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Reactions of tetramesityldisilene with azides: synthesis of disilaaziridines *

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Abstract

The reactions of several organic azides (RN_3) with tetramesityldisilene (**1**) were studied. Azides with R = Ph or Mes each gave two products, a disilaaziridine and a disilatriazoline. When R = $PhCH_2$ or Me_3SiCH_2 intermediate adducts of the azide and the disilene were found. These adducts and the disilatriazolines both react thermally to yield the respective disilaaziridines. For R = Me_3Si only a disilaaziridine was observed, the structure of which was determined by X-ray crystallography and was found to have a short Si–Si internuclear distance of 2.23 Å. Crystal data: R = trimethylsilyl, a 23.561(3), b 19.001(3), c 16.916(3) Å, monoclinic, $\beta = 106.095°$, $C2/c$, $Z = 8$. Novel five-membered silicon heterocycles were isolated from the reactions of **1** with toluenesulfonyl azide and diphenylphosphonyl azide.

Introduction

The rich chemistry of tetramesityldisilene [1] and other disilenes has been the subject of several recent reviews [2]. Reactions of disilenes have allowed the synthesis of many new organosilicon compounds which were previously inaccessible by other routes. Among these are many small ring compounds made by cycloaddition of multiple bonds with disilene, including products of reactions with oxygen [3a], diazomethane [3b], acetylenes [3c], ketones [3d], isocyanides [3e] and nitrous oxide [3f]. Several of these compounds have unique structural features which raise questions about the bonding in these species.

In this paper we discuss reactions of **1** with azides. The isolated products are novel three- and five-membered rings which were characterized by standard spectroscopic techniques, including X-ray crystallography of a disilaaziridine.

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* This manuscript is dedicated to Prof. F.G.A. Stone in view of his many important contributions to organometallic chemistry.

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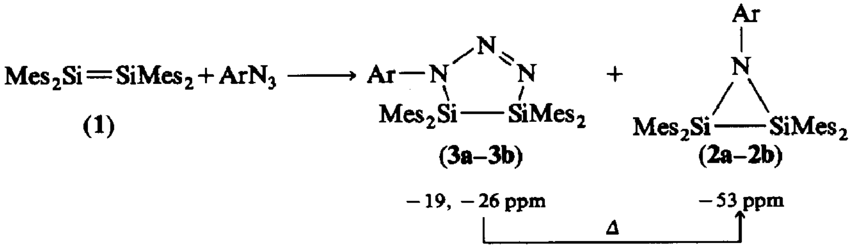
Results and discussion

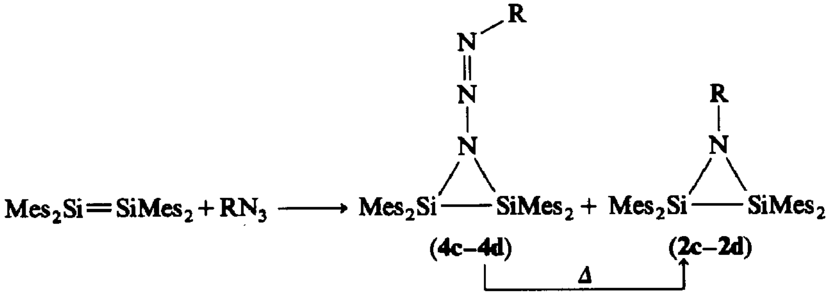
A. Reaction of 1 with aryl azides. The addition of a solution of PhN_3 in hexane to a bright yellow solution of **1** [4] in C_6D_6 at room temperature resulted in immediate decolorization of the solution and vigorous gas evolution. After 1–2 min the solution became purple, and an absorption maximum at 562 nm was observed by UV-visible spectroscopy. Three new resonances were observed in the ^{29}Si NMR spectrum at −19.5, −26.9 and −53.0 ppm. Upon standing, a white solid precipitated from solution which, when redissolved in $CDCl_3$, gave a ^{29}Si NMR with a single resonance at −53.0 ppm. The purple supernatant gave a ^{29}Si spectrum with the same three resonances in a ratio of 1/1/2. The ^1H NMR of the purple solution was consistent with the assignment of the colored compound to disilatriazoline **3a** (eq. 1). When the purple sample was heated at 80 °C for 12 h, the color faded and the signals at −19.5 and −26.9 ppm diminished as the signal at −53.0 ppm grew. Attempts to obtain pure **3a** were unsuccessful; samples were invariably contaminated by **2a**. The white solid **2a** was isolated and gave analytical data consistent with a disilaazridine structure. Reaction of **1** with $MesN_3$ under the same conditions produced similar results.



