k_2 \gg k_1$).



(4)

Experimental

General data. Unless otherwise noted, ^1H NMR (in benzene-d_6) and ^{13}C NMR (in chloroform-*d*) spectra were measured on Bruker WP-270 and AM-500 instruments, respectively. Analytical GC was done on a Hewlett–Packard 5890A instrument equipped with a 0.53 mm × 15 m open tubular column coated with 5% phenyl methyl silicone and a 3390A integrating chart recorder. Preparative GC was done on a GOW-MAC model 550P instrument equipped with a 1/4″ × 3′ column packed with 5% Dexsil 400 on Chromosorb W/AW/DMCS. The GC columns were pretreated with hexamethyldisilazane immediately prior to injection when necessary.

High resolution mass spectra were measured on a Kratos MS-80 instrument. GC-MS were recorded on a Kratos MS-25 instrument interfaced with a Carlo Erba capillary GC. Data are reported as m/z ratios with percent relative intensities in parentheses. Infrared spectroscopy was carried out on a Beckman Acculab 7 spectrophotometer. Values are reported in cm^{-1}.

Alcohols were distilled from the corresponding sodium alkoxide. Solution photolyses were conducted on dry, degassed samples in quartz tubes in a Rayonet RPR-100 Photochemical Reactor equipped with 254 nm lamps. Low temperatures were maintained by a cold stream of nitrogen and monitored by a calibrated thermocouple. Glass experiments were conducted in Suprasil cuvettes immersed in a quartz Dewar vessel filled with liquid nitrogen.

All reactions were conducted under an atmosphere of dry nitrogen in oven-dried glassware (12–24 h, 150 ° C, assembled hot under a flow of nitrogen). Solvents were dried appropriately and distilled immediately prior to use. Chlorosilanes were distilled from K_2CO_3.

Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Mesityllithium etherate, MesLi · Et$_2$O. A one liter 3-necked flask was equipped with a condenser, 500 ml dropping funnel, and a magnetic stir bar. To the flask was added bromomesitylene [17] (50.0 g, 0.25 mol) and 250 ml of Et_2O. A hexane solution of n-BuLi (1.5 *M*, 0.38 mol) was cannulated into the addition funnel and slowly added to the aryl bromide. A colorless precipitate soon formed and, upon completing the addition, the suspension was stirred for 8 h. The suspension was then transferred with a wide-bore cannula to an enclosed glass frit and filtered. The resulting colorless solid was washed several times with hexane to remove any unreacted n-BuLi and dried in a vacuum until the weight remained constant. The yields of $MesLi \cdot Et_2O$ ranged from 80–95%.

Trimesitylsilane, Mes$_3$SiH. A 500 ml, 3-necked flask was equipped with a 250 ml addition funnel, a condenser, and a magnetic stir bar. To the flask was added $MesLi \cdot Et_2O$ (42.7 g, 0.21 mol) and 150 ml of benzene. To this stirred suspension was added dropwise trichlorosilane (9.0 g, 0.07 mol) in 150 ml of benzene. After heating to reflux for 12 h, the mixture was filtered and the benzene removed by distillation. The residue was taken up in Et_2O, washed with water, dried over $MgSO_4$, filtered, and rotary evaporated. Recrystallization from acetone afforded Mes_3SiH (13.6 g, 53%): m.p. 194–195 ° C (lit. 192 ° C [18]); ^1H NMR ($CDCl_3$) δ 6.78 (s, 6H), 5.76 (s, 1H), 2.26 (s, 9H), 2.12 (s, 18H); HRMS: m/z 386.2434 (M^+, 11, calcd. for $C_{27}H_{34}Si$ 386.2421), 385(3), 371(3), 267(30), 266(100), 147(73).

Trimesitylchlorosilane, Mes$_3$SiCl. A mixture of Mes_3SiH (7.1 g, 18 mmol) and PCl_5 (4.2 g, 20 mmol) in 100 ml of carbon tetrachloride was heated to reflux in a 250 ml flask. After 24 h, the CCl_4 was removed in a vacuum and the yellow residue taken up in hexane and filtered. The solution was washed with water (the chlorosilane does not undergo hydrolysis) and then with dilute $NaHCO_3$ until the aqueous layer was non-acidic. After three more water washes, the organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. Two recrystallizations from hexane gave Mes_3SiCl (4.9 g, 65%): m.p. 171.5–172.5 °C; ^1H NMR δ 6.67 (s, 2H), 2.24 (br s, 6H), 2.09 (s, 3H); MS 420 (M^+, 0.3), 385(0.2), 300(84), 181(100) [19*].

