Cyclotrisilanes[†]

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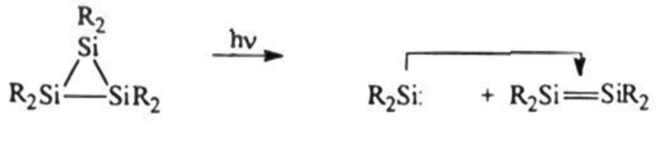
Contents

Manfred Weidenbruch was born in Bremen, Germany, in 1937. He studied chemistry at the Technical University of Aachen and received his Dr. rer. nat. in 1965 under the guidance of Martin Schmeisser. From 1966 to 1973 he worked as senior engineer in the Institute of Inorganic Chemistry in Aachen. In 1971 he finished his habilitation at Aachen Technical University. He joined the Chemistry Department of the University of Oldenburg in 1978, was Head of the Department from 1981 to 1984, and now continues as full Professor of Chemistry. His research interests are in the general field of main-group chemistry, particularly silicon compounds and, more recently, also germanium, tin, and lead compounds with emphasis on synthetic and structural studies.

I. Introduction

Cyclotrisilanes are the smallest, and at the same time, the most recently discovered members of the class of cyclooligosilanes.[1] Although they have been known for hardly more than 10 years, several review articles on the syntheses and reactivity of this compound class have already been published and, of these, the 1991 article by Masamune et al.[1d] on "Strained-Ring and Double-Bond Systems of the Group 14 Elements Si, Ge, and Sn" merits particular emphasis. Interest in cyclotrisilanes is not only directed at their strained ring systems but also at their photolytic fragmentation reactions which can give rise to the stable or marginally stable disilenes.

The synchronous cleavage of two Si–Si bonds in the ring system **A** gives rise to the silylenes **B** and the disilenes **C**. The former species usually undergo subsequent dimerization to **C** and thus increase the yield of the latter species. Hence, this photochemically-induced ring cleavage process provides a second general access to the disilenes **C** as a complementary method to the most frequently employed photolysis of open-chain trisilanes.[2,3]



This review article is concerned with the formation and properties of stable cyclotrisilanes, whereas larger cyclooligosilanes, including polycyclic and polyhedral systems, are discussed by Hengge in this issue.

Characteristic for most cyclotrisilanes are the differing courses of thermally- and photochemically-induced ring cleavage reactions which, when a suitable reaction partner is present, provide an access to disiliranes and trisiletanes—three- and four-membered ring systems each containing one heteroatom. In addition, the silylenes **B** and disilenes **C**, formed by the photolysis of **A**, undergo numerous addition reactions leading to further heterocyclic systems.

Since the addition reactions of silenes as well as silylenes and disilenes originating from other sources are discussed in detail elsewhere in this special issue, they will only be mentioned in exceptional cases in this article to avoid extensive repetitions. Furthermore, the interested reader is referred to the recently published review by Kabe and Ando,[1f] in which, among others, the formation of smaller organosilicon compounds from silylenes, silenes, or disilenes is treated in depth.

II. Formation of Cyclotrisilanes

The first cyclotrisilane **1** was prepared in 10% yield in 1982 by Masamune et al.[4] via reductive

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[†] Dedicated to Professor Peter Paetzold on the occasion of his 60th birthday.

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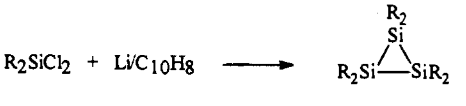
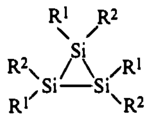
elimination of the halogen from dichlorobis(2,6-dimethylphenyl)silane using lithium naphthalenide.



1, R = $2,6\text{-}Me_2C_6H_3$

The formation of **1** impressively illustrates the conditions required in the thermal equilibrium for the successful preparation of cyclotrisilanes. On the one hand, the small endocyclic angles of 60° create a considerable strain within the three-membered ring while, on the other hand, these small angles allow correspondingly larger exocyclic angles between the bulky substituents and thus reduce the close van der Waals contacts between the hydrogen atoms of neighboring substituents, which are inevitably present in larger ring systems.

The cyclotrisilanes **2**,[5] **3**, and **4**[6,7]—in which the spatial requirements of the substituents at silicon do not differ too greatly from that of the 2,6-dimethylphenyl group—can be prepared analogously.



2, $R^1 = R^2 = 2,6\text{-}Et_2C_6H_3$

3, $R^1 = 2,4,6\text{-}Me_3C_6H_2$; $R^2 = t\text{Bu}$ (*cis-cis*-isomer)

4, $R^1 = 2,4,6\text{-}Me_3C_6H_2$; $R^2 = t\text{Bu}$ (*cis-trans*-isomer)

In some cases it appears to be more favorable to use an alkali or alkaline earth metal in place of lithium naphthalenide for the reductive dechlorination.

$$(Me_3CCH_2)_2SiCl_2 + Li \longrightarrow [(Me_3CCH_2)_2Si]_3 \quad \mathbf{5}^{8}$$

$$R_2SiCl_2 + Mg \longrightarrow (R_2Si)_3 \quad \mathbf{6}^{9}$$

$R = 2\text{-}(Me_2NCH_2)C_6H_4$

The good yield obtained in the formation of **6** from the pentacoordinated dichlorobis[2-[(dimethylamino)-methyl]phenyl]silane[10] is surprising; here, the presence of one alkyl group in an *ortho*-position on the aromatic ring is apparently sufficient to stabilize the three-membered ring system.