(1)

(**2a**, **3a**: Ar = phenyl,
2b, **3b**: Ar = 2,4,6-trimethylphenyl)

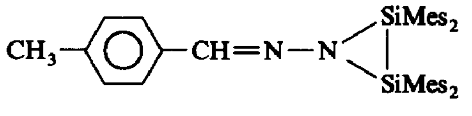
B. Reaction of 1 with alkyl azides. When one equivalent of $PhCH_2N_3$ was added to a solution of **1** in C_6D_6 vigorous gas evolution took place and the solution took on a deep orange color ($\lambda_{max} = 470$). Two new resonances were found in the ^{29}Si NMR with chemical shifts of −53.09 and −54.03 ppm, in an approximately 2/1 ratio. Heating the solution at 80 °C for 6 h caused the peak at −54.03 to disappear and the solution to decolorize. The isolated product was analyzed as the disilaaziridine **2c**. The orange color observed is probably due to the thermally unstable compound observed by ^{29}Si NMR. The symmetrical nature of the compound eliminates disilatriazoline **3c** as a plausible structure for the intermediate. The most likely structure is **4c**, the end-on adduct of the azide to the double bond of disilene (eq. 2).



(2)

(**2c**, **4c**: R = $PhCH_2$,
2d, **4d**: R = Me_2SiCH_2)

Similar acyclic triazenes are known to have absorption bands in the visible regions. For example, PhN=NN$(SiMeEt_2)_2$ is orange and other silyl substituted triazenes are also colored. Detailed studies of azide additions to olefins have been carried out but no evidence has been reported for the analogous carbon compounds as reaction products [6*]. Reactions of phosphines (R_3P) with azides are however known to proceed via an initial end-on adduct [7]. Recently, Schubert et al. reported that *p*-tolyldiazomethane adds to **1** to give a 1/1 adduct having a very similar ^{29}Si chemical shift to that of **4c**, −54.04 ppm, which was assigned the end-on adduct structure, **5** [8]



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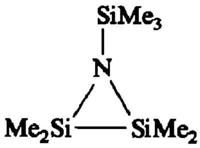
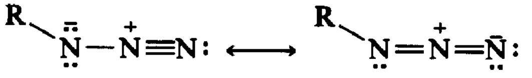


(6)

The reaction of **1** with trimethylsilylmethyl azide, $Me_3SiCH_2N_3$, gave similar results to benzyl azide, except that the solution was colorless after addition of the azide. Two new high field resonances were observed by ^{29}Si NMR (−51.6, −54.8 ppm) in a ratio of approximately 1/1. When the mixture was heated at 70 ° C for 24 h the peak at −54.8 ppm disappeared with growth of the −51.6 ppm peak. The colorless solid product gave spectral data consistent with the disilaaziridine **2d**.

Addition of trimethylsilyl azide (Me_3SiN_3) to a solution of **1** in C_6D_6 resulted in immediate decolorization of the solution and vigorous gas evolution. In this case, ^{29}Si NMR showed that only one new product was formed with resonances at +1.64 and −50.3 ppm. The solid product isolated was recrystallized from hexane and was analyzed spectroscopically as **2e**. No evidence for **4e** was obtained. One previous example of a disilaaziridine has been reported, a permethyl compound obtained under strenuous reaction conditions and giving analytical data and chemical reactions consistent with the assigned structure **6** [9*].

The reaction products of azides with disilene appear to depend on the nature of the substituent group in the azide; aryl azides produce disilaaziridines and triazolines (**3**), alkyl azides yield disilaaziridines and triazenes (**4**) and Me_3SiN_3 gives only the disilaaziridine. The reason for the differences are not clear, but the results are consistent with the model of azides as resonance hybrids of canonical structures **A** and **B**. Structure A, which should be most nucleophilic at the internal nitrogen



$$R-\overset{-}{\ddot{N}}-\overset{+}{N}\equiv N: \longleftrightarrow R-\ddot{N}=\overset{+}{N}=\ddot{\overset{-}{N}}:$$

(A) **(B)**

atom, is believed to be more important for aryl than for alkyl azides, while structure **B**, nucleophilic at the terminal nitrogen, is more favored for alkyl azides [10]. Our earlier studies indicate that structure **B** is even more strongly preferred for silyl azides [11]. The fact that no **4e** is observed in the reaction of Me_3SiN_3 with disilene may reflect the ability of the Me_3Si group to undergo rapid 1,3-rearrangement, to give **2e**.

