

THE DISILENES: CHEMISTRY OF SILICON-SILICON DOUBLE BONDS

Robert West

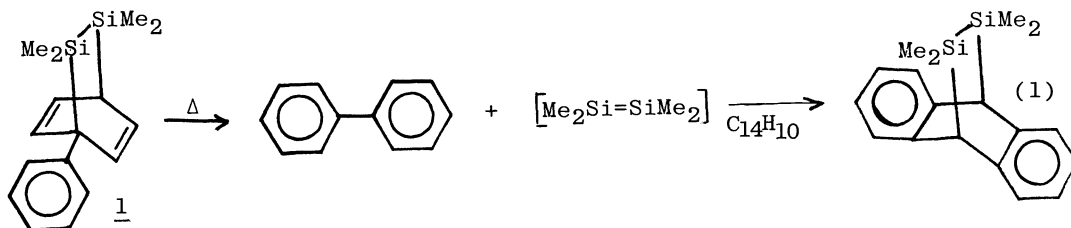
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Abstract - Three stable disilenes, Mes(R)Si=Si(R)Mes where R = mesityl, *tert*-butyl and $(\text{Me}_3\text{Si})_2\text{N}$, have been prepared by photolysis of trisilanes and dimerization of the resulting silylenes. X-ray crystallographic studies show Si=Si distances of ~ 215 pm, about 20 pm shorter than for a Si-Si single bond. The silicon and attached carbon atoms are planar in the *tert*-butylmesityl compound but anti-pyramidal in tetramesityl-disilene. Stereoisomers (*cis-trans*) have been identified for two of the disilenes and their interconversions have been investigated. Disilenes are reactive toward both polar and radical reactions. With oxygen, disilenes form adducts with unique four-membered ring structures.

INTRODUCTION

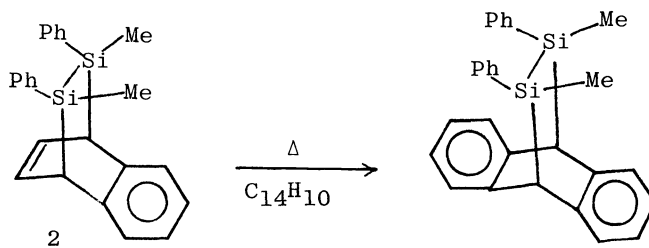
As silicon is the element most similar to carbon in its chemical properties, it is not surprising that multiple bonds involving silicon have long been sought. The pioneering research of Kipping and his students early in this century included attempts to make compounds containing Si=Si, Si=C and Si=O double bonds. In recent years evidence has appeared for transient species containing such bonds, as reaction intermediates (1). However, isolation of actual chemical compounds containing multiple bonds to silicon was reported only in 1981. That year saw the first publications of Si=C double bonds by Brook and coworkers (2), and of Si=Si double bonds from our group (3).

Evidence for the transient existence of species containing Si=Si double bonds (disilenes) was first presented ten years earlier by Peddle and Roark (4). They prepared bridged compounds such as 1, which upon thermolysis in the presence of trapping agents like anthracene transferred $\text{Me}_2\text{Si=SiMe}_2$ units:

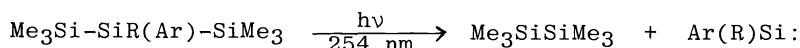
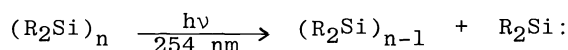


Following this publication, a number of other reports appeared interpreting experiments in terms of disilene intermediates. Particularly significant is the sequence of reactions reported by Sakurai and coworkers, involving the same type of thermolysis (5). The *cis* and *trans* isomers of the bridged disilane 2 were separated, and independently thermolyzed in the presence of trapping agents such as anthracene. The stereoisomerism of the reactants was retained in the products, and this result was interpreted as showing that *cis-trans* isomerism in disilenes must be slow.

Our own research in this area began with studies of divalent silicon species, silylenes. In 1979 we reported the isolation of dimethylsilylene, Me_2Si ,



both in argon matrices at $\sim 10\text{K}$ and in hydrocarbon glasses at liquid nitrogen temperature (6). The silylene, prepared by photolysis of the cyclic compound $(\text{Me}_2\text{Si})_6$, is indefinitely stable in hydrocarbons at 77K . We have since found that photolytic generation of silylenes is quite general, either from cyclic compounds or, for arylsilylenes, from linear trisilanes (7):

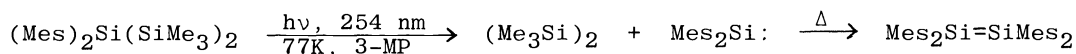


Some of the silylenes generated in hydrocarbons by this method are listed in Table 1, together with the wavelength of their low-energy electronic absorption bands. The absorption bands cover the range from 404 to 577 nm, so that silylenes occur in all the colors of the rainbow. The reasons for the marked dependence of the $n \rightarrow p$ transition of silylenes on substituents will be discussed elsewhere (7).