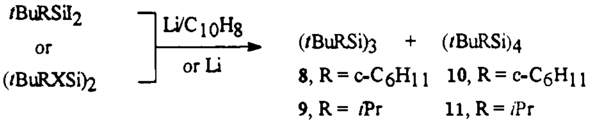
For the preparation of highly-strained cyclotrisilanes, it is advantageous to take advantage of the, in comparison to the Si−Cl bond, markedly lower Si−Br or Si−I bond energies. Thus, for example, the reaction of di-*tert*-butyldichlorosilane with a reducing agent leads only to acyclic silanes,[11,12] while the corresponding reactions of the respective dibromo- or diiodosilanes furnish hexa-*tert*-butylcyclotrisilane (**7**) in good yield.[13]

$$t\text{Bu}_2SiX_2 + Li/C_{10}H_8 \longrightarrow (t\text{Bu}_2Si)_3$$

$X = Br, I$ **7**

Compound **7** is also accessible by ultrasound-induced, reductive elimination of halogen from the dibromo- or diiodosilanes with lithium, whereas the analogous reaction of the dichloro compound leads to hexa-*tert*-butyl-1,3-dihydrocyclotetrasilane.[14]

The interplay between the bulk of the substituents and the ring size in cyclooligosilanes is apparent on going from a *tert*-butyl group to the less sterically demanding isopropyl or cyclohexyl groups since, in the latter cases, thermal equilibria of the three- and four-membered ring products are formed.[15] Further reductions in the steric situation by introduction of a methyl group lead to a distinct predominance of the four-membered ring product in the reaction mixture.[16]



$$\left.\begin{array}{c} t\text{BuRSiI}_2 \\ \text{or} \\ (t\text{BuRXSi})_2 \end{array}\right] \xrightarrow[\text{or Li}]{Li/C_{10}H_8} (t\text{BuRSi})_3 + (t\text{BuRSi})_4$$

8, R = c-C_6H_{11} **10**, R = c-C_6H_{11}

9, R = *i*Pr **11**, R = *i*Pr

When very large substituents are present in the dihalosilanes the three-membered ring product is no longer formed. In these cases, reductive elimination of halogen results in the formation of disilenes, which can formally be considered as two-membered rings. Examples of this situation are provided by the formation of the sterically congested disilenes **12**[17] and **13**[18] as well as the *cis,trans*-isomeric disilenes **14**[19] and **15**.[20]

$$R_2SiI_2 + Li/C_{10}H_8 \longrightarrow R_2Si{=}SiR_2$$

12, $R = CH(SiMe_3)_2$

$$R_2SiCl_2 + Li/C_{10}H_8 \longrightarrow R_2Si{=}SiR_2$$

13, $R = 2,4,6\text{-}i\text{Pr}_3C_6H_2$

$$R^1R^2SiCl_2 + Li/C_{10}H_8 \longrightarrow R^1R^2Si{=}SiR^1R^2$$

(*E*)-, (*Z*)-**14**

$R^1 = CH(SiMe_3)_2$,
$R^2 = 2,4,6\text{-}Me_3C_6H_2$

$$R^1R^2SiBr_2 + Li/C_{10}H_8 \longrightarrow R^1R^2Si{=}SiR^1R^2$$

(*E*)-, (*Z*)-**15**

$R^1 = 2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2$

$R^2 = 2,4,6\text{-}Me_3C_6H_2$

The triethylsilyl group possesses just sufficient bulk for the preferred formation of the three-membered ring; dehalogenation of dibromohexaethyltrisilane furnishes the persilylated cyclotrisilane **16a** in 11% yield.[21] The similarly persilylated cyclotrisilanes **16b** and **16c** are accessible by a similar route comprising reductive coupling of the corresponding dibromosilanes with lithium naphthalenide.

$$(Et_3Si)_2SiBr_2 + Na \longrightarrow [(Et_3Si)_2Si]_3 \quad \mathbf{16a}$$

$$(i\text{Pr}_2MeSi)_2SiBr_2 + Li/C_{10}H_8 \longrightarrow [(i\text{Pr}_2MeSi)_2Si]_3 \quad \mathbf{16b}$$

$$(t\text{BuMe}_2Si)_2SiBr_2 + Li/C_{10}H_8 \longrightarrow [(t\text{BuMe}_2Si)_2Si]_3 \quad \mathbf{16c}$$

In contrast, elimination of halogen from dibromobis-(triisopropylsilyl)silane leads to the tetrasilyldisilene.

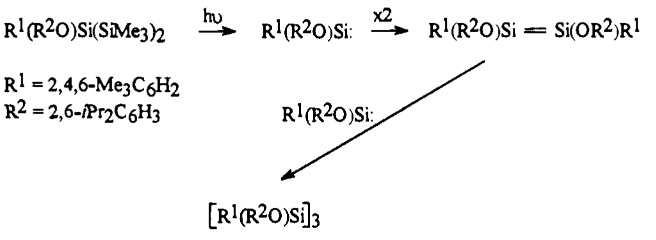
In analogy to compounds **12**–**15**, the steric requirements of the two triisopropylsilyl groups at each silicon atom are probably too large for the reaction to progress from the disilene step to the cyclotrisilane.[22]

Cyclotrisilanes with sterically less demanding groups at the silicon atoms are hardly accessible from dihalomonosilanes. As illustrated by the compounds **17** and **18**, such products can, nevertheless, be obtained in excellent yields outside the constraints of the thermal equilibria by the reductive dehalogenation of hexaalkyl-1,3-dichlorotrisilanes. However, a high degree of experimental expertise and special combinations of reducing agent and solvent are necessary to ensure success in the synthesis of these sensitive cyclotrisilanes.[23]

$$\mathrm{Cl\text{-}(R_2Si)_3\text{-}Cl} \longrightarrow \mathrm{(R_2Si)_3}$$

17, R = *i*Pr
18, R = Et$_2$CH

A further approach to cyclotrisilanes involves their stepwise construction from silylenes. The first oxygen-substituted cyclotrisilane **19** was isolated in 25% yield after photolysis of 2-mesityl-2-(2,6-diisopropylphenoxy)-1,1,1,3,3,3-hexamethyltrisilane; the following reaction sequence provides a plausible rationale for its formation:[24]



