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Isolable Compounds Containing a Silicon-Silicon Double Bond

Robert West

Summary. After 70 years of unsuccessful attempts, several stable disilenes—compounds with double bonds between silicon atoms—have now been made. The silicon-silicon double bond resembles in many ways the well-known carbon-carbon double bond of organic chemistry. However, striking dissimilarities are also found between disilenes and alkenes in both their structures and chemical reactions.

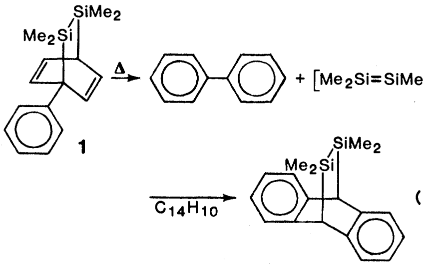
Of all the elements, silicon is the closest to carbon in its chemical properties. Since multiple bonds are pervasive in carbon chemistry, it is not surprising that multiple bonds to silicon have been sought repeatedly over the last 70 years (*1*). However, the numerous attempts to prepare multiply bonded silicon compounds were uniformly unsuccessful until recently. The persistent failure to generate such compounds led to the myth that they are inherently unstable because of the weakness of π bonds formed from 3*p* orbitals on silicon (*2*).

In the 1960's evidence began to accumulate for the possible existence of Si=C (silene), Si=Si (disilene), and Si=O (silanone) species as transient reaction intermediates. By the late 1970's it seemed likely that compounds of all three kinds had been made as transient species, and in 1976 a silene was isolated in argon matrix at approximately 10 K (*3*). However the picture was altered dramatically in 1981 when the synthesis of a silene (*4*) and a disilene (*5*), both stable at room temperature, were reported simultaneously.

The chemistry of the silicon-silicon double bond has developed considerably in the past 3 years (*6*). It is now clear that many disilenes can be prepared, including compounds that are surprisingly stable. In this article the present knowledge of disilenes will be summarized with particular attention to the ways in which the Si=Si double bond both resembles and differs from the familiar C=C double bond of olefins.

Transient Disilenes

Evidence suggesting the presence of a disilene as an intermediate in a chemical reaction was first presented by Roark and Peddle in 1971 (*7*). These workers prepared bridged compounds such as **1** which, upon thermolysis in the presence of trapping agents, transferred the $\mathrm{Me_2Si{-}SiMe_2}$ moiety. For example, the reaction with anthracene proceeds according to Eq. 1. The results were interpreted in terms of the transient formation of tetramethyldisilene, $\mathrm{Me_2Si{=}SiMe_2}$.



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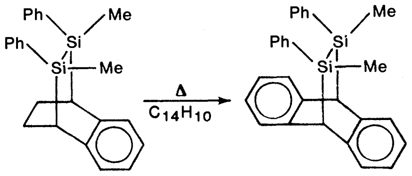
Subsequent to this finding, a number of other reports appeared in which experimental results were interpreted in terms of disilene intermediates (*8*). A particularly cogent example is the sequence of reactions reported by Sakurai and coworkers in which a similar thermolysis was observed (*9*). The *cis* and *trans* isomers of the bridged disilane **2** were separated and each was heated in the presence of anthracene. The geometrical conformation of the reactant was retained in the trapped product, as shown for the *cis* isomer in Eq. 2. This result was taken as an indication that *cis-trans* isomerism in the (putative) disilene intermediate must be slow. Also especially important in the light of what was to follow were several communications indicating that divalent silicon species might undergo dimerization to disilenes (*10*).



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Synthesis of Stable Disilenes

Our own investigations in this area begin with studies of silylenes: unstable, divalent silicon species that can be generated photochemically from polysilanes. An important and well-studied example is dimethylsilylene (**3**), formed by photolysis of the six-membered ring polysilane as shown in Eq. 3 (*11*). Cyclic polysilanes are appropriate precursors

$$(\mathrm{Me_2Si})_6 \xrightarrow[254\ \mathrm{nm}]{h\nu} (\mathrm{Me_2Si})_5 + \underset{\mathbf{3}}{[\mathrm{Me_2Si:}]} \qquad (3)$$

for dialkylsilylenes, but for silylenes containing at least one aryl group the linear trisilane is usually a more convenient starting material, as shown in Eq. 4. Although they are

$$\mathrm{Me_3Si{-}SiR(Ar){-}SiMe_3} \xrightarrow{h\nu} \mathrm{Me_3SiSiMe_3} + \mathrm{R(Ar)Si:} \qquad (4)$$

highly reactive species, dimethylsilylene and other silylenes are inert in rigid hydrocarbon matrices at 77 K as well as in argon matrices at still lower temperatures.