TABLE 1. Electronic absorption bands of silylenes, $\text{RR}'\text{Si}$

Silylene	λ_{max}	Color
$(\text{Me}_3\text{Si})_2\text{N}-\text{Si}-\text{Mes}$	404	yellow
$\text{cyclo}(\text{CH}_2)_4\text{Si}$	436	yellow
$\text{cyclo}(\text{CH}_2)_5\text{Si}$	449	yellow
$(\text{CH}_3)_2\text{Si}$	469	yellow
$\text{Cl}-\text{Si}-\text{Mes}$	487	orange
$\text{CH}_3-\text{Si}-\text{C}_6\text{H}_5$	490	red
$(\text{C}_6\text{H}_5)_2\text{Si}$	495	red
$\text{CH}_3-\text{Si}-\text{Mes}$	497	red
$(\text{CH}_3)_3\text{C}-\text{Si}-\text{Mes}$	505	red
$\text{HC}\equiv\text{C}-\text{Si}-\text{Mes}$	524	purple
$\text{C}_6\text{H}_5-\text{Si}-\text{Mes}$	530	purple
Mes_2Si	577	blue

When the hydrocarbon glasses containing silylenes are carefully annealed, the absorption band due to the silylene disappears and is replaced by a band near 380 nm (for alkylsilylenes) or 420 nm (for most arylsilylenes). Upon complete melting of the matrix, in most cases the yellow secondary products also disappear and the ultimate product is a linear polysilane. However if the substituent groups are both mesityl, the yellow annealing product persists in hydrocarbon solution to room temperature and above (2,7). Evaporation of the hydrocarbon leaves yellow, stable tetramesityldisilene:

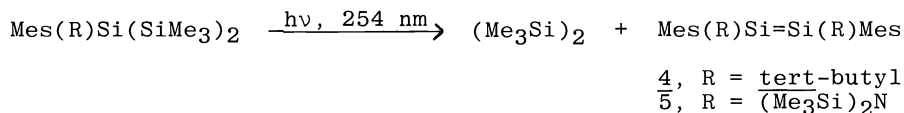


3

It is not necessary to prepare the intermediate silylene; simple irradiation of the precursor in hydrocarbon solution produces 3 in yields $>90\%$.

Subsequently, compound 3 has been prepared from a dichloride precursor with lithium and ultrasonic activation (8); and a closely-related compound, tetrakis(2,6-dimethylphenyl)disilene, has been made by photolysis of the corresponding 3-membered cyclosilane ring (9).

At Wisconsin, we have studied a number of the chemical and physical properties of tetramesityldisilene, which are unprecedented and remarkable (10). In addition the photolytic route has been employed to synthesize two new disilenes, 4 and 5, both bearing two different groups on each silicon atom (11):



These disilenes prove to have surprisingly great thermal stability; 3 is stable to its melting point of 178°C, and 4 survives heating to 225°C.

STRUCTURAL CHEMISTRY OF DISILENES

X-ray crystallography

Crystal structures have been determined for 3 (12), and for the *trans* isomer of 4 (13), by x-ray diffraction. The two molecular structures are rather different, and both are revealing about the nature of silicon-silicon double bonding.

The structure of 4 will be considered first. An ORTEP diagram is shown in Figure 1. In molecules of 4 the two silicon and four attached carbon atoms

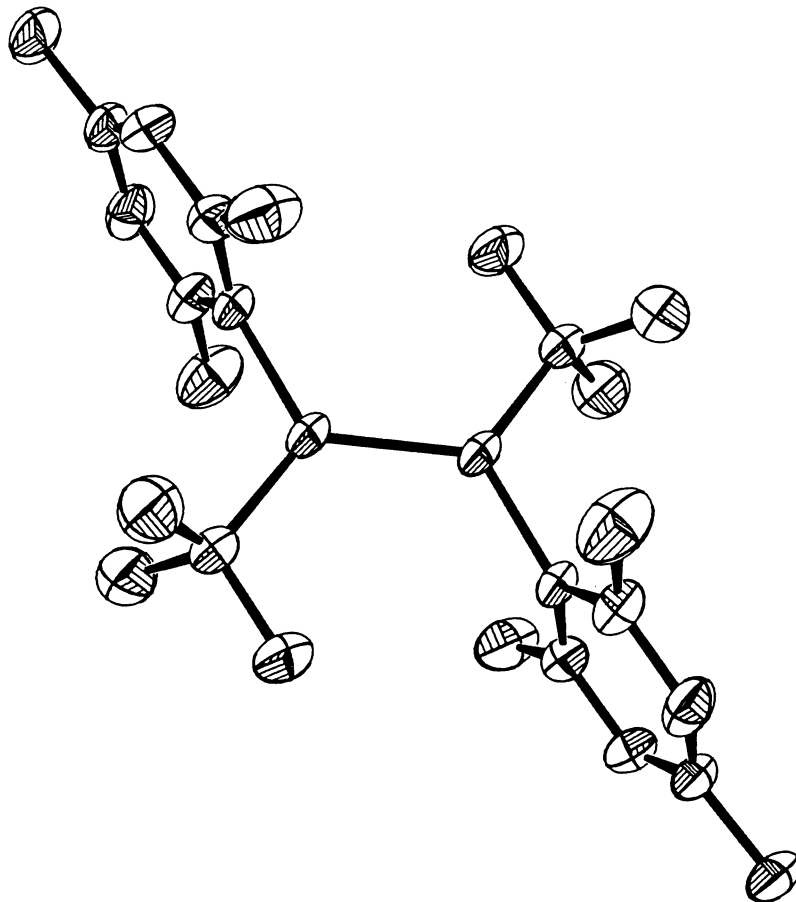


Fig. 1. ORTEP diagram showing carbon and silicon atoms in *t*-Bu(Mes)Si=Si(Mes)*t*-Bu, 4.

are essentially coplanar; the sum of bond angles about silicon is 359.8° . The mesityl groups are inclined at angles of 88° to the plane of the silicon and attached carbon atoms. In this configuration little conjugation between the pi systems of the aromatic rings and that of the silicon-silicon double bond is possible.