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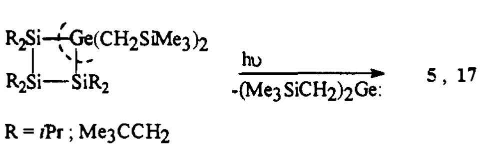
Various photolytic ring-contraction reactions leading to cyclotrisilanes are of more mechanistic than preparative interest. However, the photolyses usually do not stop at the three-membered ring product but ultimately lead to less stable disilenes by a further extrusion of silylene. Thus, for example, the photolysis of octaisopropylcyclotetrasilane proceeds by way of the cyclotrisilane **17**, which can be detected by UV spectroscopy, to tetraisopropyldisilene and subsequent products derived therefrom.[25]

$$(i\mathrm{Pr_2Si})_4 \xrightarrow[-i\mathrm{Pr_2Si:}]{h\nu} \mathbf{17} \xrightarrow[-i\mathrm{Pr_2Si:}]{h\nu} \left\{ i\mathrm{Pr_2Si{=}Si}i\mathrm{Pr_2} \right\}$$

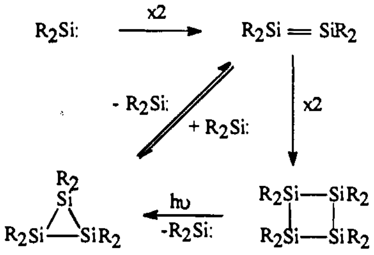
Flash photolysis of nonplanar cyclotetrasilanes also gives rise to cyclotrisilanes, whereas planar cyclotetrasilanes are degraded to disilenes under identical conditions.[26]

Germatrisilacyclobutanes[27] undergo preferential cleavage of germylene to furnish the detectable cyclotrisilanes **5** and **17**.[28,29] This reaction course is not surprising in view of the greater stability of germylenes in comparison to silylenes.

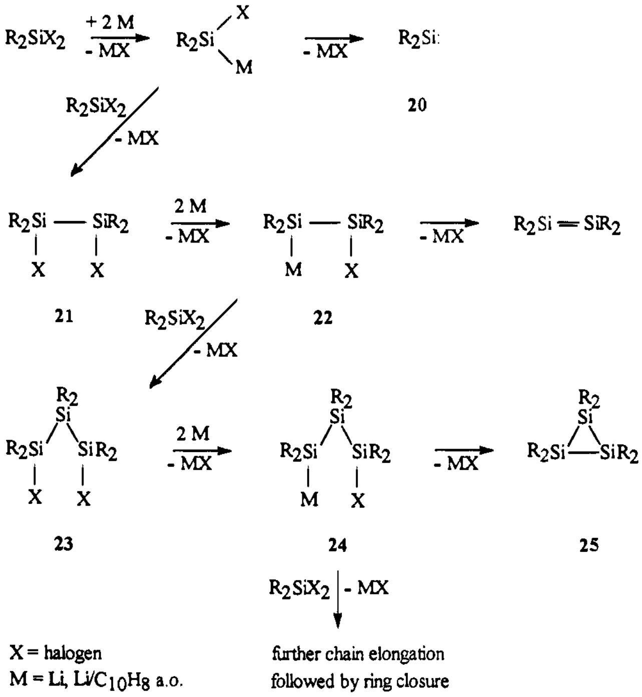


The currently used routes for the synthesis of cyclotrisilanes are summarized in Schemes 1 and 2.

Scheme 1



Scheme 2



Scheme 1 illustrates the stepwise construction of the three-membered ring from photochemically-generated silylenes. Although the dimerization to disilenes[3] and ring contraction steps are well substantiated there is, as yet, no experimental evidence for the [2 + 1]-cycloaddition of silylenes to disilenes or for the [2 + 2]-cycloaddition of two disilene molecules.

The putative steps in the reductive dehalogenations of dihalosilanes and 1,2-dihalodisilanes are illustrated in Scheme 2. This is the most frequently used route for the synthesis of cyclooligosilanes and the individual steps are based on a plausible suggestion by Masamune.[1d]

The reaction sequence is initiated by metalation of an Si–X bond to give the silylenoid which can either furnish the silylene **20** by α-elimination or can react further with the dihalosilane to produce the 1,2-dihalodisilane **21**. Although silylenes of the type **20** having the coordination number 2 and being shielded exclusively by steric factors are still unknown, a thermally-stable silylene[30] was reported very recently and its stability attributed to a combination of steric and electronic effects.

Further metalation of the disilane **21** furnishes the compound **22** which is either converted by β-elimination to a disilene or by reaction with a further molecule of the dihalosilane to the 1,3-dihalotrisilane **23**. Decisive for the choice of reaction route are the steric requirements of the substituent R: in the case of extremely bulky groups the reaction stops at the disilenes, whereas with somewhat less sterically demanding groups, the reaction ultimately yields the target cyclotrisilanes by way of compounds **23** and **24**. On further reductions in size of the substituents, the chain-lengthening reaction continues until a thermal equilibrium of favorable ring sizes for the respective substituent can be obtained by α,ω-elimination.

As demonstrated for compounds **17** and **18**,[23] it is also possible to generate cyclotrisilanes outside of the constraints of the thermal equilibrium. Starting from trisilanes of the type **23**, the three-membered ring compounds **25** are accessible by way of the metalated derivatives **24** since the possible alternative formation of six-membered ring or acyclic products can be excluded in the case of medium-sized substituents such as Pr^i or Et_2CH.

III. Molecular Structures and Physical Properties of Cyclotrisilanes

To date, crystal structure analyses of eight cyclotrisilanes have been reported; the most important structural data are summarized in Table 1. Both the Si–Si bond lengths and the endocyclic angles reveal the presence of equal-sided and isosceles triangles with, at most, very slight deviations from equality. Exceptions are the *cis,trans*-isomeric compounds **4** and **19** which exhibit a marked asymmetry in their structures as a result of the two different substituents at each silicon atom. However, it is interesting to note that the analogous *cis,trans*-compound **8** has, within the limits of experimental error, an equilateral triangular structure.