Robert West is a professor of chemistry at the University of Wisconsin, Madison 53706.

The photolytic method is quite general, and a large number of silylenes have now been observed in hydrocarbon glasses (*12*). Some of them are listed in Table 1, together with the wavelength of maximum absorption for their lowest-energy electronic transitions. Because these maxima span the range from 404 to 577 nm in the visible region, the silylenes appear in a beautiful array of colors.

If a trapping agent such as triethylsilane is present in the matrix and the matrix is allowed to melt, the silylenes are intercepted by insertion into the Si–H bond of the silane (Eq. 5). With no trapping agent present, the ultimate

$$\text{Precursor} \xrightarrow[77\text{ K}]{h\nu,\ 254\text{ nm}} \text{RR'Si:}$$

$$\xrightarrow[\Delta]{\text{Et}_3\text{Si–H}} \text{Et}_3\text{Si–SiRR'–H} \qquad (5)$$

products obtained upon melting the matrix are usually polysilane polymers $(\text{RR'Si})_n$. However, if the substituent groups R and R′ are large enough, only dimerization of the silylene takes place, forming the disilene. To stabilize the Si=Si bond, it is only necessary to have large substituents on the silicon atoms which by their steric bulk prevent polymerization.

This procedure was used in the first synthesis of a stable disilene, tetramesityldisilene (**4**), as shown in Eq. 6 (*5*) (mesityl, 2,4,6-trimethylphenyl, hereafter abbreviated Mes).

$$\text{Mes}_2\text{Si(SiMe}_3)_2 \xrightarrow[\text{pentane, 77 K}]{h\nu,\ 254\text{ nm}}$$

$$(\text{Me}_3\text{Si})_2 + \text{Mes}_2\text{Si:} \xrightarrow{\text{warm}}$$

$$\underset{\mathbf{4}}{\text{Mes}_2\text{Si=SiMes}_2} \qquad (6)$$

In practice it is not necessary to prepare the intermediate silylenes: simple irradiation of the silylene precursor in hydrocarbon solution at −50°C produces **4** in high (more than 90 percent) yield (*12*). Two other disilenes, **5** and **6**, have been prepared in a similar fashion (Eq. 7) (*13*).

$$\text{Me}_3\text{Si–Si(R)Mes–SiMe}_3 \xrightarrow[\text{pentane}]{h\nu,\ 254\text{ nm}}$$

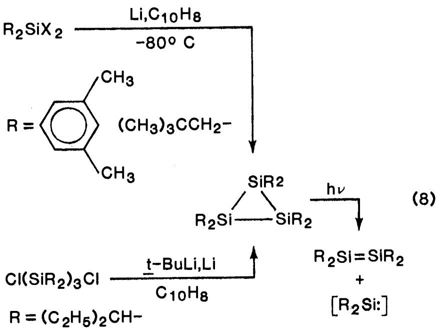
$$(\text{Me}_3\text{Si})_2 + \text{Mes(R)Si=Si(R)Mes} \qquad (7)$$

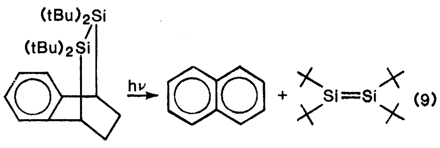
where R is mesityl in **4**, *tert*-butyl in **5**, and $(\text{Me}_3\text{Si})_2\text{N}$ in **6**. The products can be obtained as yellow or orange solids simply by evaporation of the solvent.

Disilenes can also be synthesized by photolysis of cyclotrisilanes (*14–16*), which may be generated by coupling reactions from dihalosilanes or 1,3-dichlorotrisilanes, as shown in Eq. 8. Direct dechlorination of dimesityldichlorosilane with lithium metal and ultrasonic activation leads to **4**, albeit in impure form (*17*). Finally, tetra-*tert*-butyl-disilene has been obtained by thermolysis of the bridged naphthalene derivative (*18*), as shown in Eq. 9.

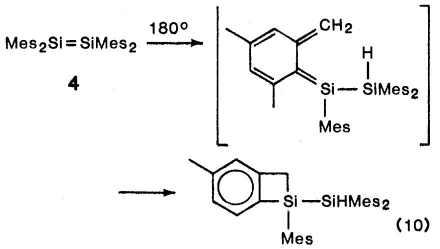
Table 1. Electronic absorption bands of silylenes, RR′Si.