Disilene **3** has a somewhat more complex structure. In addition to a slight (5°) twist at the Si-Si double bond, each of the silicon atoms is moderately anti-pyramidalized, as seen from Fig. 2. The plane formed by the silicon

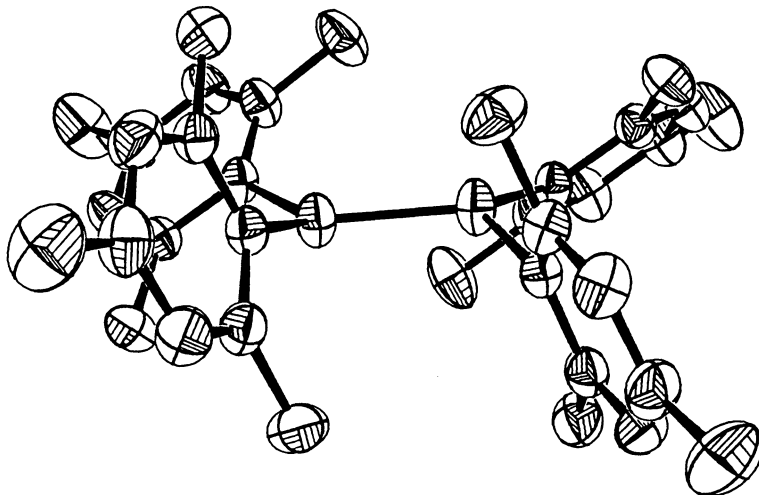


Fig. 2. ORTEP diagram for carbon and silicon atoms in tetramesityldisilene, **3**, showing pyramidalization at silicon atoms.

and two attached carbon atoms is at an angle of 18° to the silicon-silicon internuclear line. Quantum mechanical calculations for the parent disilane, $H_2Si=SiH_2$, suggest that the silicon-silicon double bond may lead either to a planar or pyramidal arrangement about silicon; the energy required for pyramidal distortion is predicted to be very small (14). Our crystallographic results are fully in agreement with these theoretical studies.

In **3**, two of the aromatic rings, in a *cis* relationship to each other, are rotated so that their pi systems are nearly orthogonal to the silicon pi bond, like the aryl groups in **4**. However the other pair of *cis* aromatic rings are much more nearly coplanar with the mean plane of the silicon and attached carbon atoms, in a conformation resembling that of *cis*-stilbene (Fig. 3). These two rings are so disposed that conjugation with the Si-Si pi system is possible.

A most important parameter is the silicon-silicon bond length, 216.0 pm in **3** and 214.3 pm in **4**. These distances are about 20 pm shorter than the Si-Si single bond distances, which typically ranges from ~ 234 to 236 pm. The decrease in internuclear distance going from the single to the double bond is at least as large as that for analogous carbon-carbon bonds (typical distances are C=C, 154 and C=C, 136 pm), although on a percentage basis the decrease is of course smaller for silicon. The short silicon-silicon distance in disilenes implies the presence of a true pi-bond between the silicon atoms.

Cis and trans isomers

Disilenes **4** and **5**, being differentially substituted at silicon, can exist in two stereoisomeric forms. Compound **4** is produced mainly as the *trans* isomer, but photolysis at 350 nm converts it to a photostationary 63:37 *trans:cis* mixture. When irradiation is ceased, interconversion of *cis* to *trans* **4** takes place slowly to give the equilibrium mixture of 98:2 *trans:cis*. At 25° in benzene, the half-time for isomerization is 500 ± 5 h. The change can easily be followed by 1H or ^{29}Si spectroscopy (11).

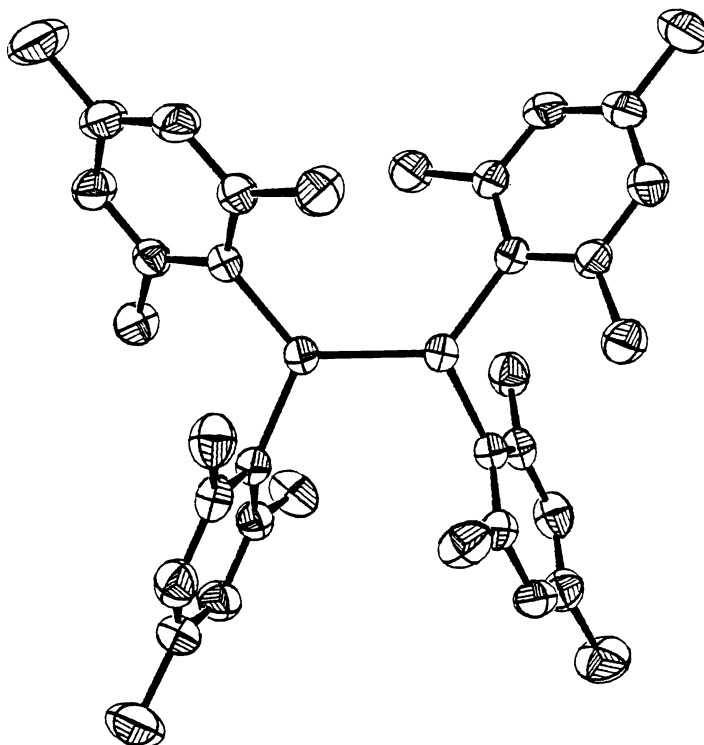


Fig. 3. ORTEP diagram for carbon and silicon atoms in 3, showing arrangement of aromatic rings.

