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Synthesis and Reactivity of a Stable Silylene

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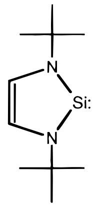
Abstract: The synthesis and several reactions of the stable silylene **1** (1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene) are described. X-ray crystal structures are given for two intermediates in the synthesis of **1**, the diimine **7** and its dilithium salt **8**, and for a byproduct, the spiro compound **10**. **1** reacts with ethanol and water by inserting into the O−H bond, and with iodomethane by insertion into the C−I bond. The silanol from reaction of **1** with water condenses to a disiloxane, **13**. From **1** and sulfur and selenium, cyclic compounds containing Si_2E_2 rings are obtained (E = S or Se). Crystal structures are presented for disiloxane **13** and for the sulfur and selenium cycloadducts, **15** and **17**.

Introduction

Silylenes (R_2Si:), the silicon analogues to carbenes in organic chemistry, are key intermediates in numerous thermal and photochemical reactions of organosilicon compounds and hence are extremely important in the field of silicon chemistry.[1] Until recently, silylenes have been observed only at low temperatures in argon or hydrocarbon matrixes, disappearing quickly at temperatures above 77 K. Stable divalent silicon compounds were isolated in the late 1980s, such as the π-complex decamethylsilicocene $(Me_5C_5)_2Si$[2] synthesized by Jutzi and co-workers, and the phosphorus complex $[Me_2PC(SiMe_3)PMe_2]_2$-Si.[3]

Following the discovery of analogous stable carbenes by Arduengo and co-workers,[4] we described the synthesis and characterization of the stable silylene **1**.[5]



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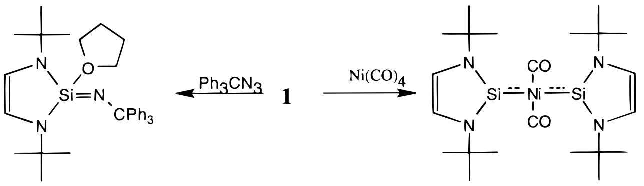
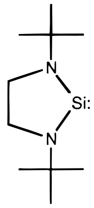
Scheme 1



The structure of **1** was established by gas-phase electron diffraction. This silylene has truly remarkable thermal stability; it can be sublimed or distilled at 85 °C (1 Torr), survives heating in toluene at 150 °C indefinitely, and decomposes only at its melting point of 220 °C. The properties of **1** may reflect the electron donation from the nitrogen to the silicon, stabilizing the lone-pair orbital on the silicon atom, as well as aromatic delocalization in the 6 π-electron ring.[6,7] Since the synthesis of **1**, three additional stable silylenes **2**,[8] **3**,[9] and **4**[10] have been reported.



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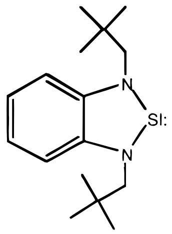

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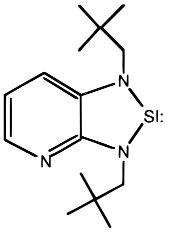

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A few reactions of **1** have been described to date. These include the reaction with nickel carbonyl, yielding the bis(silylene) nickel complex, **5**,[11] and with triphenylmethyl azide to give the silanimine, **6** (Scheme 1).[12]

The latter reaction provides a novel method for synthesis of Si=N doubly bonded compounds, previously formed via

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(1) For reviews, see Gaspar, P. P.; West, R. In *Chemistry of Organosilicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, pp. 2463−2568; Nefedov, O. M.; Egorov, M. P.; Ioffe, A. I.; Menchikov, C. G.; Zuev, P. S.; Minikin, V. L.; Simkin, B. Y.; Glukhovtsev, M. N. *Pure Appl. Chem.* **1992**, *64*, 265.

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(4) Arduengo A. J., III; Rasika Dias, A. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

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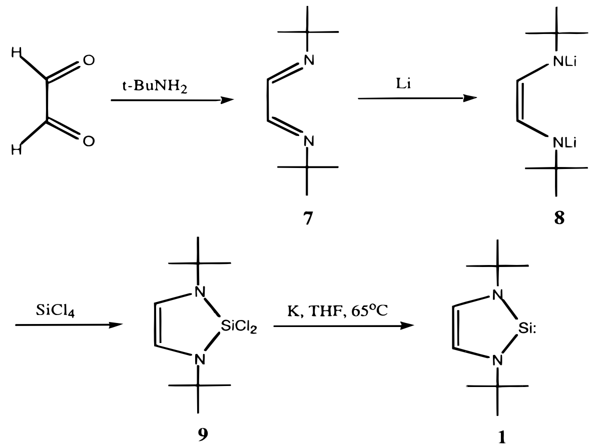
(9) (a) Gehrhus, B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Blaeser, D. *J. Chem. Soc. Chem. Commun.* **1995**, 1931. (b) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Heinicke, J.; Boese, R.; Bläser, D. *J. Organomet. Chem.* **1996**, *521*, 211. (c) Gehrhus, B.; Lappert, M. F. *Polyhedron* **1998**, *17*, 999.

(10) Heinicke, J.; Oprea, A. Abstracts from the 11th International Symposium on Organosilicon Chemistry, Montpellier, France, **1996**, PA28.

10.1021/ja9733999 CCC: $15.00

Scheme 2



elimination reactions.[13] In both reactions, **1** behaves analogously to phosphines, with which it is isolobal.