In comparison to the normal length of 234 pm, the Si–Si bonds in all the cyclotrisilanes are more or less markedly lengthened. As to be expected, the bond length increases in **6** are the smallest since here the aryl groups each possess only one *ortho*-substituent and the donor atoms of the dimethylamino groups are oriented away from the silicon atoms. While the values for the remaining cyclotrisilanes are in the order of 240 pm, the Si–Si bond lengths of compound **7** with 251.1 pm are clearly longer.

The weakening of the Si–Si bonds associated with the increases in length is also reflected in the electronic spectra of the compounds as a pronounced red shift of the absorption bands at longest wavelength with increasing steric demands of the substituent does occur. However, only alkyl-substituted compounds should be compared directly since the aryl substituents can cause a pronounced per-

Table 1. Bond Lengths (pm) and Bond Angles (deg) in Cyclotrisilanes $(R^1R^2Si)_3$

compd	R^1	R^2	d(Si–Si)	∠SiSiSi	ref
6[a]	$R^1 = R^2 = 2\text{-}(Me_2NCH_2)C_6H_4$		235.2; 237.2; 236.8 236.4; 235.6; 235.7	60.2; 59.5; 60.2 59.9; 60.2; 59.9	31a
5[a]	Me_3CCH_2	Me_3CCH_2	238.7; 236.7; 236.7 241.4; 237.8; 237.8	59.5; 60.3; 60.3 59.0; 60.5; 60.5	32
cis,trans-**19**	$2,4,6\text{-}Me_3C_6H_2$	$2,6\text{-}iPr_2C_6H_3O$	234.2; 238.0; 240.7	58.6; 60.1; 61.3	24
1	$2,6\text{-}Me_2C_6H_3$	$2,6\text{-}Me_2C_6H_3$	237.5; 242.2; 242.2	58.7; 60.7; 60.6	4
cis,trans-**4**	*t*Bu	$2,4,6\text{-}Me_3C_6H_2$	239.5; 241.3; 244.1	59.1; 59.8; 61.0	7
cis,trans-**8**	*t*Bu	$c\text{-}C_6H_{11}$	241.9; 242.2; 242.2	60.0; 60.0; 60.0	15
cis,trans-3	*t*Bu	$2,4,6\text{-}Me_3C_6H_2$	242.5; 242.8; 243.1	60.1; 60.1; 59.9	7
7	*t*Bu	*t*Bu	251.1; 251.1; 251.1	60.0; 60.0; 60.0	13

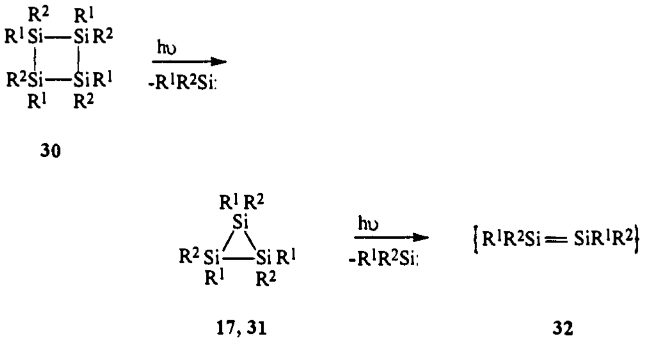
[a] The asymmetric unit contains two crystallographic independent molecules.

Table 2. Electronic Absorptions and ^{29}Si Chemical Shifts of Cyclotrisilanes $(R^1R^2Si)_3$

compd	R^1	R^2	λ_{max}, nm (log ϵ)	$\delta(^{29}Si)$	ref(s)
17	*i*Pr	*i*Pr	299 (sh, 2.5), 323 (sh, 2.4)		33
8	$c\text{-}C_6H_{11}$	*t*Bu	301 (2.8), 322 (2.7)		15
9	*i*Pr	*t*Bu	301 (2.7), 322 (2.6)		15
18	Et_2CH	Et_2CH	304 (2.4), 328 (2.5)		23
7	*t*Bu	*t*Bu	360 (sh, 2.7), 387 (2.8)	−4.0	13, 15
5	Me_3CCH_2	Me_3CCH_2	310 (2.5)	−81.68	8
1	$2,6\text{-}Me_2C_6H_3$	$2,6\text{-}Me_2C_6H_3$	260 (4.6), 344 (sh, 3.0)		4
26	$2,4,6\text{-}Me_3C_6H_2$	$2,4,6\text{-}Me_3C_6H_2$	262 (4.7), 348 (sh, 3.0)		33
2	$2,6\text{-}Et_2C_6H_3$	$2,6\text{-}Et_2C_6H_3$	353 (2.6), 387 (2.5)	−50.8	5, 34
cis,cis-**27**	$2,6\text{-}Et_2C_6H_3$	$2,4,6\text{-}Me_3C_6H_2$	351 (2.9), 380 (2.8)	−52.69	35
cis,trans-**28**	$2,6\text{-}Et_2C_6H_3$	$2,4,6\text{-}Me_3C_6H_2$	329 (2.6), 382 (2.4)		35
cis,trans-**29**	*t*Bu	C_6H_5		−33.42, −37.33	36
cis,trans-**4**	*t*Bu	$2,4,6\text{-}Me_3C_6H_2$	334 (3.0), 363 (3.0)		6
cis,cis-3	*t*Bu	$2,4,6\text{-}Me_3C_6H_2$	379 (2.7), 412 (2.7)		6
16	Et_3Si	Et_3Si	335 (3.1)	−174.38	21
cis,trans-**19**	$2,4,6\text{-}Me_3C_6H_2$	$2,6\text{-}iPr_2C_6H_3O$	353, 380	+7.32, +7.34	24
6	$R^1 = R^2 = 2\text{-}(Me_2NCH_2)C_6H_4$		368 (3.4)	−64.65	9, 31b

turbation of the electronic structure. The influence on the transition energy is most apparent in **19** since this is the only cyclotrisilane known to date with a donor atom attached directly to each silicon atom (Table 2).