For compound 5, both isomers have been obtained pure. This possibility arises because the less stable cis isomer is formed with very high stereoselectivity in the initial photolytic synthesis. Photolysis at -60°C in pentane and crystallization at -78°C produces cis-5 in $>95\%$ yield. In benzene at 25° , the cis isomer transforms to the equilibrium distribution, 88:12 trans:cis, with a half-time of 51 h. The pure trans isomer can be obtained by recrystallization from this equilibrium mixture.

The observed rates of cis-trans isomerism for disilenes 4 and 5 are consistent with relatively small activation energies for this process. It is interesting to compare these results with the high-temperature studies of transient disilenes reported by Sakurai and coworkers, mentioned above (5). Possibly isomerism is slower in nonhindered disilenes, or perhaps the reaction shown in equation (2) does not actually proceed through free disilene.

SPECTROSCOPY

Nuclear magnetic resonance spectra

The ^{29}Si nmr chemical shift should be distinctive for the sp^2 hybrid silicon atoms in disilenes. In Table 2 are shown ^{29}Si chemical shifts for several silicon compounds. Disilanes, and other polysilicon compounds typically exhibit values well upfield from TMS. The three compounds so far reported with $\text{Si}=\text{C}$ double bonds show strongly deshielded silicon atoms with δ +41 to +55 ppm (15). The chemical shifts for disilenes 3, 4 and 5 fall from +49 to +95 ppm, even more strongly deshielded.

The isotropic ^{29}Si chemical shift in solution is the trace of the anisotropic chemical shift tensor; the principal values of this tensor can give information about the anisotropy of the electronic environment about the silicon atom. Solid state ^{29}Si spectra for 3 and of tetramesityldisilane (6) were taken to obtain the tensor elements for these species (16). Figure 4 shows the ^{29}Si solid state spectrum of these compounds along with the literature ^{13}C solid state spectra for ethylene and ethane (17). Table 3 lists the derived principal values for the chemical shift tensors.

TABLE 2. Chemical shifts for some silicon compounds

Compound	δ
$\text{Me}_3\text{SiSiMe}_2\text{Ph}$	-21.7
$\text{Me}_3\text{SiSiMe}_3$	-19.8
Me_4Si	0.0
$(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{CMe}_3$	+41.4
$(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{adamantyl}$	+41.8
$(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{CEt}_3$	+54.2
$(\text{Me}_3\text{Si})_2\text{N}(\text{Mes})\text{Si}=\text{Si}(\text{Mes})\text{N}(\text{SiMe}_3)_2$	+49.4, +6.3 (<u>cis</u>) +61.9, +6.8 (<u>trans</u>)
$\text{Mes}_2\text{Si}=\text{SiMes}_2$	+63.6
$\text{Me}_3\text{C}(\text{Mes})\text{Si}=\text{Si}(\text{Mes})\text{CMe}_3$	+90.3 (<u>trans</u>) +94.7 (<u>cis</u>)

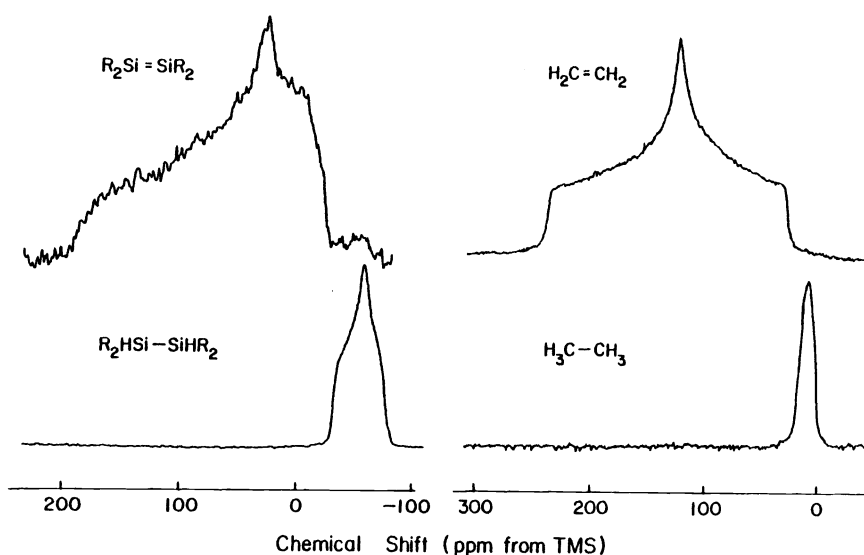


Fig. 4. Solid-state ^{29}Si nmr (left) and ^{13}C nmr (right) spectra obtained by the cross-polarization technique. R stands for mesityl(2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2$).