In this paper we report details of the synthesis of **1** as well as several reactions involving insertion of the silylene into various chemical bonds. While the work reported in this paper was under way, a paper on reactions of silylene **3** appeared;[9b] the reactions of **3** with CH_3I, ethanol, and chalcogens reported in that study gave results similar to those reported here.

Results and Discussion

The synthetic pathway for **1** is outlined in Scheme 2. Diimine **7**, formed from glyoxal and *tert*-butylamine in aqueous solution, is lithiated to the dilithium derivative **8**, which reacts with silicon tetrachloride to give **9**, the five-membered ring precursor to **1**. Dehalogenation of **9** to **1** requires treatment with potassium metal in refluxing tetrahydrofuran (THF) for several hours.

Although diimine **7** is often depicted as having s-cis conformation (as in Scheme 2), X-ray crystallographic analysis showed that in the solid state it adopts the s-trans conformation. A thermal ellipsoid diagram for **7** is shown in Figure 1.

The result is not surprising in that the s-trans arrangement minimizes the repulsion between p-orbitals on the two nitrogen atoms. The nearly planar structure allows maximal overlap of the nitrogen p-orbitals and the $C{=}C$ π-bond. The s-cis conformer may however be present in equilibrium with the s-trans form in solution, and in fact tom Dieck and Franz have proposed a mechanism for formation of **8** in which the s-cis conformer of **7**, present in equilibrium in solution, undergoes reduction to an anion radical and then to the s-cis dianion.[14]

An X-ray structure was also obtained for the dilithium salt of the diimine, **8**, an unsymmetrical dimer (Figure 2). Both of the nitrogen atoms in **8** are virtually planar and are in the cis-conformation (torsion angles: N−C−C−N 0.9° and 0.5°). The two dianion moieties are united by two lithium atoms (Li(1B), Li(1C)). In one-half of the molecule, Li(1B) coordinates to the two nitrogen atoms (N(3B), N(6B)), creating a five-membered ring. A second lithium, Li(1C), coordinates in η^4-fashion to the carbon and nitrogen atoms in the ring. These two lithium atoms further coordinate in η^1-fashion to the nitrogen atoms in the other half of the molecule, thus forming the dimer. The remaining two lithium atoms (Li(1A), Li(1D)) are each coordinated η^4 to one of the dianion moieties, as well as singly coordinated to an oxygen atom of a diethyl ether molecule.

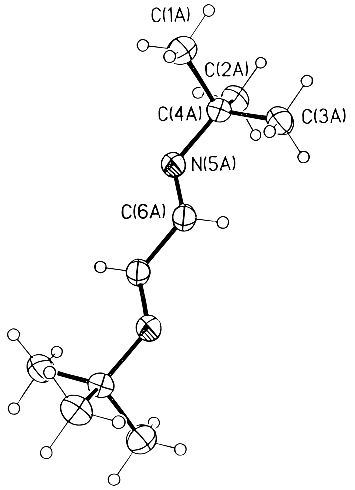


Figure 1. Crystal structure of **7** (50% probability ellipsoids). Selected bond lengths: C(6A)−N(5A) = 1.269(2) Å, C(6A)−C′(6A) = 1.477(2) Å. Selected bond angles: C(6A)−N(5A)−C(4A) = 120.70(11)°, N(5A)−C(6A)−C′(6A) = 119.8(2)°.

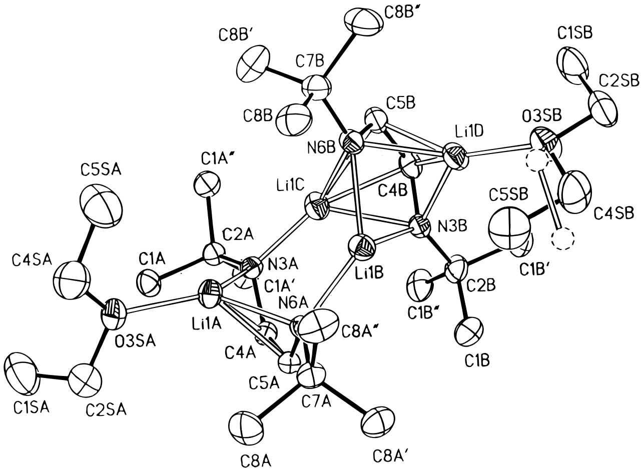


Figure 2. Crystal structure of **8**, the dilithium salt of the diimine (50% probability ellipsoids).

The dilithium salt **8** is treated with excess $SiCl_4$ to form **9**, the dichloride precursor to the silylene. Because **9** is difficult to separate from the starting diimine, repeated vacuum distillations are often necessary. The final step in the synthesis is the reduction of **9** by using molten potassium in refluxing THF. The success of this reaction appears to depend on the purity of the starting dichloride **9**. Because **1** and **9** are very difficult to separate, the reaction requires careful monitoring with ^1H NMR. Careful monitoring is also necessary to ensure that the silylene is not overreduced. The silylene may be isolated by vacuum sublimation (85 °C, 0.1 Torr), but it can also be distilled if a large enough quantity is available.

A side product, spiro compound **10**, is usually produced, probably formed from the reaction of **1** with residual diimine. Reaction of **1** with **7** led to **10** in high yield. Crystals of **10** were isolated by sublimation at 220 °C (0.1 Torr); the crystal structure is shown in Figure 3.

The five-membered rings in **10** are planar, and lie in orthogonal planes. The Si−N bond length in **10** is slightly longer than in **1** [1.753(5) vs 1.738(2) Å] and the N−C distances are slightly shorter [1.400(9) vs 1.145(2) Å].