Silyene	λ_{max} (nm)	Color
$(\text{Me}_3\text{Si})_2\text{N–Si–Mes}$	404	Yellow
$\text{Cyclo(CH}_2)_4\text{Si}$	436	Yellow
$\text{Cyclo(CH}_2)_5\text{Si}$	449	Yellow
$(\text{CH}_3)_2\text{Si}$	469	Yellow
Cl–Si–Mes	487	Orange
$\text{CH}_3\text{–Si–C}_6\text{H}_5$	490	Red
$(\text{C}_6\text{H}_5)_2\text{Si}$	495	Red
$\text{CH}_3\text{–Si–Mes}$	497	Red
$(\text{CH}_3)_3\text{C–Si–Mes}$	505	Red
HC≡C–Si–Mes	524	Purple
$\text{C}_6\text{H}_5\text{–Si–Mes}$	530	Purple
Mes_2Si	577	Blue





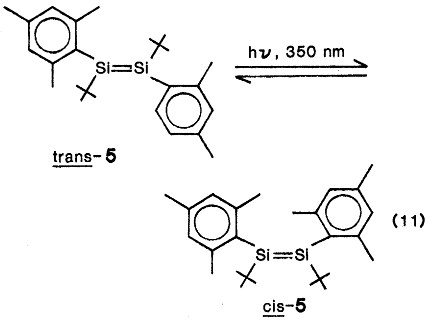
Some of the disilenes are remarkably stable, especially considering the long history of unsuccessful attempts to isolate them. Compound **4** is inert to its melting point of 178°C, and **5** is even more stable, surviving heating to 220°C. The thermolysis reaction has been studied for **4**, which decomposes above 180°C according to Eq. 10 to give a benzosilacyclobutane. A possible pathway for this transformation is 1,5-sigmatropic rearrangement to a sila-*o*-xylylene intermediate (Eq. 10) and subsequent ring closure.



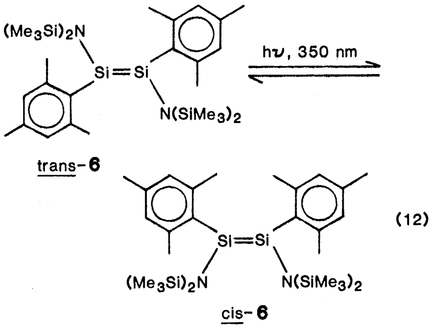
For reasons that are not clear, disilenes bearing only alkyl groups seem to be less stable than those with some aryl substituents. To date, tetraalkyldisilenes are known only in solution; none has been isolated in pure form.

Cis and *Trans* Isomers

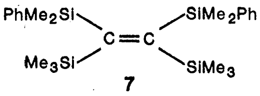
Because they have different substituents at each silicon atom, disilenes **5** and **6** can exist in *cis* and *trans* stereoisomeric forms. In the photochemical synthesis **5** is produced mainly as the *trans* isomer, which can be obtained pure by recrystallization. Irradiation at 350 nm converts *trans*-**5** to a photostationary mixture containing 37 percent *cis* and 63 percent *trans* (*13*) (Eq. 11). When irradiation is stopped, the *cis* isomer slowly rearranges to the *trans* until an equilibrium mixture of the two isomers is attained. In benzene at 25°C, the half-time for interconversion is 3220 ± 50 hours, and the final equilibrium composition is *trans*:*cis*, 98:2.



For disilene **6**, a fortunate coincidence makes it possible to prepare both isomers in pure form: the initial photochemical synthesis leads mainly to the less stable *cis* isomer, which can be crystallized from hydrocarbon solution. Isomerization to equilibrium mixture *trans*: *cis*, 94:6 takes place with a half-time of 40 ± 3 hours at 25°C (*13*) (Eq. 12).



The disilenes thus resemble olefins in that *cis* and *trans* stereoisomers can be isolated, but they differ from typical alkenes in that *cis-trans* interconversion is much more rapid. From measurements of the rate of isomerization at different temperatures, activation energies of 31 kcal/mol for **5** and 25 kcal/mol for **6** have been obtained. For ordinary alkenes such as ethylene, the corresponding value is much higher, about 65 kcal/mol. However, alkenes such as **7** in which the double bond is substituted by bulky groups have energies of activation for *cis-trans* interconversions in the same range as those for the disilenes (*19*).