TABLE 3. Principal values of chemical shift tensors

		σ_{11}	σ_{22}	σ_{33}
^{29}Si	$\text{Mes}_2\text{Si}=\text{SiMes}_2$	180	27	-15
^{29}Si	$\text{Mes}_2\text{HSi}-\text{SiHMes}_2$	-31	-56	-73
^{13}C	$\text{H}_2\text{C}=\text{CH}_2$	234	120	24
^{13}C	$\text{H}_3\text{C}-\text{CH}_3$	14	14	10

The large anisotropy of the ^{13}C chemical shift found for ethylene (210 ppm) results from the highly asymmetric charge distribution in this molecule, due to the C=C pi bond. In contrast ethane, which contains only sigma bonds, shows very little anisotropy (4 ppm). Similarly the anisotropy of the ^{29}Si chemical shift disilane, which contains only sigma bonds, is small; the ^{29}Si nmr anisotropy for

3 is huge, 195 ppm. From this similarity in behavior of chemical shift anisotropy in the disilene and in olefins, it appears that the electronic structure of the double bond in 3 is similar to that in carbon-carbon double bonds.

The unusual hybridization at silicon is also indicated by the large value for the ^{29}Si - ^{13}C one-bond coupling constant, shown in Table 4.

TABLE 4. One bond ^{29}Si - ^{13}C coupling constants in representative organosilicon compounds

	f_s	$^1J_{^{29}\text{Si}-^{13}\text{C}}$ (Hz)
$\text{Me}_3\text{SiSiMe}_3$	1/16	43.6
Me_4Si	1/16	50.2
$\text{Mes}_2\text{HSiSiHMes}_2$	1/12	63.5
PhSiMe_3	1/12	66.5
$\text{PhC}\equiv\text{C-SiMe}_3$	1/8	83.6
$\text{Mes}_2\text{Si}=\text{SiMes}_2$	1/9	90.0
$(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{R}$	1/9	84.0

R = adamantyl

The one-bond coupling constant should be proportional to the degree of s character in the bond, which is roughly equal to f_s , the product of formal s character in the individual hybrid orbitals contributing to the bond (18). (For $\text{sp}^n\text{-sp}^m$, $f_s = (1/n+1) \times (1/m+1)$). The large value of 90 Hz for the Si-C one-bond coupling constant in 3 is consistent with sp^2 hybridization at silicon in this molecule; a similar high value is observed for the Si=C doubly bonded compound shown in the table.

The proton nmr spectrum of 3 at room temperature is quite simple, showing only three resonances at 2.05 (3H), 2.43 (6H) and 6.67 (2H). This spectrum is not consistent with the solid state structure, which should show different chemical shifts for the protons on different rings. The simple proton spectrum suggests that conformational equilibration is occurring at room temperature. This interpretation is strengthened by the nmr at lower temperatures, which shows splitting of the resonances corresponding to the *o*-methyl and aromatic hydrogens, Fig. 5, with coalescence temperatures of -43 and -57 respectively. An average activation barrier of 12 kcal/mole is

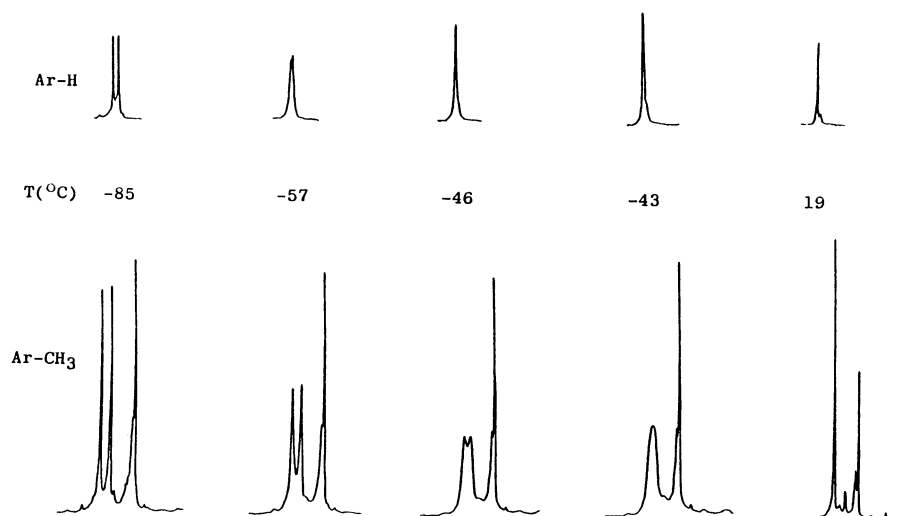


Fig. 5. Variable temperature ^1H nmr for tetramesityldisilene in toluene- d_8 .

calculated for the dynamic process leading to averaging of the proton signals. Although the nature of the process is unknown most likely it involves rotation of mesityl groups around the Si-C bond.