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[11] Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33.

[12] Denk, M.; Hayashi, R. K.; West, R. *J. Am. Chem. Soc.* 116, **1994**, 10813.

[13] For a review, see Hemme, I.; Klingebiel, U. *Adv. Organomet. Chem.* **1996**, *39*, 159.

[14] tom Dieck, H.; Franz, K.-D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 249.

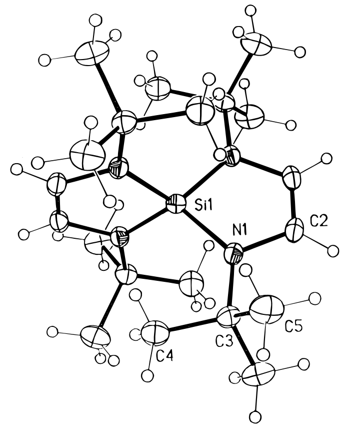
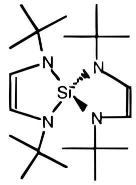


Figure 3. Structure and thermal ellipsoid diagram of the spiro compound **10**. Selected bond lengths: Si(1)−N(1) = 1.738(2) Å, N(1)−C(2)= 1.415(2) Å, C(2)−C′(2) = 1.341(4). Selected bond angles: N(1)−Si(1)−N′(1) = 92.40(11)°, N(1)−Si(1)−N(2) = 118.62(6)°, Si(1)−N(1)−C(2) = 109.42(14)°, N(1)−C(2)−C′(2) = 114.38(11)°. Torsion angles; Si(1)−N(1)−C(3)−C(4) = 0.0°, Si(1)−N(1)−C(2)−C′(2) = 0.0°.



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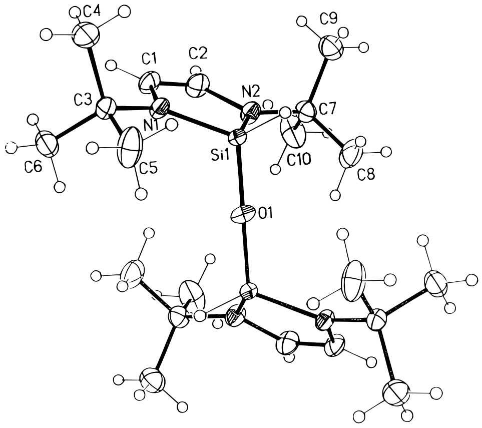
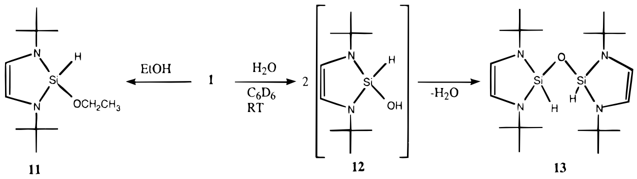


Figure 4. Molecular structure of **13** (50% probability ellipsoids).

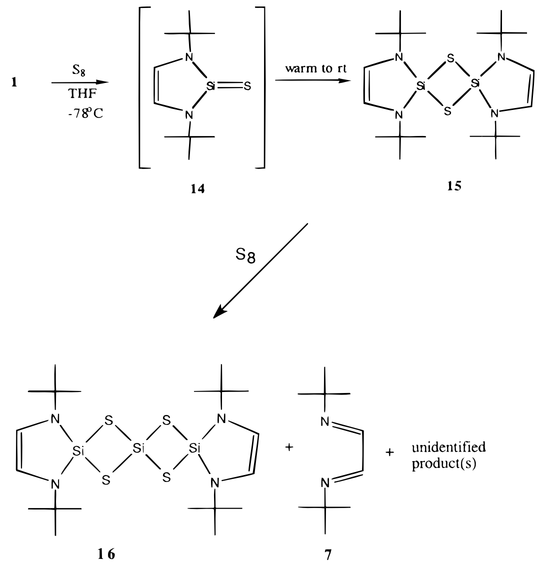
Table 1. Selected Bond Lengths (Å) and Angles (°) for 13

Si−O	1.6272(4)	Si−N(1)	1.7249(12)
Si−N(2)	1.7386(12)	N(1)−C(1)	1.427(2)
N(2)−C(2)	1.428(2)	C(1)−C(2)	1.347(2)
Si−O−Si′	167.53(11)	N(1)−Si−N(2)	93.45(6)
Si−N(1)−C(1)	108.69(9)	Si−N(1)−C(3)	130.57(9)
C(1)−N(1)−C(3)	120.75(11)		
Si−N(1)−C(1)−C(2)	−1.3(2)	N(1)−C(1)−C(2)−N(2)	0.4(2)

Scheme 3



Scheme 4



Reactions of 1. As pointed out in an earlier communication,[5] silylene **1** is far less reactive than typical transient silylenes. Thus, it does not insert into Si−H bonds or react with acetylenes, nor does it behave as a Lewis acid, even in the presence of relatively strong bases (THF, triethylamine, pyridine). However, like the more reactive transient silylenes, **1** does insert into O−H bonds of hydroxyl compounds. With ethanol, the product is the alkoxysilane **11**. Water reacts with **1** initially to give silanol **12**, which eventually self-condenses to disiloxane **13** (see Scheme 3), isolated as colorless plates from C_6D_6. The X-ray structure of **13** is portrayed in Figure 4.[15]

Selected bond lengths and angles for **13** are summarized in Table 1. The steric hindrance from the four closely spaced *tert*-butyl groups may be responsible for the large Si(1)−O-Si(1′) bond angle of 167.53(11)° and is probably the reason the sp^3-nitrogen atoms are in a planar configuration (the sum of surrounding bond angles is 360.0°) rather than the typical pyramidal arrangement. Further, the two silicon-containing rings in **13** are also virtually planar.