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Structural Properties of Disilenes

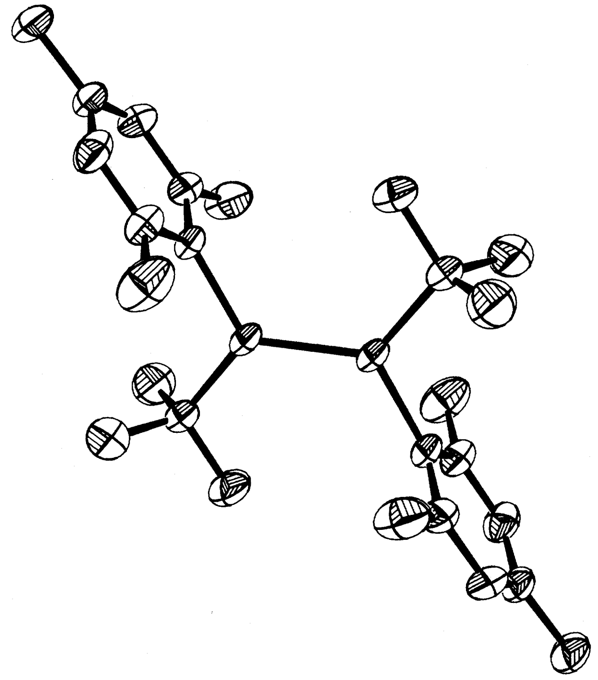
The structures of **4** and of the *trans* isomer of **5** have been determined by x-ray crystallography (*20, 21*). The two structures are different, and together they reveal a great deal about the nature of silicon-silicon double bonding.

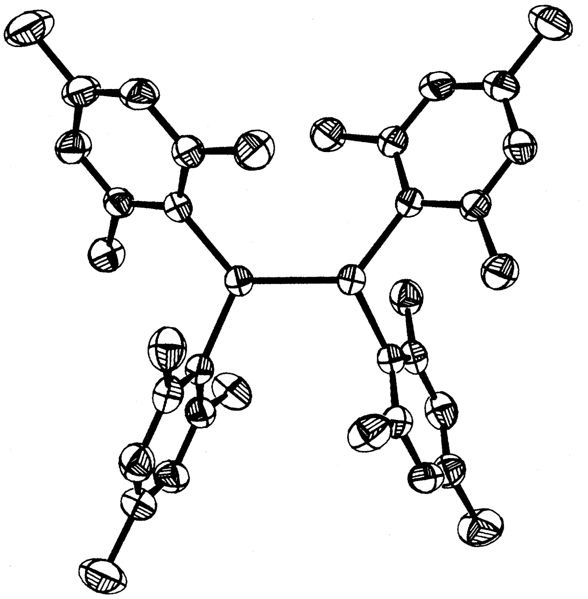
Because the structure of **5** is simpler, it will be useful to consider it first. An ORTEP diagram (Fig. 1) shows the general arrangement of the atoms, which is analogous to that in olefins. The two silicon atoms are coplanar with the four attached carbon atoms, and the bond angles at silicon are near 120°. As seen in the diagram, the two mesityl groups are inclined at almost perpendicular angles to the central molecular plane; the actual interplanar angles are 88°. In this conformation, little conjugation is possible between the mesityl groups and the Si=Si π bond.

A similar view of disilene **4** is given in Fig. 2. Two of the aromatic rings, in a *cis* arrangement, are tipped so that their π systems are almost orthogonal to the Si=Si π bond, like the aromatic rings in **5**. However, the other two mesityl groups are nearly coplanar with the mean plane of the silicon and attached carbon atoms, a conformation resembling that of the carbon compound *cis*-1,2-diphenylethene (stilbene). These two mesityl rings are arranged so that conjugation between their π systems and the Si=Si bond is possible.

Further complexities in the structure of **4** are shown in Fig. 3. The arrangement of atoms around silicon is not coplanar but moderately pyramidalized. The plane formed by each silicon and its two attached carbon atoms is at an angle of 18° to the line joining the silicon atoms. In addition the Si=Si bond is slightly twisted by 6°. The pyramidal arrangement at silicon is consistent with several molecular orbital calculations for disilene ($H_2Si{=}SiH_2$), which indicates that the potential energy curve for out-of-plane bending of the SiH_2 groups is shallow and that the planar and antipyramidal arrangements are almost equal in energy (*21*). Thus both theoretical and crystallographic results suggest that, in this respect, the Si=Si bond differs substantially from the C=C bond in alkenes.