Electronic spectra

As expected from their differing colors, compounds 3, 4 and 5 exhibit distinctive electronic absorption spectra, illustrated in Fig. 6. The lowest

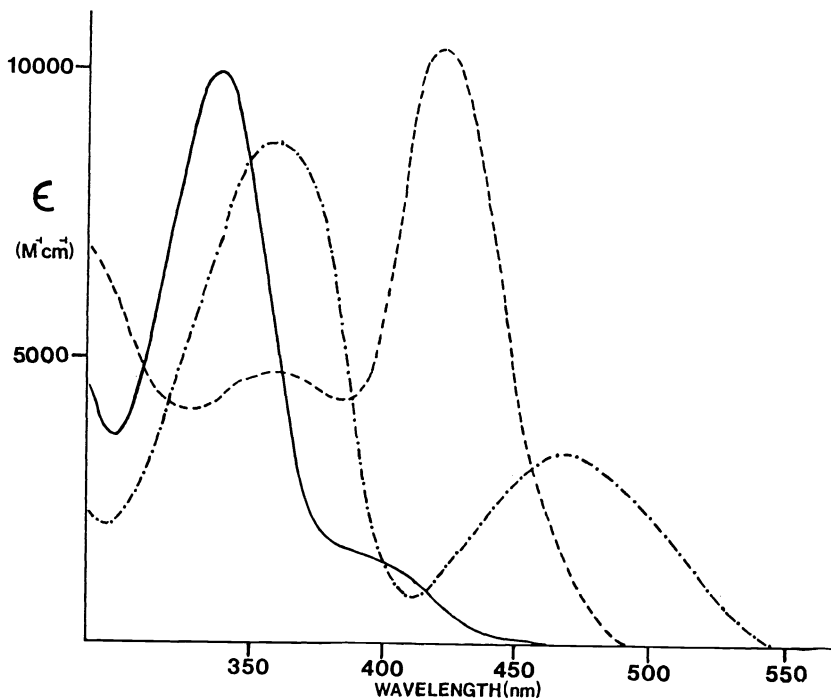


Fig. 6. Electronic absorption spectra for 3 (---), 4 (—), and 5 (-·-·-).

energy absorption is observed for the nitrogen-substituted compound 5. The low energy may reflect interaction of the nitrogen lone pairs with the Si=Si double bond, raising the energy of the ground state. Compound 3, with mesityl groups which may conjugated with the disilene bond, has an intermediate value of λ ; and the shortest wavelength absorption is found for 4, which (at least in the conformation found in the solid) cannot benefit from such conjugation.

The absorption and emission spectra of 3 have been investigated in somewhat greater detail. At 77K in a hydrocarbon glass, additional absorptions are found for 3, shown in Fig. 7. Also displayed in Fig. 7 are the emission and excitation spectra for the compound, as well as their polarizations. The identical value of 0.5 for the emission and excitation spectra indicate that a single electronic transition is involved. The curious feature of the spectra is that the excitation spectrum, although it follows the absorption spectrum closely, is shifted to longer wavelength. Moreover the fluorescence lifetime of 2 ns is much shorter than the theoretical lifetime of 17 ns calculated from the integrated intensity of the long-wavelength absorption band. The likely explanation of these anomalies is that more than one conformer of 3 is present in solution; nonfluorescing conformer(s) are 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 (19).

The infrared and Raman spectra of 3 have also been investigated and will be published elsewhere (7, 20).

CHEMICAL REACTIONS

Most of the chemical studies so far have been done with the tetramesityl compound 3 (10). The silicon-silicon double bond in 3 participates both in polar and radicaloid reactions, and is decidedly more reactive than a

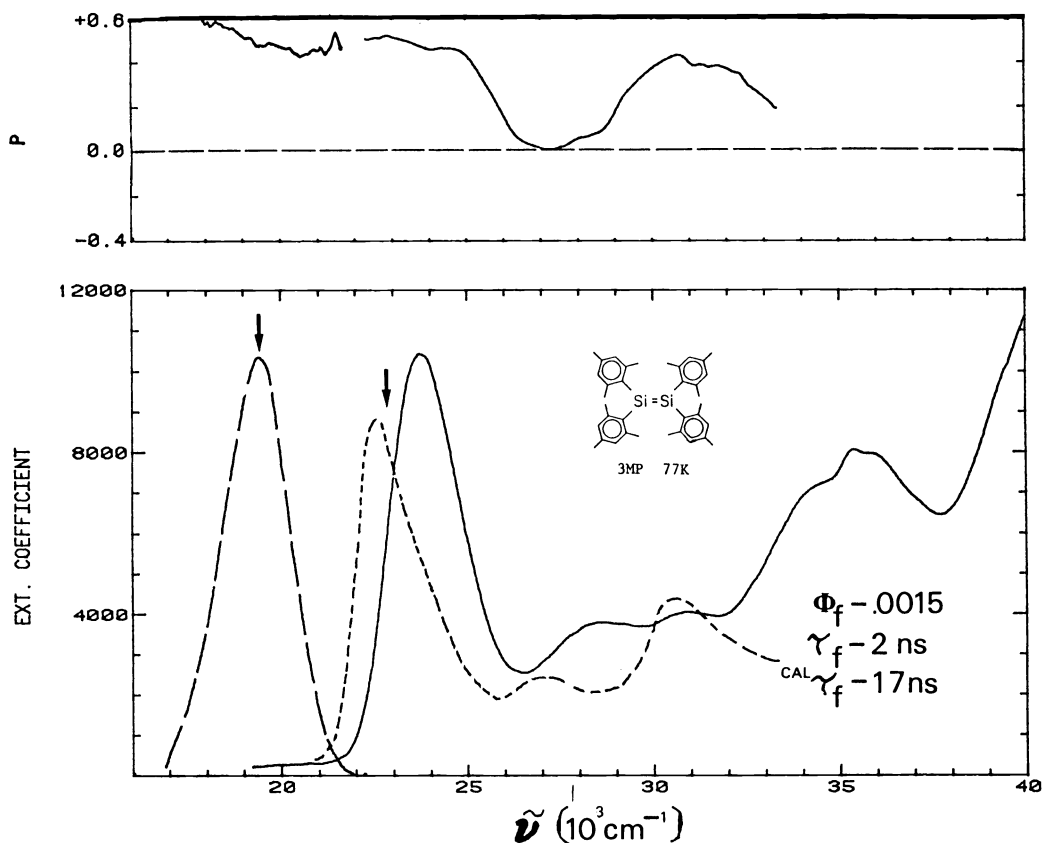
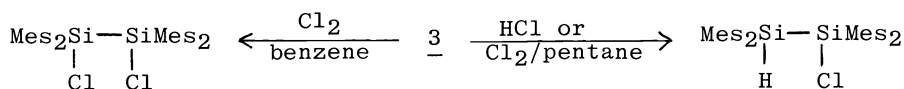