When **1** is reacted with exactly 1 equiv of sulfur in THF at −78 °C with gradual warming to room temperature, one major product is obtained, according to ^{1}H NMR [ppm] = 5.81(s, 4H, CH), 1.41(s, 36H, CH_3) in d^6-benzene and ^{29}Si NMR spectroscopy [ppm] = −42.7(s) in THF. Using variable-temperature ^{29}Si NMR to monitor the progress of the reaction, one can detect a short-lived intermediate with a shift of +122.7 ppm at −78 °C. This strongly deshielded silicon can reasonably be attributed to intermediate **14**, a compound containing a silicon−sulfur double bond[16] (see Scheme 4). This ephemeral species may dimerize to give compound **15**. Pale yellow plate-shaped crystals of **15** were grown from C_6D_6; Figure 5 depicts the crystal structure.

A centrosymmetric spirocyclic dimer, **15** has virtually orthogonal rings. Notably, steric congestion from neighboring methyl groups in the *tert*-butyl side chains forces two of the Si−S bonds in the ring core (2.2113(5)Å) to be considerably longer than the other two (2.1186(5)Å). The shorter Si−S bonds are free of such congestion. Although the SiNCCN rings in **15**

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(15) This crystal structure is in agreement with one obtained by workers at the Du Pont Co. We thank A. J. Arduengo III and J. C. Calabrese for communication of their independent results.

(16) Okazaki and co-workers have published the only Si═S double bond-containing compound known to date, in Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11578.

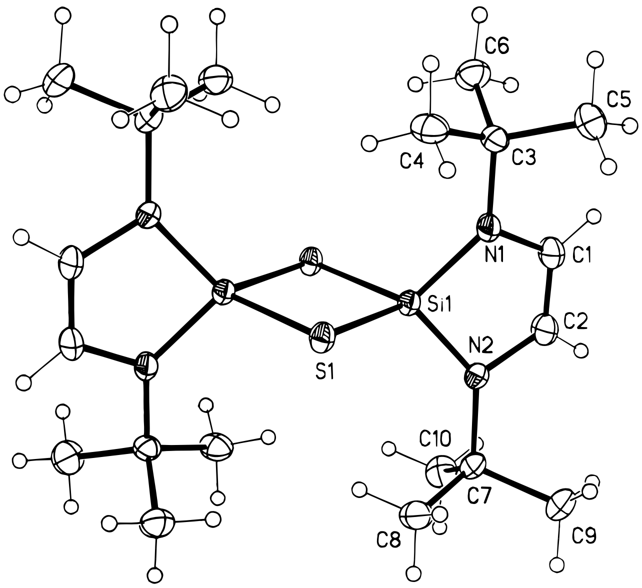


Figure 5. Molecular structure of **15** (50% probability ellipsoids).

Table 2. Selected Bond Lengths (Å) and Angles (°) for **15**

Si−S	2.2113(5)	Si−S′	2.1186(5)
Si−N(1)	1.7351(12)	Si−N(2)	1.7376(12)
N(1)−C(1)	1.4199(18)	N(2)−C(2)	1.4279(18)
C(1)−C(2)	1.329(2)		
SI−S−Si′	84.888(18)	S−Si−S′	95.112(18)
N(1)−Si−N(2)	93.23(5)	Si−N(1)−C(1)	105.84(10)
Si−N(1)−C(3)	134.64(9)	C(1)−N(1)−C(3)	118.06(11)
Si−N(1)−C(1)−C(2)	−16.06(17)	N(1)−C(1)−C(2)−N(2)	0.3(2)

are not planar, the sp^3 nitrogen atoms in the ring are virtually planar (the sum of the bond angles about N is 358.6°). Presumably, the nitrogen atom flattens to reduce steric hindrance in the molecule. See Table 2 for a summary of relevant data.

Interestingly, if this reaction is performed with slightly more than 1 equivalent of sulfur, a different result is observed. Although **15** is initially formed, it gradually undergoes further reaction to form a new product. Over a period of several hours, ^{1}H NMR peaks corresponding to **15** slowly disappear while new peaks simultaneously emerge. Peaks corresponding to the diimine **7** also appear in the spectrum. According to the integration, the diimine and the new product are present in equimolar quantities. Two peaks are present in the ^{29}Si NMR spectrum at −38.1 ppm and −44.3 ppm, indicating two magnetically nonequivalent silicon atoms. The mass spectrum registers a molecular mass of 548 g mol^{-1} for the product. All of these data are consistent with our tentative identification of the product as compound **16**, shown in Scheme 4.

Further, when the silylene is reacted with a larger excess of sulfur, additional diimine **7** is produced. A mixture of oligomeric products is also formed, according to the numerous weak, broad peaks in the vinyl region of the ^{1}H NMR. This series of reactions demonstrates the high lability of the enediamine ligand on the silicon atom in the five-membered ring.

The reaction between **1** and elemental selenium is quite slow, requiring 3−4 h to complete at 25 °C in a sealed NMR tube, and affords only one major product, **17** (Scheme 5). Light yellow transparent crystals were successfully grown from C_6D_6, and the crystal structure obtained is shown in Figure 6. Table 3 summarizes selected data for **17**.