The carbon-carbon bond length decreases markedly from single to double bonds; typical values are 154 pm for C–C and 136 pm for C=C. The Si=Si bond lengths in **4** and **5** are 216.0 and 214.3 pm, respectively, about 20 pm less than the typical Si–Si bond distance (*20*). The decrease in bond length from single to double bonds appears to be slightly larger for silicon than for carbon, although the percent decrease is a little larger for carbon. These results are consistent with a true 3pπ-3pπ double bond in the disilenes.





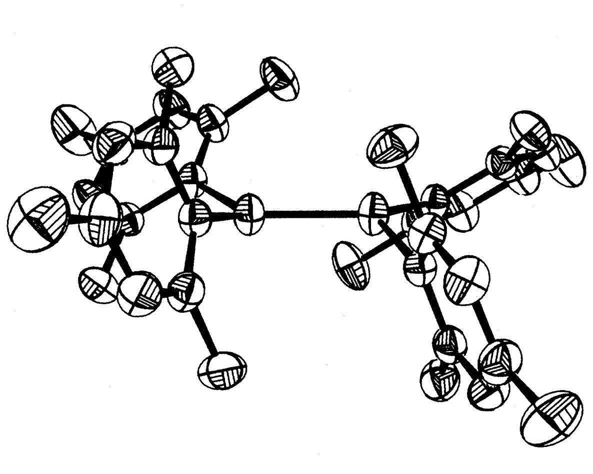
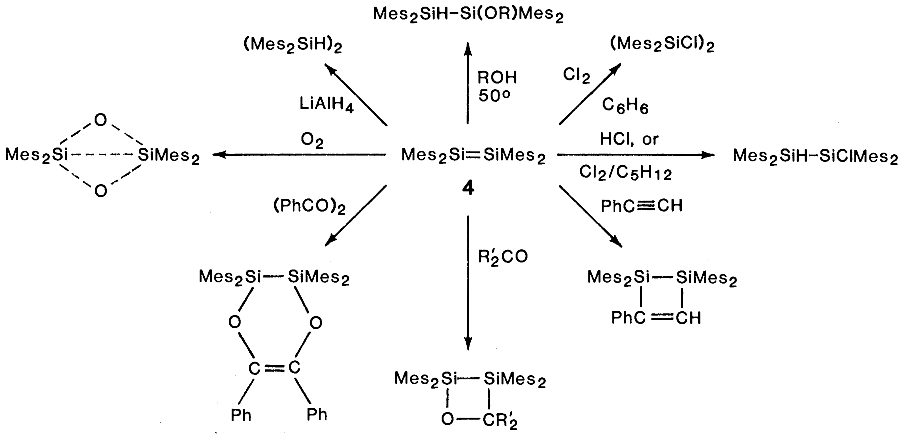


Fig. 1 (left). ORTEP diagram showing carbon and silicon atoms in *trans-t*-Bu(Mes)Si=Si(Mes)*t*-Bu (**5**). Fig. 2 (top right). ORTEP diagram for carbon and silicon atoms in tetramesityldisilene (**4**) showing arrangement of aromatic rings. Fig. 3 (bottom right). ORTEP diagram for carbon and silicon atoms in tetramesityldisilene (**4**) showing pyramidalization at silicon atoms.

Chemical reactions. Most of the reactions of disilenes to date have been done with **4** simply because it was the first such compound to be synthesized. Compound **4** resembles olefins in undergoing addition reactions that break the π bond but leave the σ bond intact. However, the double bond in **4** is far more reactive than that in alkenes.

Among reactions of **4** that resemble those of olefins are the addition of HCl or of Cl_2 in benzene (Scheme 1). Addition of bromine to the Si=Si bond has also been reported (*14*). However, when **4** is treated with chlorine in pentane or cyclohexane solution, the major product obtained is from addition of HCl rather than Cl_2 (*22*). Evidently **4** reacts with chlorine in alkanes via a free radical mechanism; this is a minor reaction for olefins but becomes the dominant pathway for **4**.