Fig. 7. Absorption (—), emission (---) and excitation (----) spectra for tetramesityldisilene. Polarization of the absorption and emission spectra is shown above.

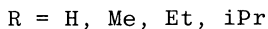
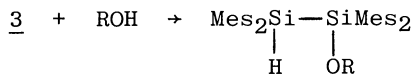
typical C=C double bond. Most reactions of this compound proceed to single products in yields greater than 90%.

Addition of typical double bond reagents takes place readily, so long as steric hindrance does not become limiting. Thus hydrogen chloride adds immediately across the Si=Si double bond, as does chlorine when the reaction is carried out in benzene. However if **3** is treated with Cl₂ in pentane or cyclohexane, the main product is the HCl adduct:

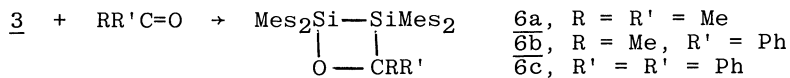


Products of free-radical chlorination of the alkane are also found; **3** apparently catalyzes such chlorination, and adds the HCl which is formed as byproduct.

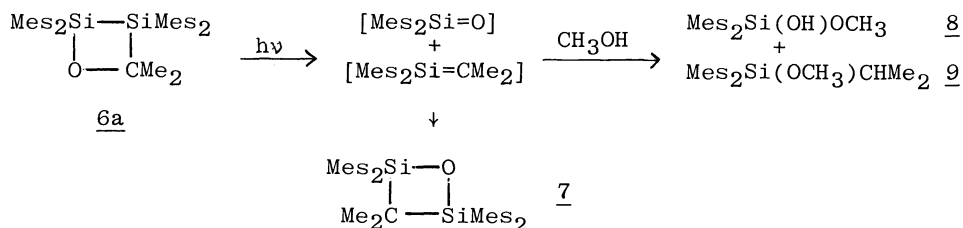
Unlike olefins, **3** (also **4** and **5**) will add alcohols across the double bond. The reaction requires warming to about 50°C. Water will also add in the presence of a cosolvent:



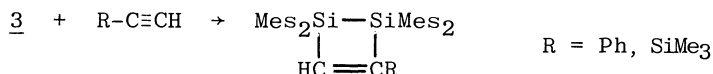
Carbonyl compounds also react with **3** to give cycloaddition products, **6a-c**:



Photolysis of the acetone adduct 6a has been studied, with quite interesting results. Irradiation at 254 nm in inert solvents converts 6a quantitatively into its isomer 7. However in the presence of methanol, the trapping products 8 and 9 are produced instead. The irradiation apparently produces silanone and silene intermediates by fragmentation of the four-membered ring; in the absence of a trapping agent these recombine in a head-to-tail fashion to give 7 (10).

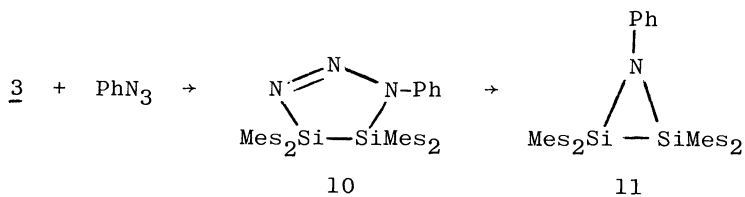


Cycloaddition reactions also take place with certain acetylenes, such as phenylacetylene and trimethylsilylacetylene to produce the 1,2-disilacyclobutenes. However 3 is unreactive toward anthracene, 1-hexyne, phenyltri-

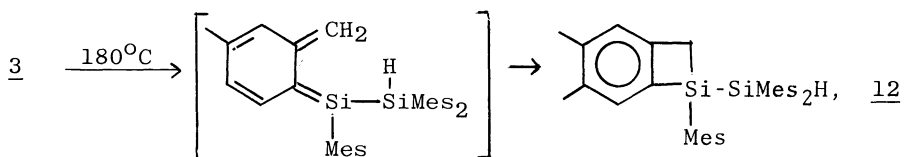


methylsilylacetylene, and dienes such as 2,3-dimethylbutadiene, all of which serve as trapping reagents for transient, unhindered disilenes. Steric blocking may impede these potential cycloaddition reactions.