Like **15**, **17** is also a centrosymmetric spirocyclic dimer. The endocyclic bond angles of the planar four-membered ring at the center of the molecule are slightly larger at silicon (95.21(2)°, 94.66(2)°) than at selenium (84.79(2), 85.34(2)°). The steric congestion from neighboring methyl groups in the *tert*-butyl side chains is also evident in this molecule, as two of the Si−Se bonds in the ring core (2.3645(6)Å, 2.3697(6)Å) are noticeably longer than the other two (2.2625(6)Å, 2.2664(6) Å)

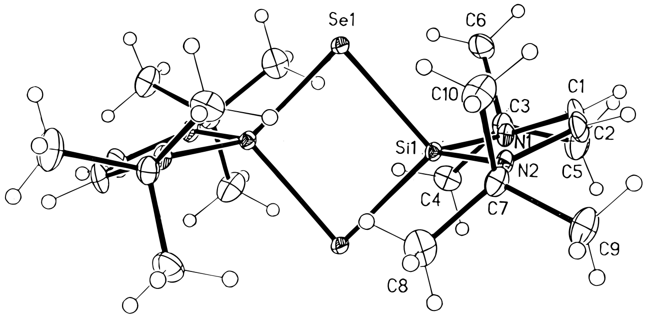
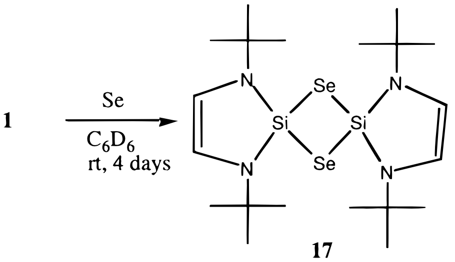


Figure 6. Molecular structure of **17** (50% probability ellipsoids).

Table 3. Selected Bond Lengths (Å) and Angles (°) for **17**

Si−Se	2.3645(6)	Si−Se′	2.2625(6)
Si−N(1)	1.739(2)	Si−N(2)	1.738(2)
N(1)−C(1)	1.417(3)	N(2)−C(2)	1.423(3)
C(1)−C(2)	1.321(3)		
Si−Se−Si′	84.79(2)	Se−Si−Se′	95.21(2)
N(1)−Si−N(2)	93.26(9)	Si−N(1)−C(1)	106.3(2)
Si−N(1)−C(3)	133.78(14)	C(1)−N(1)−C(3)	118.8(2)
Si−N(1)−C(1)−C(2)	13.3(3)	N(1)−C(1)−C(2)−N(2)	−0.1(3)

Scheme 5



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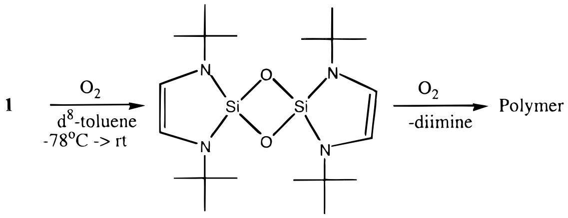
Scheme 6



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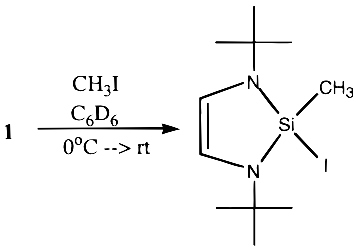
Reaction of **1** with excess dry oxygen gas at −78 °C in d^8-toluene initially affords a red solution, which upon warming, lightens to a pale yellow. The major product of this reaction is a colorless, insoluble polymer (most likely SiO_2), but a small amount of minor product is also observed. Mass spectrum and ^{1}H NMR data for this product were consistent with the formation of dimer **18**, but insufficient amounts of the minor product prevented any further characterization. This reaction could possibly proceed through the initial formation of a transient silanone, which could then dimerize to yield compound **18** (Scheme 6). Excess oxygen could further react to form a silicate-like polymer with simultaneous liberation of the diimine **1**, which was also seen in the reaction products.

Scheme 7



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The reaction between **4** and white phosphorus, P_4, was interesting in that as the two were mixed, the color of the reaction mixture transformed from a pale yellow to a deep orange-red, and a glassy substance insoluble in THF formed on the sides of the reaction vessel. However, ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, and mass spectroscopy clearly indicated that the silylene was still the only organic species present in solution and so it seemed not to react. Apparently, the silylene simply catalyzed the conversion of white phosphorus to the more-stable allotropic form, red phosphorus.

The reaction between **1** and methyl iodide in a sealed NMR tube affords an intense yellow solution containing the expected insertion product **18**, shown in Scheme 7.

Experimental Section

All reactions and manipulations were conducted under an argon atmosphere with standard Schlenk techniques. Glyoxal, *tert*-butylamine, silicon(IV) chloride, phosphorus, selenium, and sulfur were purchased and used without further purification. Lithium and potassium were purchased in mineral oil and washed with hexane or pentane before use.

Proton NMR spectra were recorded on either a Bruker AC-250 or a Bruker AC-300 spectrometer. Silicon-29 NMR spectra were collected on a Bruker 500 MHz spectrometer. Carbon-13 NMR spectra were taken on a Bruker AC-300 spectrometer. Solid-state ^{29}Si NMR spectra were determined on a Varian 500 MHz spectrometer.