In the series of cyclooligosilanes, a marked bathochromic effect can be observed with decreasing ring size. Thus, for example, the three-membered ring compounds **8** and **9** have lower transition energies than the four-membered ring compounds **10** and **11** with the same substituent patterns.[15] A similar trend can be deduced from the photolytic degradation of the cyclotetrasilanes **30** which proceeds by way of **17** and **31** as well as other transient cyclotrisilanes, which are unstable under the photolysis conditions, to the similarly unstable disilenes **32** and their subsequent products. A stepwise red shift of the absorption bands at longest wavelength is observed on going from **30** via **31** to **32**; these bands occur between 300 and 330 nm for the cyclotrisilanes **17** and **31**, and between 390 and 400 nm for the disilenes **32**.[25]



30

17, 31

32

a : $R^1 = R^2 = i\text{Pr}$
b : $R^1 = \text{Me}, R^2 = t\text{Bu}$
c : $R^1 = R^2 = i\text{Bu}$
d : $R^1 = R^2 = Me_3SiCH_2$

In spite of the—sometimes—considerable lengthening of the Si−Si bonds, the ^{29}Si nuclei in the cyclotrisilanes are rather well shielded (Table 2). The ^{29}Si-NMR signals for the alkyl- and aryl-substituted cyclotrisilanes appear in the range −4 to −82 ppm while that for the persilylated cyclotrisilane **16** occurs at −174 ppm. Only in the case of *cis,trans*-**19** is a slight deshielding noticeable, presumably as a consequence of the Si−O bonds.

Two ^{29}Si-NMR resonances are observed for *cis,trans*-**19** and *cis,trans*-**29**, presumably resulting from the asymmetry of the rings; in the case of **29** it was thus possible to determine the $^1J(^{29}Si,^{29}Si)$ coupling constant as 24.1 Hz. This is only about half as large as the ^1J values of the unstrained oligosilanes which are in the range 50−80 Hz,[37] and thus apparently reflects the low s character of the s bonds within the Si_3 skeleton.

In contrast, CPMAS (cross-polarization magic-angle spinning) ^{29}Si-NMR investigations on the cyclotrisilanes **7** and **26**, as well as tetramesityloxadisilirane (**98**), reveal unusually large chemical shift anisotropies,[38] which are about three times as large as that for the cyclohexasilane $(MePhSi)_6$, and are similar to the values for tetramesityldisilene.[39] The values for **7** are 90, −7, and −97 ppm and the corresponding data for **26** can be taken from Figure 1.

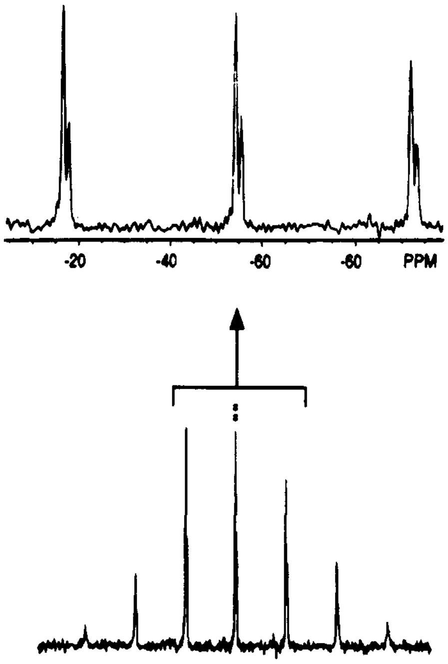
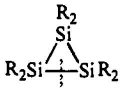


Figure 1. (a) Center portion of the ^{29}Si MAS spectrum of hexamesitylcyclotrisilane (**26**) and (b) ^{29}Si-MAS spectrum of **26** at 2.34 T. The asterisks (**) mark the isotropic shifts. (Reprinted from ref 38. Copyright 1993 American Chemical Society).

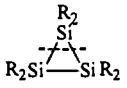
It may prove possible to resolve the contradiction between the observed small $^1J(^{29}Si,^{29}Si)$ coupling constants and the large chemical shift anisotropies, the latter having a spread that is typical for disilenes with their large $^1J(^{29}Si,^{29}Si)$ coupling constants of 155−160 Hz,[40,41] by means of suitable *ab initio* calculations. In a very recent paper, it is suggested that these large chemical shift anisotropies for cyclotrisilanes reflect paramagnetic deshielding due to the low $\sigma-\pi^*$ excitation energies in these rings.[38b]

IV. Chemical Properties of Cyclotrisilanes

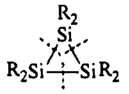
The usually high ring strain of the Si_3 skeletons is the reason why practically all of the known reactions of the cyclotrisilanes are initiated by Si−Si bond cleavage. Since three Si−Si bonds are present, the three reaction possibilities illustrated by the formulae **D**, **E**, and **F** should be realizable.



D



E



F

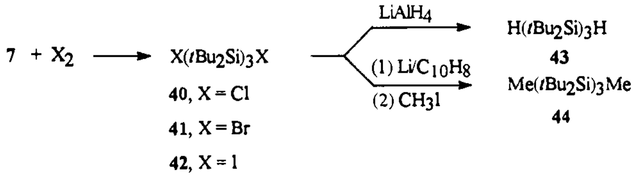
In the following sections, reactions initiated by the cleavage of one or two Si−Si bonds will be discussed.[42] In addition, the recently demonstrated cleavage of all three Si−Si bonds will be mentioned.

A. Reactions with Cleavage of One Si−Si Bond

In the absence of light or a catalyst, cyclotrisilanes react to give either acyclic trisilanes or products of ring expansion, depending on the nature of the reaction partner. Although this would provide a simple route to sterically stressed trisilanes or trisiletanes, only few reactions with chalcogens, halogens, and isocyanides have been reported to date. Most of these investigations started with the cyclotrisilane **7** which appears to be predestined for such ring cleavage reactions on account of its large Si–Si bond lengths.