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* Reference number with asterisk indicates a note in the list of references.

Table 1

Summary of crystal data and intensity collection for **2e**

Empirical formula	$C_{39}H_{53}Si_3N$
Formula weight	619
Crystal dimensions	0.3×0.5×0.5
Temperature	173 K
Cell parameters	a, 23.594(7) Å
	b, 19.011(6) Å
	c, 16.914(3) Å
	β, deg 106.04(2)
Space group	$C2/c$
Z	8
Calculated density, g/cm^3	1.14
Nicolet diffractometer (Note 2)	$P\bar{1}$ (Mo)
Absorption coefficient (μ, cm^{-1})	1.52
Scan type	ω
Scan range, deg below $2\theta K_\alpha$	1.0
deg above $2\theta K_\alpha$	1.0
Scan speed (deg/min)	2.93–29.3
Background/scan ratio	profile analysis
2θ limits, deg	3.5–48.3
$(\sin\theta/\lambda)_{\max}$	0.968
Unique data, measured	4059
$F_o > 3\sigma(F_o)$	3167
p; weight = $[\sigma^2(F) + p^2F^2]^{-1}$	0.03
Discrepancy indices, R_1	0.076
R_2	0.095
Goodness of fit	3.01
Observation/variable ratio	8.2
Final difference, $\lambda_{\max}$, e/Å^3	0.52

*C. X-Ray crystallography of **2e**.* Crystals of **2e** suitable for X-ray analysis were grown from hexane at room temperature. The structure of **2e** was solved by direct methods and was refined by blocked cascade least-squares analysis for F with $F_o > 3\sigma(F_o)$ [12]. A summary of experimental data is given in Table 1. The bonding parameters for **2e** are given in Tables 2 and 3. Other details of the crystal structure are given in the experimental section. The structure of **2e**, as shown in the thermal ellipsoid diagram in Fig. 1, proves unequivocally that **2e** has the disilaaziridine structure. The bonding to the attached ligands is unremarkable. The Si–N bond lengths in the ring are 1.77 Å, slightly longer than the normal Si–N distance (1.74 Å) [13]. The internal bond angles of the three-membered ring (3MR) are 78, 51 and 51°. The silicon and carbon framework of the molecule is very nearly planar. The sum of the bond angles C–Si–Si′, C′–Si–Si and C–Si–C′ about each silicon atom is 358°.

A most interesting feature of this molecule is the short Si–Si internuclear distance of 2.23 Å, which more closely resembles the length of a Si–Si double bond (2.15 Å) than a single bond (2.35 Å). The Si–Si distance in **2e** is consistent with a recent theoretical calculation for the parent compound, $(H_2Si)_2NH$, which predicted Si–Si 2.233 Å [14]. The structure of **2e** is very similar to that reported for the isoelectronic disilaoxirane, for which the Si–Si distance is also 2.23 Å [3f].

Table 2

Bond angles for **2e** (°). Estimated standard deviations are given in parentheses