Synthesis of Glyoxal-bis-(*N*-*tert*-butylimine), 7. To a 250-mL round-bottom flask equipped with a pressure-equalizing addition funnel, *tert*-butylamine (73.1 mL, 696 mmol) and 50 mL of distilled water were added and the solution was cooled to 0 °C. Aqueous 40% glyoxal solution (40.0 mL, 348 mmol) was added dropwise with stirring. A white precipitate formed almost immediately. After reaction mixture was stirred for an additional 45 min, the product was filtered and recrystallized from 1:1 EtOH/H_2O. Subsequent sublimation (40 °C, 0.1 Torr) yielded 43.3 g of **7** (78%) as colorless crystals. mp= 50 °C, ^{1}H NMR ($CDCl_3$) 7.87 (s, 2H, CH), 1.20 (s, 18H, CH_3); ^{1}H NMR (C_6D_6) 8.06 (s, 2H, CH), 1.10 (s, 18H, CH_3).

Synthesis of 1,3-Di-*tert*-butyl-2,2-dichloro-1,3-diaza-2-sila-4-cyclopentene, 9. In a 250-mL three-necked flask equipped with a reflux condenser and a gas inlet, diimine **7** (10.0 g, 59.4 mmol) was dissolved in 100 mL of THF (or diethyl ether) and the reaction mixture was cooled to −78 °C. Lithium wire cut into small chunks (0.91 g, 131 mmol) was added, whereupon the colorless mixture gradually darkened to a red solution. The solution was allowed to warm to room temperature for 24 h. X-ray-quality crystals of the THF-stabilized lithiated intermediate **8** were obtained at room temperature and a structure was determined. The reaction mixture was then frozen in a liquid nitrogen bath and $SiCl_4$ (68.0 mL, 594 mmol) was added. The resulting mixture was allowed to warm to room-temperature overnight. The white precipitate formed during the reaction (LiCl) was filtered off through a vacuum frit and the excess THF and $SiCl_4$ were evaporated under vacuum. Subsequent distillation (95 °C, 0.1Torr) yielded 11.1 g of **9** (70%) as a colorless crystalline solid. ^{1}H NMR (C_6D_6) δ 5.74 (s, 2H, CH), 1.24 (S, 18H, CH_3); ^{13}C NMR (C_6D_6) δ 112.6 (CH), 52.6 (**C**(CH_3)), 30.4 (C(**C**H_3)); ^{29}Si NMR (C_6D_6) δ −40.7 (s); MS *m*/*z* 287 [M$^+$].

Synthesis of 1,3-Di-*tert*-butyl-2,3-dihydro-1*H*-1,3,2-diazasilol-2-ylidene, 1. In a 100-mL three-necked flask equipped with a reflux condenser and gas-inlet, the dichloride precursor **9** (10.0 g, 37.0 mmol) was dissolved in ∼100 mL of THF. Small chunks of potassium metal (3.22 g, 82.0 mmol, 2.2 equiv) were added and the reaction mixture was heated to reflux for several hours. The reaction progress was followed by ^{1}H NMR spectroscopy. The hot reaction mixture was filtered through a glass frit and the solid was washed with 20 mL of THF. The THF was then removed in vacuo. The remaining residue was sublimed (70 °C, 0.1 Torr) to give 3.3 g (45%) of the colorless solid, **1**. ^{1}H NMR (C_6D_6) 6.75 (s, 2H, CH), 1.40 (s, 18H, CH_3); ^{13}C NMR (C_6D_6) 120.0 (CH), 54.0 (**C**(CH3)), 30.3 (C(**C**H3)); ^{29}Si NMR (C_6D_6) 78.3 (s); MS *m*/*z* 196 [M$^+$]; exact mass calcd for $C_{10}H_{20}N_2Si$ *m*/*z* 196.1396, found 196.1385.

Reaction of 1 with Diimine 7. In the drybox, 100 mg of **1** (0.51 mmol) and 86 mg of **7** (0.51 mmol) were dissolved in 2 mL of C_6D_6. The solution was sealed into an NMR tube. After 18 h at 25 °C, the ^{1}H NMR showed only starting material. The sample was then heated to 70 °C for 24 h, after which the NMR indicated about 70% conversion of the starting materials to **10**. White crystals precipitated when the tube was cooled, which were filtered off to give 65 mg of **10** (35% isolated yield), m.p. 241−243 °C. ^{1}H NMR (C_6D_6) 5.67 (s, 2H, CH), 1.31 (s, 18H, CH_3); ^{13}C NMR (C_6D_6) 108.59 (CH), 58.57 (**C**(CH3)), 30.46 (C(**C**H3)); ^{29}Si NMR (C_6D_6) −51.14 (s); MS *m*/*z* 364 [M$^+$]; exact mass calcd for $C_{20}H_{40}N_4Si$ *m*/*z* 364.3022, found 364.3018.

Reaction of 1 with Ethanol. In a dry 50 mL Schlenk flask, silylene **1** (500 mg, 2.54 mmol) was dissolved in 3.5 mL of d_6-benzene. Dry ethanol (stored over molecular sieves) was added to the reaction mixture. Only one major product (**11**) was formed, according to ^{1}H NMR and ^{29}Si NMR. ^{1}H NMR (C_6D_6) 5.81 (s, 2H, CH), 5.72 (s, 1H, Si−H), 3.64 (q, 2H, CH_2CH_3), 1.24 (s, 18H, C(CH_3)), 1.13 (t, 3H, CH_2-CH_3); ^{13}C NMR (C_6D_6) δ 112.09 (CH, d, $J = 179$ Hz), 57.12 (−O**C**H_2-CH_3, t, $J = 142$ Hz), 50.90 (**C**CH_3, s), 30.91 (CCH_3, q, $J = 129$ Hz), 18.33 (−OCH_2**C**H_3, q, $J = 148$ Hz); ^{29}Si NMR (C_6D_6) −44.91 (s). HRMS: exact mass calcd for $C_{12}H_{26}N_2OSi$ *m*/*z* 242.1814, found 242.1821.