Scheme 1

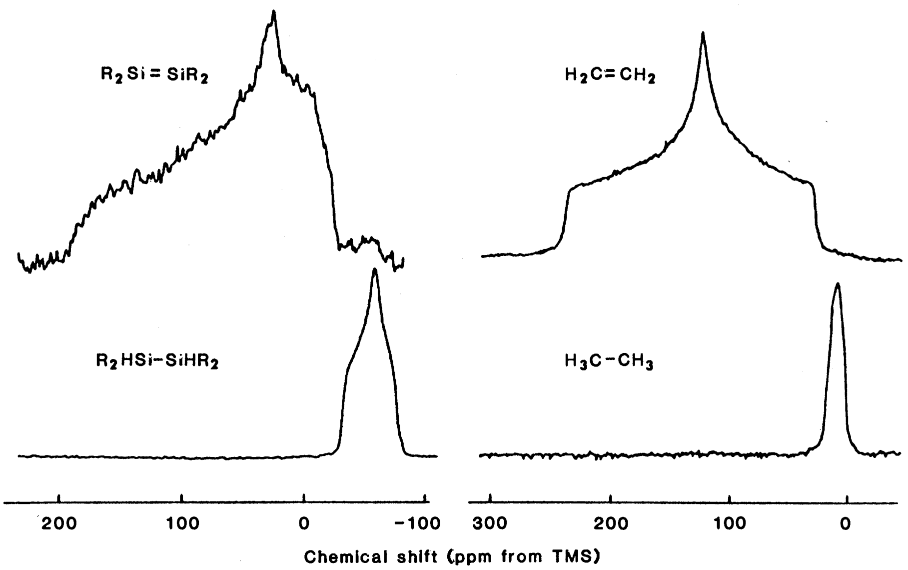


Fig. 4. Solid-state ^{29}Si NMR (left) and ^{13}C NMR (right) spectra obtained by the cross-polarization technique. R, mesityl[2,4,6-$(CH_3)_3C_6H_2$].

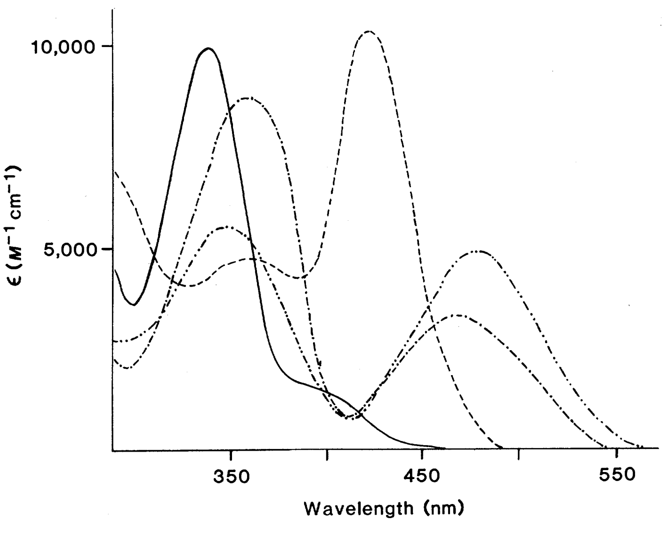
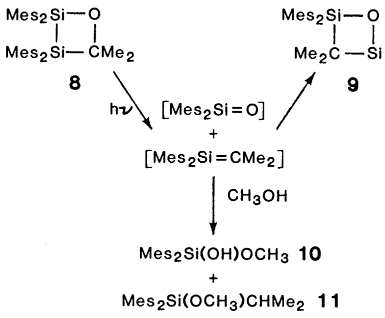


Fig. 5. Electronic absorption spectra for **4** (- - - -), *trans*-**5** (——), *cis*-**6** (-·-·-), and *trans*-**6** (-··-··-).

Disilene **4** will also add many reagents toward which olefins are normally unreactive. For example, the O–H bond of alcohols will add across the Si=Si bond at about 50°C (Scheme 1). Water will likewise add to **4** in the presence of a cosolvent. Cycloaddition reactions also take place between **4** and certain multiply bonded compounds. The acetylenes $PhC\equiv CH$ and $EtOC\equiv CH$ undergo 2 + 2 cycloaddition with **4** to give disilacyclobutenes. Many alkynes, however, do not react with **4**; examples are 1-hexyne, 3-hexyne, and phenyltrimethylsilylacetylene. Reduced steric hindrance and polarity in the C≡C bond both seem to be required for acetylene addition to take place.

In another reaction unknown for alkenes, carbonyl compounds add readily to **4** to give cycloaddition products (Scheme 1). Irradiation of the acetone cycloadduct leads to the novel rearrangement shown in Eq. 13, producing the 1,3-disila isomer **9** (*23*). However, if the irradiation is carried out in the presence of methanol, the trapping products **10** and **11** are formed instead. Our interpretation is that absorption of radiation leads to fragmentation of **8** into the transient Si=C and Si=O species shown in Eq. 13. If methanol is present these intermediates are intercepted, but in hydrocarbons they recombine in head-to-tail fashion to give isomer **9** (*22*). A different kind of reaction with a carbonyl compound has been reported between **4** and the 1,2-diketone benzil (*17*) (Scheme 1).