1. Formation of Acyclic Trisilanes

The reaction of the heavier halogens with **7** gives rise to the hexa-*tert*-butyl-1,3-dihalotrisilanes **40**–**42** which are converted to the 1,3-dihydro derivative **43** upon treatment with lithium aluminum hydride.[43]



$$42 + LiCH_3 \longrightarrow Li(tBu_2Si)_3I \xrightarrow[-\,LiI]{} 7$$

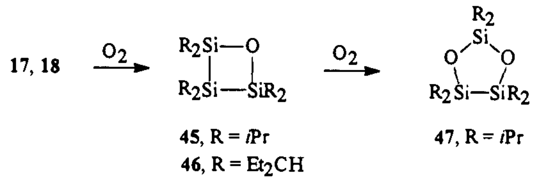
Attempts to metalate **42** with methyllithium and to convert the resultant derivative to the 1,3-dimethyl compound **44** by treatment with iodomethane surprisingly resulted in the re-formation of the cyclotrisilane **7**.[43] Since the formation of the three-membered ring apparently proceeds more rapidly than the dimetalation, this result may be considered as further evidence in favor of the mechanism for the formation of cyclotrisilanes illustrated in Scheme 2.

On the other hand, **44** is readily accessible from the reaction of **42** with lithium naphthalenide at low temperature and subsequent treatment with iodomethane.[44] The steric overload in the acyclic trisilanes **40**–**44** is apparent from the Si–Si bond lengths of 258.1 and 264.4 pm for **42**[45] and 259.3 pm for **44**;[44] these values are markedly larger even than those for **7** and approach the value of 269.7 for hexa-*tert*-butyldisilane,[46] the largest Si–Si bond length observed in a discrete molecule to date. At the same time, these values suggest that the actual bond lengths in **7** and other cyclotrisilanes may actually be longer than the measured values. For example, Si–Si separations of 265 pm can be calculated for **7** under the assumption of arched bonds![45]

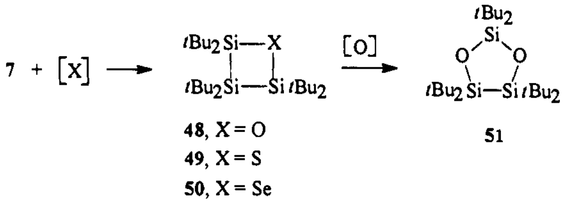
Other cyclotrisilanes can also be converted into acyclic trisilanes analogously. Thus, a kinetic investigation of the cleavage of variously sized cyclooligosilanes with iodine revealed that, in accord with the increase in ring strain energy with decreasing ring size, the reaction of **5** proceeds very rapidly and that the rate can no longer be measured by the usual methods.[47,48]

2. Formation of Trisiletanes

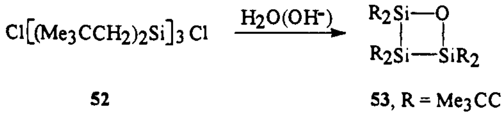
Although most cyclotrisilanes are not sensitive to atmospheric oxygen, the sterically less shielded compounds **17** and **18** are smoothly converted to the oxatrisiletanes **45** and **46** and the 1,3-dioxatrisilolane **47**.[23]



Compound **7** reacts similarly to **17** and furnishes the oxatrisiletane **48** and the 1,3-dioxatrisilolane **51** on treatment with oxygen or dimethyl sulfoxide (DMSO). Vigorous oxidation with 3-chloroperoxybenzoic acid (*m*-CPBA) leads ultimately to hexa-*tert*-butylcyclotrisiloxane. Only the monoinsertion products **49** and **50** are obtained on reaction with elemental sulfur or selenium.[49] The large reductive ability of the Si–Si bonds in **7** is reflected in its reactions with carbon dioxide and carbon disulfide which smoothly give rise to **51** and **49**, respectively.[50]

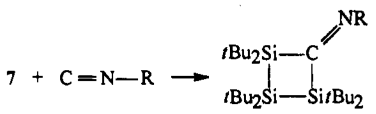


Oxatrisiletanes are not only accessible by ring expansion reactions of cyclotrisilanes but also by alkaline hydrolysis of 1,3-dichlorotrisilanes. Thus, for example, **52** furnishes the four-membered ring system **53** in very good yield.[51]



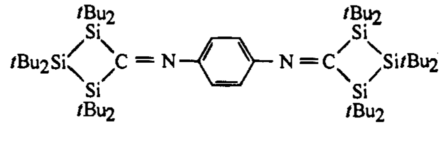
Although the high energies of the silicon–chalcogen bonds and, above all, the formation of disiloxanes should favor the formation of five- and six-membered rings, the latter is counteracted by the widening of the Si–Si–Si angle and the accordingly increased interactions between the hydrogen atoms of the neighboring, mostly bulky substituents. Thus, an X-ray crystallographic analysis of the almost planar four-membered ring of **53** reveals markedly stretched Si–Si bond lengths in spite of an only slight angle widening from about 60° in the corresponding three-membered ring product **5** to 68° in **53**.[51]

The increased lability of the formed four-membered ring can be seen even more clearly in insertion reactions into the cyclotrisilane **7**, which has the most highly strained three-membered ring of this type not only on account of the Si–Si bond distances[13] but also because of the electrochemically-determined oxidation potential.[52] Reactions of **7** with various aryl isocyanides which, like the chalcogen atoms themselves, can be formally considered as electron sextet molecules, smoothly give rise to the red- to violet-colored trisilacyclobutanimines **54**–**59**.[53,54]