Reaction of 1 with Water. In a dry NMR tube, silylene **1** (100 mg, 0.51 mmol) was dissolved in 2.0 mL of d_6-benzene. Distilled water was added (9.0 μL, 0.51 mmol), and the contents of the tube were mixed by inversion. A light yellow solution resulted, and a small amount of glassy, insoluble polymeric material appeared as well. The solution contained product **13**, according to ^{1}H NMR and mass spectral data. ^{1}H NMR (C_6D_6) δ 5.93 (s, 2H, SiH), 5.81 (s, 4H, CH), 1.28 (s, 36H, CH_3); ^{13}C NMR (C_6D_6) δ 111.74 (CH), 51.13 (**C**CH_3), 30.97 (C**C**H_3); ^{29}Si NMR (C_6D_6) δ −57.8 (s); HRMS *m*/*z* (%): 410 (100) [M$^+$], 395 (35) 354 (18), 339 (22), 297 (15), 279(33), 241 (24), 185 (53), 167 (64), 149 (82)

Synthesis of Di-*μ*-sulfo-bos-1,3-di-*tert*-butyl-2,3-dihydro-1H-1,3,2-diazasilol-2-ylidene, 15. Into a 25-mL round-bottom Schlenk flask, the silylene **1** (200 mg, 1.02 mmol) and elemental sulfur (35.9 mg, 1.12 mmol of S) were added and cooled to a temperature of −78 °C. About 4 mL of THF was slowly added to the flask. While stirring, the reaction mixture was allowed to warm to room-temperature overnight. The NMR spectrum indicated complete conversion of **1** to a single product. Pale yellow crystals were grown overnight in C_6D_6 at room temperature and a crystal structure was obtained (R = 0.082). ^{1}H NMR (C_6D_6) 5.81 (s, 4H, CH), 1.41 (s, 36H, CH_3); ^{13}C NMR (C_6D_6) δ 114.20 (CH), 54.07 (**C**CH_3), 32.01 (C**C**H3); ^{29}Si NMR (THF) −42.7 (s); ^{29}Si NMR (C_6D_6) −45.3 (s); HRMS (70 eV) *m*/*z* 456 [M$^+$]; exact mass calcd for $C_{20}H_{40}N_4S_4Si_2$ *m*/*z* 456.2233, found 456.2222.

Synthesis of 16. To an NMR tube at room temperature, silylene **1** (200 mg, 1.02 mmol), elemental sulfur (35.9 mg, 1.12 mmol), and d_6-benzene (2.0 mL) were added. The tube was sealed under vacuum and the reaction progress was monitored by ^{1}H NMR. After 3 h, all of the initially formed **15** had disappeared; ^{1}H NMR indicated a nearly quantitative yield of **16** with simultaneous formation of the diimine, **7**. ^{1}H NMR (C_6D_6) 5.79 (s), 4H, CH), 1.40 (s, 36H, CH_3); ^{13}C NMR (C_6D_6) δ 113.19 (CH), 53.75 (**C**CH_3), 30.72 (C**C**H_3); ^{29}Si NMR (C_6D_6) −38.1 (s), −44.3 (s); MS *m*/*z* 548 (100) [M$^+$], 533 (31) [M$^+$-CH_3], 492 (42),

Table 4. Crystallographic Data for **7**, **10**, **13**, **15**, and **17**

	7	**10**	**13**	**15**	**17**
formula	$C_{10}H_{20}N_2$	$C_{20}H_{40}N_4Si$	$C_{20}H_{42}N_4OSi_2$	$C_{20}H_{40}N_4S_2Si_2$	$C_{20}H_{40}N_4Se_2Si_2$
fw	168.28	364.65	410.76	456.86	550.66
cryst size (mm^3)	0.40 × 0.20 × 0.20	0.40 × 0.40 × 0.20	0.60 × 0.20 × 0.05	0.45 × 0.40 × 0.15	0.50 × 0.40 × 0.30
a (Å)	9.7132(7)	9.4247(7)	16.1243(6)	8.5552(2)	16.6607(2)
b (Å)	10.7429(8)	9.4247(7)	8.2060(3)	8.7707(3)	13.9707(2)
c (Å)	11.5731(9)	12.4437(13)	18.9102(8)	8.8137(3)	11.2951(2)
α (deg)	90	90	90	98.476(2)	90
β (deg)	110.094(2)	90	90	94.495(2)	101.706(2)
γ (deg)	90	90	90	103.736(2)	90
cryst syst	monoclinic	tetragonal	orthorhombic	triclinic	monoclinic
space group	$P2_1/n$	$I\bar{4}2m$	Pbcn	P-1	$P2_1/c$
vol (Å^3)	1134.1(2)	1105.3(2)	2502.1(2)	630.97(3)	2574.39(7)
D_{calcd} (g cm^{-3})	0.986	1.096	1.090	1.202	1.421
Z	4	2	4	1	4
temp (K)	133(2)	133(2)	133(2)	143(2)	133(2)
abs coeff (mm^{-1})	0.059	0.116	0.158	0.320	2.979
no. of reflns collected	4206	2200	9959	7096	11083
no. of indep reflns	1951	556	2790	3005	5526
θ range (deg)	3.0−25.5	2.71−25.72	2.15−28.06	2.35−29.19	3.0−25.0
R1 (final R indices)	0.0389	0.0269	0.0384	0.0321	0.0257
wR2 (final R indices)	0.0897	0.0645	0.0992	0.0822	0.0532

477 (16), 436 (43), 421 (23), 380 (33), 324 (73), 249 (26), 208 (41), 200 (39); exact mass calcd for $C_{20}H_{40}N_4S_4Si_3$ *m/z* 548.1444, found 548.1452.