Si(2)-Si(1)-N(1)	51.1(2)	Si(2)-Si(1)-C(1)	125.0(3)
N(1)-Si(1)-C(1)	111.6(3)	Si(2)-Si(1)-C(10)	124.8(2)
N(1)-Si(1)-C(10)	123.0(3)	C(1)-Si(1)-C(10)	108.3(3)
Si(1)-Si(2)-N(1)	50.9(2)	Si(1)-Si(2)-C(19)	122.1(2)
N(1)-Si(2)-C(19)	123.8(3)	Si(1)-Si(2)-C(28)	125.1(3)
N(1)-Si(2)-C(28)	111.1(3)	C(19)-Si(2)-C(28)	110.4(4)
N(1)-Si(3)-C(37)	111.8(3)	N(1)-Si(3)-C(38)	111.7(3)
N(1)-Si(3)-C(39)	113.9(3)	Si(1)-N(1)-Si(2)	78.0(2)
Si(1)-N(1)-Si(3)	139.093)	Si(2)-N(1)-Si(3)	143.0(4)
Si(1)-C(1)-C(2)	119.6(5)	Si(1)-C(1)-C(6)	122.6(5)
C(2)-C(1)-C(6)	117.8(5)	C(1)-C(2)-C(3)	120.8(6)
C(1)-C(2)-C(7)	122.1(5)	C(3)-C(2)-C(7)	117.1(7)
C(2)-C(3)-C(4)	122.0(7)	C(3)-C(4)-C(5)	117.4(6)
C(3)-C(4)-C(8)	121.0(7)	C(5)-C(4)-C(8)	121.6(6)
C(4)-C(5)-C(6)	122.6(6)	C(1)-C(6)-C(5)	119.3(7)
C(1)-C(6)-C(9)	123.8(5)	C(5)-C(6)-C(9)	116.8(6)
Si(1)-C(10)-C(11)	123.5(6)	Si(1)-C(10)-C(15)	118.1(5)
C(11)-C(10)-C(15)	118.4(7)	C(10)-C(11)-C(12)	118.4(6)
C(10)-C(11)-C(16)	126.2(7)	C(12)-C(11)-C(16)	115.4(5)
C(11)-C(12)-C(13)	122.2(6)	C(12)-C(13)-C(14)	119.1(8)
C(12)-C(13)-C(17)	121.5(7)	C(14)-C(13)-C(17)	119.4(7)
C(13)-C(14)-C(15)	121.3(7)	C(10)-C(15)-C(14)	120.4(6)
C(10)-C(15)-C(18)	123.3(8)	C(14)-C(15)-C(18)	116.3(7)
Si(2)-C(19)-C(20)	126.6(5)	Si(2)-C(19)-C(24)	117.0(5)
C(20)-C(19)-C(24)	116.4(7)	C(19)-C(20)-C(21)	120.7(6)
C(19)-C(20)-C(25)	120.4(7)	C(21)-C(20)-C(25)	118.9(6)
C(20)-C(21)-C(22)	122.2(7)	C(21)-C(22)-C(23)	117.7(8)
C(21)-C(22)-C(26)	120.9(7)	C(23)-C(22)-C(26)	121.3(7)
C(22)-C(23)-C(24)	123.0(7)	C(19)-C(24)-C(23)	120.0(6)
C(19)-C(24)-C(27)	122.2(7)	C(23)-C(24)-C(27)	117.7(6)
Si(2)-C(28)-C(29)	119.0(5)	Si(2)-C(28)-C(33)	122.6(6)
C(29)-C(28)-C(33)	118.3(5)	C(28)-C(29)-C(30)	120.1(7)
C(28)-C(29)-C(34)	123.5(5)	C(30)-C(29)-C(34)	116.2(7)
C(29)-C(30)-C(31)	121.4(7)	C(30)-C(31)-C(32)	118.0(5)
C(30)-C(31)-C(35)	120.6(7)	C(32)-C(31)-C(35)	121.4(7)
C(31)-C(32)-C(33)	122.5(7)	C(28)-C(33)-C(32)	119.2(7)
C(28)-C(33)-C(36)	123.1(5)	C(32)-C(33)-C(36)	117.6(6)

To account for the unusually short Si–Si distances found in these small rings, a bonding model was proposed in which a significant amount of the double bond character of the disilene is retained in the adduct [3f]. A theoretical model [14] consistent with our findings has been applied to organosilicon compounds by Schaefer and Grev [15], and a complete discussion of bonding in silicon three-membered ring compounds appears in a recent paper by Cremer et al. [16*]. According to the theoretical model, the bonding in three-membered rings is viewed as lying on a continuum between cyclic structures and π-complexes. The structure of the ring depends upon the ability of the bridging ligand to accept electron density from the π-bond. Because the strongly electronegative O and N ligands are excellent electron acceptors, a significant amount of π-complex character should appear in the Si_2O and Si_2N structures. Compounds in which the bridging unit is less electronegative,

Table 3

Bond lengths for **2e** (Å). Estimated standard deviations are given in parentheses