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Still another reaction of **4** that does not take place for alkenes is reduction by lithium aluminum hydride to the corre-

Table 2. Principal values of chemical shift tensors (parts per million).

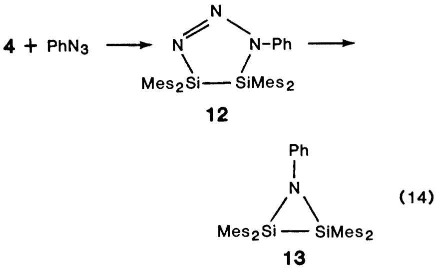
Molecule	σ_{11}	σ_{22}	σ_{33}
^{29}Si, $Mes_2Si=SiMes_2$	180	27	−15
^{29}Si, $Mes_2HSi–SiHMes_2$	−31	−56	−73
^{13}C, $H_2C=CH_2$	234	120	24
^{13}C, $H_3C–CH_3$	14	14	10

Table 3. One-bond ^{29}Si–^{13}C coupling constants (^1J) in representative organosilicon compounds. R, adamantyl.

Compound	f_s	^1J (Hz)
Me_4Si	0.063	50.2
$Mes_2HSiSiHMes_2$	0.083	63.5
$PhSiMe_3$	0.083	66.5
$(Me_3Si)_2Si=C(OSiMe_3)R$	(0.111)	84.0
$Mes_2Si=SiMes_2$	0.111	90.0

sponding dihydride $(Mes_2SiH)_2$ (Scheme 1). The same compound is obtained upon prolonged photolysis of **4** at 254 nm in hydrocarbon solution. This product is the one expected from abstraction of hydrogen by silyl radicals and therefore suggests radical character in the excited state of **4**.

Phenylazide also adds to **4** to give a purple-colored, five-membered ring product, **12**. This is an example of 1,3-dipolar addition, a type of reaction that also takes place with alkenes. Compound **12** loses nitrogen readily to produce the novel three-membered ring compound **13** (Eq. 14) (*12*).



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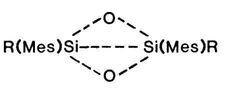
Unlike olefins, disilenes **4**, **5**, and **6** all react spontaneously with oxygen when exposed to air either in solution or in the solid state (*24*). The products have similar and quite remarkable four-membered ring structures **14a** to **14c**, which poses a new problem in chemical bonding theory. These molecules might logically be regarded as cyclodisiloxanes (**15**), but the x-ray crystal structures show that the two silicon atoms are well within bonding distance. The Si–Si distance of 231 pm for **14a** is actually shorter than the normal Si–Si single-bond length of 234 to 236 pm. [The O–Si distances in **14a** are slightly long for a siloxane bond, and the Si–O–Si angle is small (86°).] It is possible that these molecules contain partial, electron-delocalized bonds and that no single-valence bond structure can be written for them (*24*).



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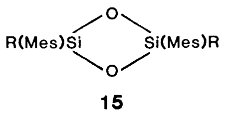

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Nuclear Magnetic Resonance and Chemical Bonding

In olefins, the ^{13}C nuclear magnetic resonance (NMR) chemical shift for the carbon atoms of the double bond is strongly deshielded compared to that for sp^3 hybridized carbon atoms. Similarly, the ^{29}Si resonances for doubly bonded silicon atoms appear at unusually low field. The chemical shifts for known disilenes lie between +49.4 parts per million (ppm) for *cis*-**6** and +94.7 ppm for *cis*-**5** compared with values of −20 to −50 ppm for typical disilanes (*13*).

The electron distribution about silicon leading to the shift of ^{29}Si resonance downfield can be more closely studied by a solid-state NMR experiment. The isotropic chemical shift value observed in solution is actually the trace of the anisotropic chemical shift tensor, whose principal values can provide information about the electronic environment of the atom under study. The solid-state ^{29}Si NMR spectra of **4** and of the corresponding disilane $Mes_2SiH–SiHMes_2$ is shown in Fig. 4, together with ^{13}C NMR spectra for ethene and ethane. The principal values of the chemical shift tensors for these molecules are given in Table 2 (*25*).

The large anisotropy of the ^{13}C chemical shift found for ethene results from the highly asymmetric charge distribution in this molecule due to the C=C π bond. In contrast ethane, in which the carbon forms only σ bonds, shows little anisotropy (*26*). Similarly in the disilane, the anisotropy of the ^{29}Si chemical shift is small, whereas in disilene **4** it is large (195 ppm). The similarity in anisotropy of magnetic shielding in **4** and ethene indicates that the electronic charge distribution in these types of molecules is also similar. If so, the bonding at the silicon atoms in the disilene can be described in terms of a p-π bond and three near sp^2 hybrid σ bonds, just like the bonding at carbon in alkenes.