Trimesitylazidosilane (1) [20]. A mixture of Mes_3SiCl (6.1 g, 15 mmol) and NaN_3 (1.1 g, 17 mmol) in 150 ml of acetonitrile was warmed to ca. 40 °C in a 250 ml flask. After stirring for 12 h, the solvent was removed in a vacuum and the residue suspended in hexane. The salts were removed by filtration and the filtrate cooled to effect crystallization of **1**. A second recrystallization afforded pure Mes_3SiN_3 (5.4 g, 84%): m.p. 164.0–164.5 °C; ^1H NMR: δ 6.70 (s, 2H), 2.29 (br s, 6H), 2.05 ppm (s, 3H); ^{13}C NMR: δ 145.2, 140.5, 131.2, 130.2, 24.1, 21.2 ppm; IR (KBr) 2140; HRMS: m/z 427.2423 (M^+, 0.3, calcd. for $C_{27}H_{33}SiN_3$ 427.2436), 399(1) 308(28), 307(100), 279(22), 264(27), 188(32). Anal. Found: C, 75.53; H, 7.80; N, 9.97. $C_{27}H_{33}SiN_3$ calcd.: C, 75.83; H, 7.77; N, 9.83%.

1,1-Dimesityl-2,2-diphenyl-2-t-butylchlorodisilane, $Mes_2Si(Cl)SiPh_2$-t-Bu. In a 250 ml flask was placed t-$BuPh_2SiCl$ (42 g, 0.15 mol, Petrarch) and 140 ml of THF. The solution was magnetically stirred while Li wire (2.5 g, 0.36 g-atom) was cut in small pieces directly into the flask. The resulting red brown solution was stirred for 4 h. A 500 ml, 3-necked flask was equipped with a 250 ml funnel and magnetic stir bar. To the flask was added Mes_2SiCl_2 [21] (37.4 g, 0.11 mol) and 100 ml of THF. The lithium reagent was cannulated into the addition funnel and added dropwise to the dichloride. Upon completion of the addition, the mixture was stirred for 12 h. A few drops of a saturated NH_4Cl solution was added to quench any unreacted lithium reagent. The solvent was removed on a rotary evaporator and the light yellow residue was suspended in hexane and filtered. Evaporation of the hexane gave a glassy solid that was recrystallized twice from acetone to give the chlorodisilane (43.7 g, 74%): m.p. 178.5–179.5 °C; ^1H NMR (CD_2Cl_2): δ 7.73 (m, 4H), 7.35 (m, 6H), 6.71 (s, 4H), 2.22 (s, 6H), 2.13 (s, 12H), 1.05 ppm (s, 9H); HRMS: m/z 540 (M^+, not observed), 483.1756, (M^+ − t-Bu, 2.8, calcd. for $C_{30}H_{32}Si_2Cl$ 483.1723), 301(33), 266(98), 265(14), 135(100) [19*].

1,1-Dimesityl-2,2-diphenyl-2-t-butylazidodisilane (2). To a 500 ml flask was added the above chlorodisilane (22.2 g, 41 mmol), NaN_3 (27 g, 0.42 mol), and 250 ml of acetonitrile. The mixture was heated to reflux for 24 h. The reaction was then cooled, the solvent removed on a rotary evaporator, and the salts suspended in hexane. Filtration and concentration of the solution resulted in a crude, colorless solid (14.4 g, 64%). A second recrystallization from hexane gave pure **2**: m.p. 190.5–191.5 °C; ^1H NMR (CD_2Cl_2): δ 7.61 (m, 4H), 7.36 (m, 6H), 6.75 (s, 4H), 2.23 (s, 6H), 2.12 (s, 12H), 1.01 ppm (s, 9H); ^{13}C NMR: δ 144.4, 140.1, 137.1, 135.3, 130.5, 130.0, 129.6, 128.0, 29.6, 24.7, 22.7, 21.1 ppm; IR (KBr): 2120 cm^{-1}; HRMS: m/z 547 (M^+, not observed), 519.2778 ($M^+ - N_2$, 0.2, calcd. for $C_{34}H_{41}Si_2N$ 519.2767), 462 (100). Anal. Found: C, 74.42; H, 7.45; N, 7.77. $C_{34}H_{41}Si_2N_3$ calcd.: C, 74.54; H, 7.54; N, 7.67%.