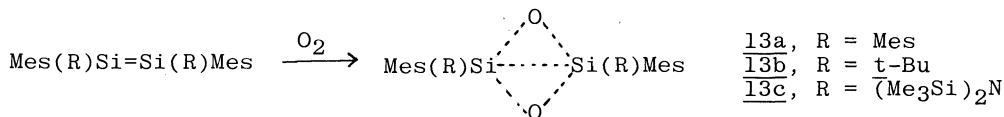
On the other hand, phenyl azide adds readily to 3 in dipolar fashion to give the unstable purple compound 10. The latter loses nitrogen spontaneously to produce the disilaziridene 11 (20):



The disilenes are surprisingly resistant to thermal degradation; 3 decomposes above 180°, or upon long heating in solution at 140°, while 4 survives unchanged up to 225°C. Thermolysis of 3 proceeds with hydrogen transfer to the benzosilacyclobutene 12. A possible pathway for this rearrangement is through the sila-o-xylylene intermediate shown below (10):



All of the disilenes combine with oxygen. The half-times for oxidation of powdered solid samples in air are minutes for 3, but hours for 4, so the latter may be exposed briefly to air without decomposition, for instance in making transfers from one vessel to another. The three disilenes give products with similar, and quite remarkable, structures, 13a-c (21):



The structures of these products might logically be written as cyclodisiloxanes - a structural type which is at present unknown. However, x-ray

crystal structure investigations of 13a-c show that the silicon atoms are well within bonding distance. The Si-Si distances are 231, 239 and 234 pm in 13a, b, and c respectively, compared with a normal Si-Si single bond distance of 234-236 pm. The O-Si distances are unequal at each oxygen, and slightly long for a siloxane bond (166 and 172 pm in 13a).

The oxygen adduct compounds 13a-c raise serious questions for chemical bonding theory. One way to explain the structures of these compounds is in terms of delocalized, electron deficient bonding within the four-atom system (21). Further speculation however should await additional theoretical and experimental studies.

CONCLUSION

Hindered disilenes are easily generated by the photolytic method. Disilenes are remarkably stable substances, considering that they were sought unsuccessfully for so many years. Spectroscopic and structural properties of these molecules are consistent with presence of a real double bond between the silicon atoms, although interconversion of cis-trans stereoisomers is relatively facile. The versatile reactivity of disilenes should lead to many new types of silicon compounds, including new species with other kinds of multiple bonds to silicon.

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REFERENCES

1. L.E. Gusel'nikov and N.S. Nametkin, Chem. Rev. **79**, 529 (1979).
2. A.G. Brook, F. Abdesaken, B. Gutekunst, A. Gutekunst and R.K. Kallury, J. Chem. Soc. Chem. Commun. 191 (1981).
3. R. West, M.J. Fink and J. Michl, 15th Organosilicon Symposium, Duke University, Durham, N.C., Mar. 1981; R. West, M.J. Fink and J. Michl, Science (Washington, D.C.) **214**, 1343 (1981).
4. D.N. Roark and G.J.D. Peddle, J. Am. Chem. Soc. **94**, 5837 (1971).
5. H. Sakurai, Y. Nakadaira and T. Kobayashi, J. Am. Chem. Soc. **101**, 487 (1979).
6. T.J. Drahnak, J. Michl and R. West, J. Am. Chem. Soc. **101**, 5427 (1979).
7. R. West, M.J. Fink, M.J. Michalczyk and J. Michl, unpublished studies.
8. P. Boudjouk, B.-H. Han and K.R. Anderson, J. Am. Chem. Soc. **104**, 4992 (1982).
9. S. Masamune, Y. Hanzawa, S. Murakami, T. Bally and J.F. Blount, J. Am. Chem. Soc. **104**, 1150 (1982).
10. M.J. Fink, D.J. De Young, R. West and J. Michl, J. Am. Chem. Soc. **105**, 1070-1071 (1983).
11. M.J. Michalczyk, R. West and J. Michl, J. Am. Chem. Soc. in press.
12. M.J. Fink, M.J. Michalczyk, K.J. Haller, R. West and J. Michl, J. Chem. Soc., Chem. Commun. in press.
13. M.J. Michalczyk, M.J. Fink, R. West, K.J. Haller and J. Michl, unpublished studies.
14. H. Lischka, H.-J. Köhler, Chem. Phys. Lett. **85**, 467 (1982) and references cited therein.
15. A.G. Brook, S.C. Nyburg, F. Ardesakan, B. Gutekunst, G. Gutekunst, R.K.M. R. Kalway, Y.C. Poon, Y.M. Chang and W. Wong-ng, J. Am. Chem. Soc. **104**, 5667 (1982).
16. K.W. Zilm, M.J. Fink, D.M. Grant, R. West and J. Michl, Organometal. **2**, 193-194 (1983).
17. K.W. Zilm, D.M. Grant, R.T. Conlin and J. Michl, J. Am. Chem. Soc. **100**, 8038 (1978); K.W. Zilm, R.T. Conlin, D.M. Grant and J. Michl, ibid. **102**, 6672 (1980).
18. G.C. Levy and J.D. Cargioli in "NMR of Nuclei Other than Protons," T. Axenrod and G.A. Webb (Eds.), Academic Press, New York, 1974, Ch. 17, p. 251; E.A. Williams and J.D. Cargioli in "Annual Reports on NMR Spectroscopy," G.A. Webb (Ed.), Vol. 9, Academic Press, New York, 1979, p. 221.
19. E. Fischer, J. Photochem. **17**, 331 (1981).
20. D.J. De Young and R. West, unpublished studies.
21. M.J. Fink, K.J. Haller, R. West and J. Michl, J. Am. Chem. Soc., in press.