Si(1)–Si(2)	2.232(4)	Si(1)–N(1)	1.772(5)
Si(1)–C(1)	1.900(6)	Si(1)–C(10)	1.908(9)
Si(2)–N(1)	1.776(5)	Si(2)–C(19)	1.881(8)
Si(2)–C(28)	1.905(6)	Si(3)–N(1)	1.741(5)
Si(3)–C(37)	1.853(9)	Si(3)–C(38)	1.858(7)
Si(3)–C(39)	1.885(9)	C(1)–C(2)	1.394(11)
C(1)–C(6)	1.419(9)	C(2)–C(3)	1.380(8)
C(2)–C(7)	1.520(10)	C(3)–C(4)	1.381(10)
C(4)–C(5)	1.380(12)	C(4)–C(8)	1.509(9)
C(5)–C(6)	1.387(8)	C(6)–C(9)	1.495(10)
C(10)–C(11)	1.415(8)	C(10)–C(15)	1.393(11)
C(11)–C(12)	1.414(12)	C(11)–C(16)	1.521(10)
C(12)–C(13)	1.349(10)	C(13)–C(14)	1.376(10)
C(13)–C(17)	1.514(14)	C14)–C(15)	1.388(14)
C(15)–C(18)	1.525(9)	C(19)–C(20)	1.420(9)
C(19)–C(24)	1.406(9)	C(20)–C(21)	1.394(12)
C(20)–C(25)	1.533(10)	C(21)–C(22)	1.346(11)
C(22)–C(23)	1.377(11)	C(22)–C(26)	1.497(13)
C(23)–C(24)	1.384(12)	C(24)–C(27)	1.503(10)
C(28)–C(29)	1.387(12)	C(28)–C(33)	1.410(10)
C(29)–C(30)	1.403(8)	C(29)–C(34)	1.535(11)
C(30)–C(31)	1.376(10)	C(31)–C(32)	1.370(11)
C(31)–C(35)	1.523(8)	C(32)–C(33)	1.388(8)
C(33)–C(36)	1.500(10)		

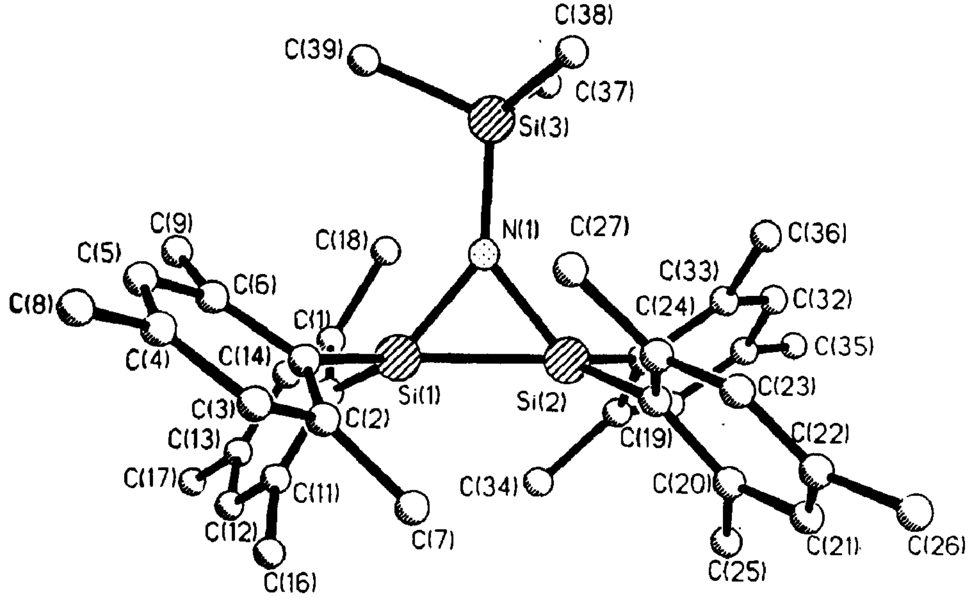
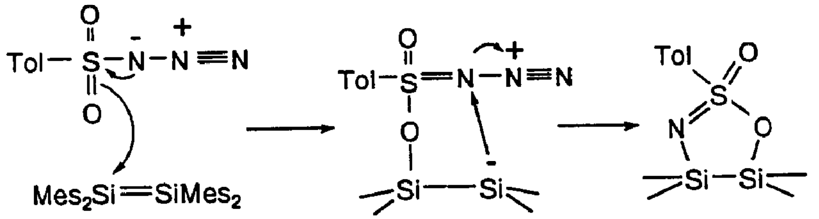


Fig. 1. Ball and stick plot of **2e**. Hydrogen atoms and some atom labels omitted for clarity.

such as disilacyclopropane [3b] and disilacyclopropanimine [3d], should have less π-complex character. In fact these compounds have Si–Si distances longer than for **2e** or disilaoxirane but still shorter than the normal Si–Si bond length.