A test of the sigma bond hybridization at silicon is available from the ^{29}Si–^{13}C one-bond coupling constant, which is proportional to the degree of s character in the bond. The latter is roughly equal to f_s, the product of s character in the individual hybrids contributing to the bond (*27*). Values of the coupling constant and of f_s are given in Table 3. The value of 90.0 Hz for **4** is entirely consistent with sp^2 hybridization of silicon orbitals in the Si–C bond (*28*). A high value for the same coupling constant in the doubly bonded compound (Table 3) suggests that it too has near sp^2 hybridization at silicon (*29*).

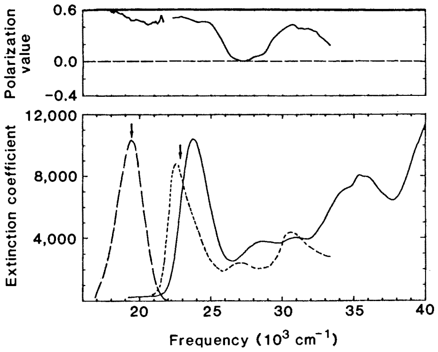

Fig. 6. Absorption (——), emission (– – –), and excitation (- - - -) spectra for tetramesityldisilene. Polarization of the absorption and emission spectra is shown above.

Electronic Spectra and Thermochromism

Disilenes **4**, **5**, and **6** differ in their appearance: the *cis* and *trans* isomers of **5** are pale yellow, **4** is bright yellow, *trans*-**6** is orange, and *cis*-**6** is red. These differences are reflected in the electronic spectra (*13*) (Fig. 5). The low energies of absorption (ϵ) observed for the isomers of **6** may reflect interaction of the lone pairs of electrons on nitrogen with the Si=Si bond, raising the energy of the ground state. Compound **4**, with mesityl groups which may be conjugated with the disilene bond, has an intermediate wavelength absorption; and the shortest wavelength absorption is found for **5**, which (at least in the conformation found in the solid) cannot benefit from such conjugation.

The absorption and emission spectra of **4** have been investigated in somewhat greater detail (*30*). At 77 K in a hydrocarbon glass, additional absorptions are found for **4**, shown in Fig. 6. Also displayed are the emission and excitation spectra for the compound and the polarizations of the spectra. The identical polarization value of 0.5 for the emission and excitation spectra indicate that a single electronic transition is responsible. The curious feature of the spectra is that the excitation spectrum, although it follows the absorption spectrum closely, is shifted to longer wavelength. More-over the fluorescence lifetime of 2 nsec is much shorter than the theoretical lifetime of 17 nsec calculated from the integrated intensity of the long-wavelength absorption band. The likely explanation of these anomalies is that more than one conformer of **4** is present in solution; a nonfluorescing conformer (or conformers) is mainly responsible for the absorption spectrum, and the emission is due to a minor amount of a strongly fluorescent isomer. Similar effects have been observed for conformers of molecules related to stilbene (*31*).

Conformational effects are probably also involved in the remarkable thermochromism exhibited by **4** in the solid state. When **4** is heated above room temperature, it gradually changes from bright yellow to orange to red, melting at 178°C to a red liquid. All of these changes are reversible if the liquid is cooled promptly. Similar thermochromism has been reported for some tetrasilylalkenes and is attributed to twisting of the C=C bond with increasing temperature, raising the energy of the ground state (*32*). Although the thermochromic behavior of **4** is not yet understood, it almost surely reflects temperature-dependent conformational changes of some kind. On the other hand, disilenes *trans*-**5** and *trans*-**6** show no, or at most slight, color changes with temperature.

Conclusion

From results gathered over the last 3 years, it is evident that stable molecules containing silicon-silicon double bonds can be synthesized by several routes. The key to stabilizing such disilenes lies in having large substituents bonded to the silicon atoms so that polymerization is blocked. Physical evidence indicates that the multiple bond in disilenes is similar electronically to the familiar carbon-carbon double bond, but the silicon-silicon double bond can adopt nonplanar conformations that are not found for olefins. Disilenes react chemically by addition across the double bond, as do alkenes. However, tetramesityldisilene also undergoes a wide variety of addition reactions unknown in organic chemistry, producing a number of new and unusual types of molecules. These studies are in their infancy, and further surprising results may be anticipated.

References and Notes

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