Dimesitylchlorosilane, Mes_2SiHCl. A one liter, 3-necked flask was equipped with a 125 ml funnel, a condenser, and a magnetic stir bar. To the flask was added $MesLi \cdot Et_2O$ (74.5 g, 0.37 mol) and 300 ml of benzene, after which trichlorosilane (25.5 g, 0.19 mol) and 80 ml of benzene were syringed into the addition funnel. The chlorosilane was added dropwise (2 h) and the mixture was stirred overnight. Filtration and rinsing of the salts, followed by solvent removal, gave a light yellow residue that was purified by Kugelrohr distillation to give Mes_2SiHCl (41.5 g, 74%): m.p. 65–68 °C (lit. 63–64 °C [22]); ^1H NMR: δ 6.63 (s, 4H), 6.35 (s, 1H), 2.42 (s, 12H), 2.03 ppm (s, 6H); IR (KBr): 2192, 1600; HRMS 302.1261 (M^+, 0.2, calcd. for $C_{18}H_{23}SiCl$ 302.1252), 266(5), 120(67), 105(100) cm^{-1} [19*].

Dimesitylfluorosilane, Mes_2SiHF. A mixture of Mes_2SiHCl (17.9 g, 59 mmol), KF (5 g, 86 mmol), and 200 ml of acetonitrile was magnetically stirred in a 500 ml flask until the reaction was found to be complete by GC. Following solvent removal, the salts were extracted overnight with hexane in a Soxhlet extractor. Recrystallization from hexane gave Mes_2SiHF (13.4 g, 80%): m.p. 123.5–126.0 °C; ^1H NMR: δ 6.66 (s, 4H), 6.25 (d, J 53.3 Hz, 1H), 2.38 (d, J 1.5 Hz, 12H), 2.05 ppm (s, 6H); HRMS: m/z 286.1547 (M^+, 21.7, calcd. for $C_{18}H_{23}SiF$ 286.1553), 271(15), 166(33), 165(10), 120(100).

t-Butyldimesitylsilane, $t\text{-}BuMes_2SiH$. A 100 ml flask was equipped with a condenser and a magnetic stir bar. Mes_2SiHF (5 g, 17.5 mmol) and 40 ml of pentane were added to the flask, to which was subsequently added 17.9 mmol of t-BuLi (1.7 *M* in pentane) via syringe. The resulting solution was heated to reflux for 8 h. A few drops of a saturated NH_4Cl solution were then added to the flask and the organic layer was washed with water, dried over $MgSO_4$, filtered, and rotary evaporated. Recrystallization from acetone gave $t\text{-}BuMes_2SiH$ (5 g, 88%): m.p. 118.5–119.5 °C; ^1H NMR: δ 6.74 (s, 4H), 5.19 (s, 1H), 2.46 (s, 12H), 2.09 (s, 6H), 1.24 ppm (s, 9H); HRMS: m/z 324.2274 (M^+, 2.5, calcd. for $C_{22}H_{32}Si$ 324.2265), 267(74), 57(100).

t-Butyldimesitylchlorosilane, $t\text{-}BuMes_2SiCl$. A mixture of $t\text{-}BuMes_2SiH$ (4 g, 12 mmol), PCl_5 (5.1 g, 24 mmol), and 50 ml of carbon tetrachloride was brought to reflux in a 100 ml flask for 12 h. The solution was then cooled and solvent removed in a vacuum. Hexane was added to precipitate the excess PCl_5. After filtration, the hexane was washed with water, followed by dilute $NaHCO_3$ until the washes were non-acidic (the chlorosilane does not hydrolyze). Two recrystallizations from hexane afforded $t\text{-}BuMes_2SiCl$ (2.7 g, 63%): m.p. 122.0–123.0 °C; ^1H NMR: δ 6.65 (s, 4H), 2.42 (s, 12H), 2.04 (s, 6H), 1.31 ppm (s, 9H); HRMS: m/z 358.1887 (M^+, 0.1, calcd. for $C_{22}H_{31}SiCl$ 358.1883), 301(100), 238(2.3).