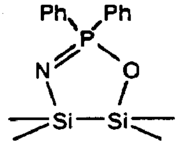
D. Reactions of ***1*** *with* $TosN_3$ *and* $Ph_2P(O)N_3$. The addition of one equivalent of *p*-toluenesulfonyl azide to a yellow solution of **1** in C_6D_6 resulted in an immediate discharge of the yellow color and vigorous gas evolution. The ^{29}Si NMR spectrum had two new resonances at −2.25 and −12.28 ppm. The peaks were very broad, 5 and 3 Hz at half-height, respectively. The ^{1}H NMR of the reaction mixture was very complicated but showed only two new *p*-tolyl groups in approximately a 2/1 ratio. An ^{29}Si INEPT-INADEQUATE experiment was attempted to determine whether the two nonequivalent silicon atoms were linked by a sigma bond [17]. The coupling constant between the two Si atoms is 94 ± 1 Hz, indicating that the silicon atoms are directly bonded [18]. The mass spectrum of the isolated compound contained a parent ion whose molecular weight corresponded to the formal addition of the nitrene TosN: to **1**. Based on the spectral data acquired, the only reasonable structure for the adduct is **7a** (eq. 3). The reaction probably proceeds by an initial nucleophilic attack of oxygen on the disilene, followed by ring closure with simultaneous loss of N_2 to form the unusual ring system **7a** (eq. 3). The ^{1}H NMR of **7a** is complicated due to the presence of the chiral sulfur atom. Two enantiomers would be expected to form, each of which would contain four nonequivalent mesityl groups giving rise to a total of 16 resonances in the *ortho-* and *para*-methyl region. This may also contribute to the broad lines observed in the ^{29}Si NMR.



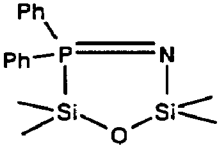
(3)

(**7a**)

The addition of one equivalent of diphenylphosphoranyl azide ($Ph_2P(O)N_3$) to a solution of **1** in C_6D_6 resulted in vigorous gas evolution and an instantaneous decolorization of the solution. One new resonance was found in the ^{31}P NMR at +4.50 ppm. The ^{29}Si NMR spectrum had four signals with chemical shifts at +7.41, +7.13, −17.03, −17.35 ppm. The colorless solid isolated following workup was analyzed as a formal 1/1 adduct of the nitrene to the disilene. A coupling constant ^{1}J(Si–Si) of 94 Hz was measured from ^{29}Si satellites, excluding structures such as **8** in which the two silicon atoms are not directly bonded. This, taken with the observation of nearly equal values for the ^{2}J(Si–P) coupling constants (20 and 22 Hz) [19] led to the assignment of structure **7b** for the product.



(**7b**)



(**8**)

Experimental

All reactions were done in a dry box equipped with a Vacuum Atmospheres recirculating gas purification system. All solvents were dried, distilled and degassed prior to use. ^1H NMR spectra were recorded on a Bruker 270 MHz spectrometer. ^{29}Si (71.55 MHz), ^{15}N (36.51 MHz) and ^{31}P (145.78 MHz) NMR spectra were taken on a Bruker AM-360 MHz instrument. The silicon spectra were referenced to external tetramethylsilane, phosphorus to external H_3PO_4 (85%) and ^{15}N to external NH_4NO_3. Chemical shifts are given in ppm. All spectra were recorded in benzene unless otherwise noted.

Phenyl azide (Pfaltz & Bauer), benzyl azide, trimethylsilyl azide (Alfa), and diphenylphosphoranyl azide (Aldrich) were used without further purification. Mesityl azide [20], tosyl azide [21] and trimethylsilylmethyl azide [22] were all synthesized according to literature procedures. Tetramesityldisilene was synthesized by a modification of the method of Fink et al. using 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane as the precursor [4]. Irradiation of 1 g of trisilane in 75 ml of 2/1 pentane/THF with 254 nm light for 20 h at −60 °C led to an isolated yield of 70–80% of **1** following workup.

*N-Phenyl-1,2-disila-1,1,2,2-tetramesitylaziridine (**2a**).* A solution of 20% PhN_3 in hexane was added to a yellow solution of **1** (290 mg, 5.5×10^{-4} mol) in hexane. The azide was added slowly via syringe until the yellow color was completely discharged. Vigorous gas evolution was noted upon addition of the azide and the solution slowly became purple. The solvent was removed in vacuo and the residue was redissolved in C_6D_6 (2 ml). Upon standing at room temperature, a white precipitate was formed. The solution was filtered and 50 mg of the colorless solid **2a** was isolated. The filtrate was sealed under vacuum in a 5 mm NMR tube and after NMR analysis was heated to 80 °C for 12 h. At this time the solution contained only **2a** and another 150 mg of the disilaaziridine was isolated. ^1H NMR $CDCl_3$ δ 7.05(s), 5H; 6.60(s), 8H: 2.43(s), 24H; 2.01(s), 12H. ^{29}Si NMR (C_6D_6) δ −53.0. MS calcd. for $M^+ - H$: 622.3313, found: 622.3345 (1.3%); calcd. for $M^+ - CH_3$: 608.3157, found: 608.3133 (23.0%). No parent ion was observed. Yield: 44%.