Reaction of 1 with Selenium. In an oven-dried NMR tube, silylene **1** (300 mg, 1.50 mmol), elemental selenium (120 mg, 1.50 mmol), and d_6-benzene (3 mL) were added. The silylene dissolved in the solvent, but the selenium remained as a dark gray solid in the reaction mixture. The NMR tube was sealed under vacuum, and the tube contents were mixed by repeated inversions of the tube. After just a few minutes, the solution turned a dark yellow and small amounts of white precipitate began to appear. The progress of the reaction was monitored by ^{1}H NMR. After mixing over a period of 3 h, all of the silylene was converted, giving a nearly quantitative yield of the product, **17**. After several days, light yellow, transparent crystals were obtained from a solution of d_6-benzene at room temperature, mp = 220 °C. ^{1}H NMR (C_6D_6) 5.90 (s, 2H, CH), 1.53 (s, 18H CH_3); ^{13}C NMR (C_6D_6) 113.8 (s, CH), 54.43 (s, **C**(CH_3)), 31.91 (s, C(**C**H_3)); ^{29}Si NMR (C6D6) d −68.17 (s); MS *m/z* 551 [M$^+$].

Reaction of 1 with Dioxygen. In a dry NMR tube, silylene **1** (100 mg, 0.51 mmol) was dissolved in 2.0 mL of d_8-toluene. Excess oxygen (predried through a column of Drierite and phosphorus pentoxide) was bubbled through the solution at −78 °C. An initial color change to red gradually lightened to a pale yellow. A colorless, glassy insoluble product appeared. The reaction mixture was allowed to warm to room temperature. Although the polymeric material seems to be the major product, trace amounts of a minor product, **18**, were found in solution. However, no product was isolated. ^{1}H NMR (d_8-toluene) 5.70 (s, 4H, CH), 1.36 (s, 36H, CH_3) ^{29}Si NMR (d_8-toluene) −70.9 (s); HRMS *m/z* 424 [M$^+$]; exact mass calcd for $C_{20}H_{40}N4Si_2O_2$ *m/z* 424.2690, found 424.2670.

Reaction of 1 with White Phosphorus. In an oven-dried Schlenk flask, a small chunk of phosphorus was placed. Excess water was evaporated in vacuo, and the remaining chunk of P_4 was broken up. Pieces of phosphorus were then removed, until only 80 mg (0.65 mmol) remained in the flask. About 5 mL of THF was added to the flask. In a separate Schlenk flask, **1** (500 mg, 2.54 mmol) was weighed and dissolved in 10 mL of THF. The silylene solution was slowly added to the flask containing the phosphorus suspension at a temperature of −78 °C. The solution changed from a faint yellow to a deep orange after ∼5 min of stirring. The solution was allowed to warm to room temperature.

Despite the color change, ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, and MS data all indicated that the silylene remained unchanged in the solution. However, an orange/red residue was present in the flask as well. This residue could be red phosphorus, a more thermodynamically stable allotropic form of phosphorus than P_4 (white).

Reaction of 1 with Iodomethane. In a dry NMR tube, the silylene **1** (100 mg, 0.51 mmol) was dissolved in 2.0 mL of d_6-benzene). At 0 °C, predistilled CH_3I (32 *μ*L, 0.51 mmol) was added. An immediate color change was observed, from a faint, pale yellow to a dark, intense yellow. The tube was sealed under vacuum. Compound **19** appears as the only major product. ^{1}H NMR (C_6D_6) 5.78 (s, 2H, CH), 1.21 (s, 18H, C(CH_3)), 1.13 (s, 3H, $SiCH_3$); ^{13}C NMR (C_6D_6) *δ* 113.70 (CH), 52.65 (**C**CH_3), 31.75 (C**C**H_3); ^{29}Si NMR (C_6D_6) *δ* 37.11; HRMS *m/z* 338 [M$^+$]; exact mass calcd for $C_{11}H_{23}N_2ISi$ *m/z* 338.0671, found 338.0662.

Crystal Structure Determination. Intensity data for **7**, **8**, **10**, **13**, **15**, and **17** were collected on a Siemens P4 diffractometer equipped with graphite-monochromated Mo Kα radiation and a charge-coupled device area detector. The structures of all compounds were solved by direct methods and refined by full-matrix least-squares refinement on F^2 (SHELXTL, version 5). Hydrogen atoms were initially determined by geometry and refined by a riding model. Nonhydrogen atoms were refined with anisotropic displacement parameters. For compound **8**, two groups were found in the asymmetric unit. Two of the ether side chains were best modeled as having two orientations with refined occupancies of 0.839(8) for C(4SB) and C(5SB), 0.161(8) for C(4B′) and C(5B′), 0.729(8) for C(4SC) and C(5SC), and 0.271(8) for C(4C′) and C(5C′). Details of the data collection and refinement are given in Table 4.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles for **7**, **8**, **10**, **13**, **15**, and **17**; proton NMR spectra for **1**, **7**, **9**, **10**, **11**, **13**, **15**, **16**, and **17** (76 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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