1,1-Dimethyl-2,2-dimesityl-2-t-butyldisilane, $Me_2SiHSiMes_2\text{-}t\text{-}Bu$. A 250 ml, 3-necked flask was equipped with an overhead stirrer. To the flask was added $t\text{-}BuMes_2SiCl$ (5 g, 14 mmol), Me_2SiHCl (16.5 mmol, Petrarch), and 100 ml of THF. The solution was stirred and cooled with an ice bath while Li wire (0.22 g, 32 mg-atom) was cut into small pieces directly into the flask. The solution was stirred overnight and the resulting suspension was filtered through a plug of glass wool to remove unreacted Li. The THF was removed on a rotary evaporator and replaced with 100 ml of hexane. The hexane was washed with water to remove the LiCl, dried over $MgSO_4$, and filtered. After solvent removal, the disilane (4.4 g, 86%) was recrystallized from abs. EtOH: m.p. 125.5–126.0 °C; ^1H NMR: δ 6.72 (s, 4H), 4.35 (sept, J 4.4 Hz, 1H), 2.32 (br s, 12H), 2.10 (s, 6H), 1.28 (s, 9H), 0.22 (d, J 4.4 Hz, 6H); HRMS 382.2505 (M^+, 1.5, calcd for $C_{24}H_{38}Si_2$ 382.2512), 325(75), 205(8), 177(52).

$(i\text{-}Pr)_2SiH\text{–}SiMes_2\text{-}t\text{-}Bu$ was synthesized in the same fashion from $(i\text{-}Pr)_2SiHCl$ [23] and was recrystallized from hexane: m.p. 93.5–95.5 °C; ^1H NMR: δ 6.72 (s, 4H), 4.22 (s, 1H), 2.35 (bf s, 12H), 2.09 (s, 6H), 1.34 (s, 11H, t-Bu + Me_2CH), 1.23 (d, J 7.1 Hz, 6H), 1.03 ppm (d, J 7.4 Hz, 6H); HRMS: m/z 438 (M^+, not observed), 381.2452 ($M^+ - 57$, 8.2, calcd for $C_{24}H_{37}Si_2$ 381.2434), 323(19), 177(100).

1,1-Dialkyl-2,2-dimesityl-2-t-butylchlorosilanes, R_2SiClSiMes$_2$-t-Bu (R = Me, i-Pr). These compounds were synthesized from the above silanes (yields 80–90%) in the same manner as Mes$_3$SiCl and t-BuMes$_2$SiCl and were characterized as follows. Me$_2$SiCl–SiMes$_2$-t-Bu: recrystallized twice from acetone, m.p. 187.0–187.5 °C; the ^{1}H NMR of this compound consists of a sharp singlet for each methyl group (except t-Bu) at probe temperature. δ 6.79 (s, 2H), 6.61 (s, 1H), 6.56 (s, 1H), 2.70, 2.59, 2.09, 2.06, 1.99, 1.81, 0.58, 0.42 (s, 3H each), 1.36 ppm (s, 9H). HRMS: m/z 416.2127 (M^+, 0.2, calcd. for $C_{24}H_{37}Si_2Cl$ 416.2122), 401(1), 359(49), 381(1), 324(4), 177(100) [19*]. To eliminate the possibility that a rearrangement had occurred in this reaction, a small amount of the chlorodisilane was reduced with LiAlH$_4$ to give back Me$_2$SiH–SiMes$_2$-t-Bu.

(i-Pr)$_2$SiCl–SiMes$_2$-t-Bu was recrystallized twice from acetone: m.p. 154.0–154.5 °C; the ^{1}H NMR spectrum of this compound exhibited very broad resonances at probe temperature. δ 6.83, 6.80, 6.61, 6.54 (br s, ArH), 2.82, 2.62, 2.08, 2.07, 1.91, 1.87 (br s, ArMe), 1.44 (s, 9H), 1.34, 1.29, 1.09, 0.37 ppm (br s).

*1,1-Dialkyl-2,2-dimesityl-2-t-butylazidodisilanes, R_2SiN_3–SiMes$_2$-t-Bu (**3**; R = Me, **4**; R = i-Pr).* Both **3** and **4** were synthesized by the reaction of the above chlorodisilanes with NaN$_3$ in acetonitrile (80–85%).