*N-Phenyl-1,2-disila-1,1,2,2-tetramesityltriazoline (**3a**).* ^1H NMR (C_6D_6) δ 7.10(s), 5H; 6.62(br), 8H; 2.56(s), 12H; 2.46(s), 12H; 2.04(s), 6H; 2.02(s), 6H. ^{29}Si NMR (C_6D_6): δ −19.5, −26.9. UV-λ_{max} 562 nm. The product was not isolated.

*N-Mesityl-1,2-disila-1,1,2,2-tetramesitylaziridine (**2b**).* The reaction of $MesN_3$ with **1** was conducted as described above using 100 mg of **1** (1.88×10^{-4} mol) and 50 μl of $MesN_3$. The solution turned purple upon addition (λ_{max} 563 nm), but the purple product was not isolable. ^1H NMR (C_6D_6) δ 6.64(s), 8H: 6.60(s), 2H; 2.57(s), 6H; 2.46(s), 24H; 2.05(s), 12H; 2.01(s), 3H. ^{29}Si NMR (C_6D_6): δ −54.1 ppm. MS calcd. for M^+: 665.3859, found: 665.3840. For **3b**, ^{29}Si NMR (C_6D_6): δ −18.9, −16.5.

*N-Benzyl-1,2-disila-1,1,2,2-tetramesitylaziridine (**2c**).* Twenty-five mg of benzyl azide was added to a solution of **1** (100 mg, 1.9×10^{-4} mol) in hexane. The solution turned orange immediately and gas evolution was noted. The sample was evaporated in vacuo and the orange residue was redissolved in C_6D_6 (1 ml) and sealed into a 5 mm NMR tube. After NMR analysis the tube was heated at 80 °C for 6 h. At this time the solution was colorless and contained only one compound by ^{29}Si NMR analysis. The sample was taken back into the dry box and the solvent was removed to yield the colorless solid **2c**. The orange intermediate was not isolated. ^1H NMR

(C_6D_6) δ 7.11, 6.91(m), 5H; 6.61(s), 8H; 4.62(s), 2H; 2.24(s), 24H, 2.04(s), 12H. ^{29}Si NMR (C_6D_6): δ −53.07. MS calcd. for M^+: 637.3547, found: 635.3557. Yield: 65 mg (54%).

*N-Benzyl-1,2-disila-1,1,2,2-tetramesityltriazene (**4c**).* ^{1}H NMR (C_6D_6 δ 7.12–6.91(m), 5H; 4.91(s), 2H; 2.44(s), 24H; 2.03(s), 12H. ^{29}Si NMR (C_6D_6) δ −54.03 ppm. UV-λ_{max} 470 nm.

*N-(Trimethylsilylmethyl)-1,2-disila-1,1,2,2-tetramesitylaziridine (**2d**).* The reaction was carried out as described above for benzyl azide using 200 mg of **1** (3.76×10^{-4} mol) and 49 mg of $Me_3SiCH_2N_3$. ^{1}H NMR (C_6D_6) δ 6.67(s), 8H; 3.14(s), 2H; 2.38(s), 24H; 2.10(s), 12H; −0.01(s), 9H. ^{29}Si NMR (C_6D_6): δ +0.08, −51.7. MS calcd. for $M^+ - CH_3$: 618.3394, found: 618.3406. No parent ion was observed.

*N-(Trimethylsilylmethyl)-1,2-disila-1,1,2,2-tetramesityltriazene (**4d**).* ^{1}H NMR (C_6D_6) δ 6.67(s), 8H; 3.68(s), 2H; 2.47(s), 24H; 2.05(s), 12H. ^{29}Si NMR (C_6D_6): δ +1.2, −54.9. The product was not isolated.