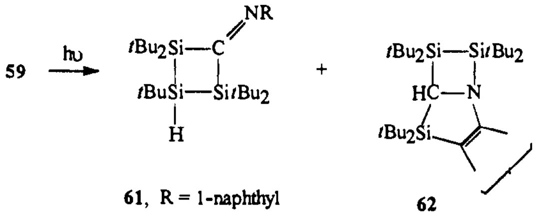
54, R = Ph
55, R = 4-NO$_2$C$_6$H$_4$
56, R = 4-CNC$_6$H$_4$
57, R = 2,4,6-Me$_3$C$_6$H$_2$
58, R = 2,6-*i*Pr$_2$C$_6$H$_3$
59, R = 1-Naphthyl

Further reaction of **7** with **56** yields the double insertion product **60**; an X-ray crystallographic analysis of **60** reveals a widening of the Si–Si–Si angle from 60° to almost 80°; a similar result was also observed for **58**.[53,54]



60

As a consequence of this angle widening and the resultant strong interactions between the hydrogen atoms of neighboring *tert*-butyl groups, the compounds **54**–**60** are unstable toward the action of light. On exposure to daylight slow and upon irradiation rapid, decomposition reactions or rearrangements to compounds of the types **61** and **62** occur.[54]



61, R = 1-naphthyl **62**

Compound **64**, which is formed from the acylsilane **63** and triethylgermyllithium possibly by a [2 + 2]-cycloaddition of disilene and silene intermediates, also has the trisilacyclobutane skeleton with a widened Si–Si–Si angle of 77°.[55]

63, Ad = 1-adamantyl **64**

Reductive couplings of the trisilanes **65** and **66** with the dichlorogermane **67** give rise to the germatrisiletanes **68** and **69** which undergo extrusion of germylene under photolysis conditions and thus open a possible access to cyclotrisilanes (*vide supra*).[29]

$$\mathrm{Cl(R_2Si)_3Cl + (Me_3SiCH_2)_2GeCl_2 \xrightarrow{Li} (R_2Si)_3Ge(CH_2SiMe_3)_2}$$

65, R = *i*Pr **67** **68**, R = *i*Pr
66, R = Me$_3$CCH$_2$ **69**, R = Me$_3$CCH$_2$

Both **68** and **69** possess folded four-membered rings with the smallest endocyclic angle at the respective germanium atom.

B. Reactions with Cleavage of Two Si–Si Bonds

Not only cyclotrisilanes containing at least one aryl group on each silicon atom[3] but also some persilylated three-membered ring derivatives are cleaved by photolysis into disilenes and silylenes with the respective silylene undergoing dimerization to furnish more disilene. Stable tetraalkyldisilenes cannot be prepared in this way. Thus, although photolysis of **7** proceeds through cleavage of two Si–Si bonds with formation of disilene and silylene, the two species initially remain together in the form of an adduct and can only be separated when suitable trapping reactions are possible. The cyclotrisilane **6** also behaves abnormally: under thermal conditions all Si–Si bonds are cleaved to furnish the silylene exclusively. Because of these peculiarities, the ring cleavage reactions of **6** and **7** are discussed in separate sections.

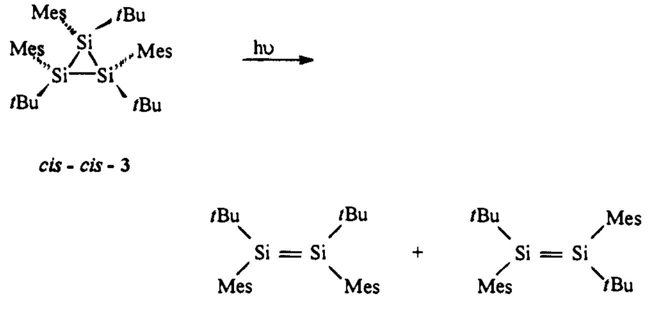
1. Formation of Disilenes

Concomitantly with the original synthesis of **1**, the first cyclotrisilane to be isolated, Masamune et al.[4] reported its photolysis which gave rise to the disilene **70** in almost quantitative yield. Since **70** could not be obtained in a crystalline form suitable for structure determination, the 2,6-diethylphenyl-substituted compound **2** was prepared analogously; light-induced cleavage of the latter yielded >50% of the disilene **71** which possesses an Si–Si bond length of 214.8 pm in the typical range for a tetraaryldisilene.[5]

$$\mathbf{1, 2} \xrightarrow{h\nu} \mathrm{R_2Si\!: + R_2Si=SiR_2}$$

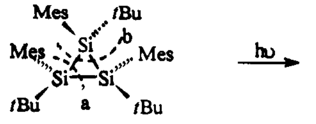
70, R = 2,6-Me$_2$C$_6$H$_3$
71, R = 2,6-Et$_2$C$_6$H$_3$

Information on the photolysis process is provided by the cleavage reactions of the *cis,cis*- and *cis,trans*-isomeric cyclotrisilanes (R^{1}R^{2}Si)$_3$. Thus, photolysis of *cis,cis*-**3** gives the (*Z*)- and (*E*)-isomeric disilenes **72** and **73** in a ratio of 7.1:1 which is indicative of retention of configuration during the reaction. The concomitant formation of the (*E*)-isomer can be attributed to the two possibilities for the dimerization of *tert*-butyl(mesityl)silylene which can give rise to both **72** and **73**.[6]



cis - *cis* - **3**

(*Z*) - **72** (*E*) - **73**



(*Z*) - **72** + (*E*) - **73**
0.38 : 1

cis - *trans* - **4**

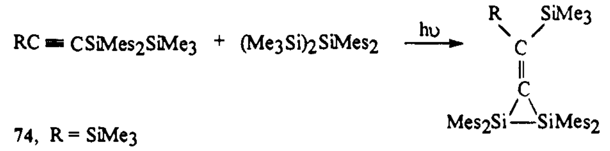
The product distribution from the photolysis of the *cis,trans*-compound **4** clearly indicates that pathway a is preferred over pathway b.[6]