Azidodisilane (**3**) was recrystallized from acetonitrile: m.p. 92.0–93.0 °C; ^{1}H NMR: δ 6.79 (br s, 2H), 6.60 (br s, 2H), 2.60, 2.57, 1.98, 1.83, 0.31, 0.25 (br s, 3H each), 2.08 (br s, 6H), 1.27 ppm (s, 9H); HRMS: m/z 423 (M^+, not observed), 395.2472 ($M^+ - 28$, 0.6, calcd. for $C_{24}H_{37}Si_2N$ 395.2464), 380(5), 338(100), 177(56). Anal. Found: C, 68.18; H, 8.97; N, 9.86. $C_{24}H_{37}Si_2N_3$ calcd.: C, 68.03; H, 8.80; N, 9.92%. Azidodisilane **4** was recrystallized from acetone: m.p. 121.0–122.0 °C. The ^{1}H NMR spectrum consists of very broad resonances at probe temperature. δ: 6.78 (br s, 2H), 6.61 (br s, 2H), 2.67, 2.08, 1.89, 1.27 (br s, 6H), 1.37 (s, 9H), 1.00 (br s, 3H), 0.56 ppm (br s, 3H); HRMS: m/z 479 (M^+, not observed), 394.2395 ($M^+ - 57$, -28, 15, calcd for $C_{24}H_{36}Si_2N$ 394.2386), 177(100). Anal. Found: C, 69.85; H, 9.58; N, 8.72. $C_{28}H_{45}Si_2N_3$ calcd.: C, 70.08; H, 9.45; N, 8.77%.

*Photochemistry of **1**.* A magnetically-stirred solution of **1** (100 mg) in 3-methylpentane (3-MP) was photolyzed in the Rayonet for 3 h (at room temperature or at −90 °C). The solution was concentrated in a vacuum and cooled to effect precipitation of **6** as a light yellow, slightly impure solid. The only peaks observed by ^{1}H NMR, ^{13}C NMR and mass spectroscopy are assigned to **6**: ^{1}H NMR: δ 6.82, 6.74 (s, 1H, Ar*H*), 6.72 (s, 4H, Ar*H*), 4.28 (s, 2H, ArCH_2N), 2.36 (s, 3H, *p-Me*ArN), 2.31 (s, 12H, *o-Me*Ar), 2.16 (s, 3H, *o-Me*ArN), 2.11 ppm (s, 6H, *p-Me*Ar); ^{13}C NMR (CD$_2$Cl$_2$): δ 150.9, 143.2, 142.6, 138.8, 136.1, 134.4, 132.4, 129.6, 121.6, 50.4, 23.7, 23.5, 21.5, 21.2 ppm; HRMS: m/z 399.2381 (M^+, 3.8, calcd. for $C_{27}H_{33}SiN$ 399.2374), 384(19), 280(9), 279(5), 269(3).

*Trapping of **5** with EtOH.* A solution of **1** (ca. 2 × 10^{-2} *M*) in 3-MP containing 5% EtOH was photolyzed in the Rayonet for 30 min at room temperature. The volatiles were removed in a vacuum and (MeO)$_4$Si was added as a ^{1}H NMR internal standard. The yields of **7a** and **6** were found by integration. Preparative GC failed to completely separate these compounds, so it was necessary to work on a GC-isolated sample that was enriched in **7a**, but still contained a small amount of **6**. The spectrum of **7a** was deduced from this enriched sample: ^{1}H NMR: δ 6.70 (s, 4H), 3.64 (q, *J* 7.1 Hz, 2H), 3.53 (br s, 1H), 2.42 (s, 12H), 2.24 (s, 6H), 2.09 (s, 3H), 2.06 (s, 6H), 1.13 (t, *J* 7.1 Hz, 3H) (ring protons of aryl amino group obscured by resonances of **6**); GC-MS: m/z 445 (M^+, 39), 326(3), 325(7), 311(100). Similarly, the ^{1}H NMR spectrum of the t-BuOH adduct **7b** was obtained: δ 6.66 (s, 4H), 2.54 (s, 12H), 2.41 (s, 6H), 2.02 (s, 6H), 1.30 ppm (s, 9H) (the aryl and p-Me resonances due to the amino mesityl group are obscured by the resonances of **6**).

A mixture of **6** and **7a** was produced upon photolysis of **1** (1.5×10^{-3} M) in 3-MP containing 0.5% alcohol at 77 K. The same mixture (ca. two parts of **6** to one part of **7a**) also resulted when a cold, dilute solution of EtOH in 3-MP was injected into a yellow solution of **5** and **6** at −140 °C.