*N-(Trimethylsilyl)-1,2-disila-1,1,2,2-tetramesitylaziridine (**2e**).* A yellow solution of 500 mg (0.94 mmol) of **1** was placed into a 10 mm NMR tube. To this was added 0.13 ml of Me_3SiN_3 (0.94 mmol). The solution was immediately decolorized and gas evolution was noted. The tube was sealed and the reaction mixture was analyzed by NMR spectroscopy. Next, the tube was opened in the drybox, concentrated in vacuo and the colorless residue was recrystallized from hexane at room temperature to yield **2e** as an air-stable solid. ^{1}H NMR (C_6D_6): δ 6.66(s), 8H; 2.45(s), 24H; 2.05(s), 12H; 0.32(s), 9H. ^{29}Si NMR (C_6D_6) δ −208.7 ppm. MS calcd. for M^+: 619.3472, found: 619.3486 (0.5%). UV-λ_{max} 237.321 nm (hexane). M.p. 250 ° C (dec). Yield: 45.5%.

*X-ray crystallography of **2e**.* A suitable crystal of **2e** was grown from hexane by slow evaporation at room temperature. Data was collected at −100 ° C on a Nicolet P$\bar{1}$ diffractometer equipped with a graphite monochromated molybdenum radiation source, using a modified LT1 low temperature apparatus. Unit cell parameters were determined by least squares refinements based on 25 centered reflections. Four standard reflections representing diverse regions of reciprocal space were monitored every 100 reflections during data collection. Little deviation in peak intensities were observed during data collection and no absorption corrections were applied.

The structure was solved by direct methods using the SHELXTL software package. Blocked cascade least squares refinements of the structure used the reflections with $F_o > 3\sigma(F_o)$. In the final refinement cycles the nonhydrogen atoms were assumed to vibrate anisotropically while the hydrogen atoms were included as idealized isotropic fixed contributors (C–H bond length = 0.96 Å; $U_{(hydrogen)} = 1.2\ U_{(carbon)}$). The final discrepancy indices R_1 and R_2 are given in Table 1.

*Reaction of **1** with tosyl azide.* The reaction was done in a manner similar to that described above for Me_3SiN_3 using 250 mg of **1** and 92 mg of $TosN_3$. Upon addition of the azide, the yellow solution immediately decolorized and gas evolution was noted. Following NMR analysis of the reaction mixture, the tube was opened in the drybox, the solvent was evaporated in vacuo and the residue was redissolved in hexane. Upon standing, a white precipitate of **5a** was formed which was isolated by filtration. ^{1}H NMR (C_6D_6) δ 7.79(d), 2H; 6.76(s), 2H; 6.62(s), 4H; 6.59(s), 2H; 2.63(s), 6H; 2.58(s), 6H; 2.44(s), 6H; 2.11(s), 3H; 2.04(s), 3H; 2.03(s), 3H; 2.01(s), 6H; 1.97(s), 3H; 1.76(s), 3H. ^{29}Si NMR (C_6D_6): δ 02.25, −12.28 ^1J(Si–Si) 95 Hz.

MS calcd. for M^+: 701.3179, found: 701.3172 (15.7%). IR (KBr pellet): ν(S=O) 1170 cm^{-1}. M.p. 207–209 ° C.

Reaction of 1 with diphenylphosphoranyl azide. The reaction was carried out as described above for Me_3SiN_3 using 100 mg of **1** (1.9×10^{-4} mmol) and 0.045 ml of $Ph_2P(O)N_3$. The yellow solution was decolorized immediately upon addition of the azide and gas evolution was noted. After NMR analysis of the reaction mixture, the tube was opened in the drybox, the solvent was removed in vacuo and the residue was recrystallized from hexane to yield the colorless amorphous solid **5b**. ^{1}H-NMR (C_6D_6): δ 7.39(d), 4H; 7.18(t), 4H; 7.05(d), 2H; 6.91(s), 4H; 6.89(s), 4H; 2.76(s), 12H; 2.63(s), 12H; 2.33(s), 6H; 2.31(s), 6H. ^{29}Si NMR (C_6D_6 δ +7.41, +7.13 (^2J(Si–Si) 22 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.32, 144.98, 139.02, 138.31, 129.29, 128.85, 128.76, 128.72, 128.20, 124.34, 120.12, 120.06, 24.96, 24.91, 20.97, 20.93. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ +4.50. Yield: 70.4%.

Supplementary material available. Tables of hydrogen atom coordinates and anisotropic thermal parameters for **2e** (six pages), a listing of observed and calculated structure factor amplitudes for **2e** (18 pages) can be obtained from the authors.

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