Photochemistry of 2. A stirred solution of the azidodisilane (0.42 g, 0.8 mmol) in 5 ml each of 3-MP and t-BuOH was photolyzed at room temperature until no starting material remained by ^{1}H NMR spectroscopy. The volatiles were removed in a vacuum and the residue dissolved in a minimal amount of hexane. Cooling afforded a colorless solid (0.25 g, 50%) that was recrystallized from acetone to give pure **9a**: m.p. 144.5–145.0 °C; ^{1}H NMR (CD_2Cl_2): δ 7.68 (m, 4H), 7.15 (m, 6H), 6.52 (br s, 4H), 2.29 (br s, 12H), 2.04 (s, 6H), 1.32 (s, 9H), 1.12 ppm (s, 9H); HRMS: m/z 593.3513 (M^+, 0.2, calcd. for $C_{38}H_{51}Si_2NO$ 539.3496), 536(0.3), 521(2), 480(100), 360(98), 120(31), 105(37); IR (nujol) 3390, 1125, 925. Anal. Found: C, 76.78; H, 8.58; N, 2.34. C, 76.84; H, 8.65; N, 2.36%. In the same fashion, **9b** and **9c** were obtained upon photolysis of **2** in i-PrOH and EtOH, respectively. The yields of the trapped products were determined by NMR integration. **9b** (85%): ^{1}H NMR (CD_2Cl_2): δ 7.66 (m, 4H), 7.33 (m, 6H), 6.67 (s, 4H), 4.14 (sept, J 6.2 Hz, 1H), 2.27 (s, 18H), 1.20 (d, J 6.2 Hz, 6H), 1.13 ppm (s, 9H); ^{13}C NMR: δ 144.2, 138.8, 137.0, 135.6, 133.3, 129.8, 129.3, 127.4, 66.5, 28.2, 25.8, 24.5, 21.3, 19.4 ppm; HRMS: m/z 579.3349 (M^+, 0.1, calcd. for $C_{37}H_{49}Si_2NO$ 579.3340), 522(22), 480(43), 402(31), 360(78), 120(55), 105(74). **9c** (80%): ^{1}H NMR (CD_2Cl_2): 7.66 (m, 4H), 7.34 (m, 6H), 6.73 (s, 4H), 3.50 (q, J 7.0 Hz, 2H), 2.32 (s, 12H), 1.11 (s, 9H), 1.06 (t, J 7.0 Hz, 3H); ^{13}C NMR: δ 144.3, 139.0, 136.8, 135.8, 133.2, 129.8, 129.3, 127.5, 58.5, 27.9, 24.3, 21.3, 19.4, 18.3 ppm; HRMS: m/z 565.3199 (M^+, 0.1, calcd. for $C_{36}H_{47}Si_2NO$ 565.3184), 508(29), 480(39), 360(37), 120(15), 105(23).

The alkoxydisilazanes **9a**–**9c** were also formed when the photolysis of **2** was conducted at low temperatures (−60 to −140 °C) in the presence of alcohol and when **2** was photolyzed by itself at −140 °C followed by addition of a cold, dilute solution of alcohol.

Attempts to observe the UV-visible spectrum of **8** invariably failed, even though the solutions were faintly orange in color to the eye. This is probably due to the fact that, at −140 °C, the solution is turbid and the signal-to-noise ratio is low as a result of light scattering.

Photochemistry of 3 and 4. Alkoxydisilazanes **11a** and **11b** were formed in the photolysis of **3** and **4**, respectively, in the presence of t-BuOH. NMR integrations were used to determine the yields of **11a** and **11b**, which were isolated by preparative GC and characterized as follows. **11a** (80%): ^{1}H NMR: δ 6.70 (s, 4H), 2.41 (br s, 12H), 2.10 (s, 6H), 1.27 (s, 9H), 1.17 ppm (s, 9H), −0.01 (s, 6H); IR (neat): 3380, 3010, 2960, 2920, 2850, 1725, 1605, 1200, 1050, 940, 850 cm^{-1}. HRMS: m/z 469 (M^+, not observed), 412.2404 (M^+ − t-Bu, 0.3, calcd. for $C_{24}H_{38}Si_2NO$ 412.2482): 396(4), 356(29), 236 (100). **11b** (83%): ^{1}H NMR: δ 6.72 (br s, 4H), 2.71 (br s, 12H), 2.10 (s, 6H), 1.35 (br m, 2H), 1.32 (s, 9H), 1.22 (s, 9H), 1.05 (d, J 7.5, 6H). 0.99 ppm (d, J 7.2, 6H); MS: m/z 525 (M^+, not observed), 381(6), 323(13), 297(15), 177(100).

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8 A product analogous to **6** is probably also produced in the photolysis of $Mes_2(Me_3Si)SiNi_3$ in argon at 20 K. See ref. 2.
9 Compound **6** could result from an intermediate nitrene or an excited state of the azide.
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