It was recently shown that the synthesis of stable disilenes by photolysis of cyclotrisilanes is not limited to the aryl derivatives but may also be applied with success to persilylated three-membered ring derivatives. Thus, for example, irradiation of **16b** and **16c** gave rise to the unambiguously characterized compounds tetrakis(diisopropylmethylsilyl)disilene and tetrakis(*tert*-butyldimethylsilyl)disilene. These persilylated disilenes, as well as tetrakis(triisopropylsilyl)disilene accessible from the respective dibromosilane, exhibit unexpectedly large Si=Si bond lengths of 220–225 pm.[22]

2. Formation of Disiliranes

Disiliranes, three-membered ring compounds with two silicon atoms and one heteroatom in the ring, are derived from cyclotrisilanes by the formal replacement of one SiR_2 group by a heteroatom. The discovery of thermally stable disilenes also helped the disiliranes to an unforeseen boom since many of them are accessible by simple addition or [2 + 1]-cycloaddition reactions at the Si=Si double bond. However, the unusual structural parameters of some compounds also posed the question as to the nature of the chemical bonds within these three-membered rings. Synthetic methods, selected structural parameters, and suggestions for the chemical bonds of disiliranes are summarized in this section.

The first disilacyclopropanes **76** and **77** were obtained by concomitant photolysis of the ethynyldisilanes **74** and **75** with 2,2-dimesitylhexamethyltrisilane and the structure of **77** was elucidated. The more probable reaction route to this three-membered ring system comprises the [2 + 1]-cycloaddition of dimesitylsilylene to an intermediarily formed 1-silapropadiene.[56,57]

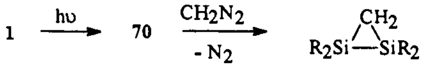


74, R = SiMe$_3$

75, R = Ph

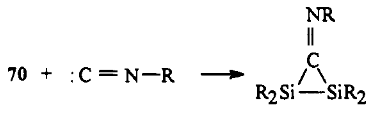
76, R = SiMe$_3$, 77, R = Ph

The disilacyclopropane **78** can be prepared by addition of diazomethane to the disilene **70**, generated photolytically from the cyclotrisilane **1**.[58] However, it could not be clarified whether the cleavage of nitrogen occurred before the addition or whether an initial [2 + 3]-cycloaddition was followed by elimination of nitrogen.



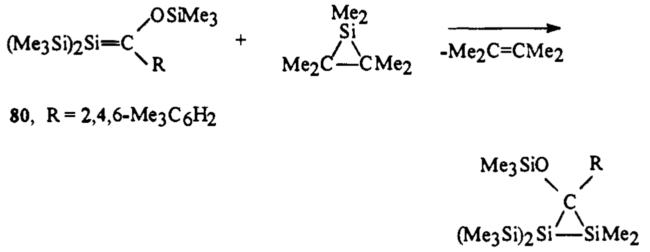
78, R = 2,6-Me$_2$C$_6$H$_3$

The reaction of **70** with 2,6-dimethylphenyl isocyanide proceeds similarly and gives rise to the yellow-colored disilacyclopropanimine **79**.[59]



79, R = 2,6-Me$_2$C$_6$H$_3$

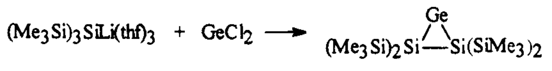
A further disilacyclopropane is the compound **81** formed from the silene **80** and hexamethylsilirane;[60,61] however, **81** readily undergoes rearrangement reactions.[62]



80, R = 2,4,6-Me$_3$C$_6$H$_2$

81

The first germadisilirane, **83**, was the surprising result isolated from the reaction of the silyllithium compound **82** with germanium(II) chloride.[63]

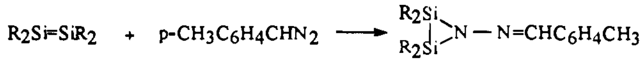


82

83

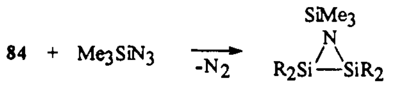
Hexamesitylsiladigermirane, possessing a three-membered ring composed of one silicon atom and two germanium atoms, is also known. Photolysis of this compound gives rise to dimesitylgermylene and a relatively stable germasilene, a molecule containing a formal Ge=Si bond.[64,65] Trapping reactions with triethylsilane, however, clearly demonstrated that this germasilene is readily converted via 1,2-mesityl shift to a silyl-substituted germylene, identified by way of subsequent reactions with the Si–H bond of triethylsilane.[66]

In contrast to diazomethane which reacts with **70** to furnish the disilirane **78**, the analogous reaction of **84** with the diazo compound **85** furnishes the azadisilirane **86**.[67]



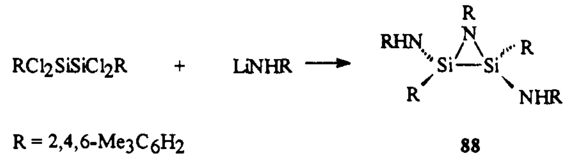
84, R = 2,4,6-Me$_3$C$_6$H$_2$ 85 86

The reactions of **84** with azides similarly give rise to different results: with aryl azides disilatriazolines are formed while alkyl azides furnish [2 + 1]-cycloadducts. On heating, both classes of compounds undergo elimination of nitrogen to furnish azadisiliranes (disilaazirines). The reaction with trimethylsilyl azide yields product **87** directly without isolation of an intermediate.[68]

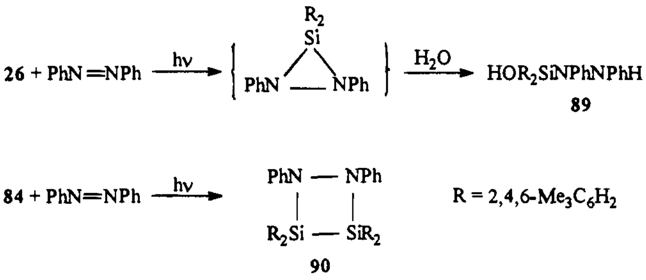


87, R = 2,4,6-Me$_3$C$_6$H$_2$

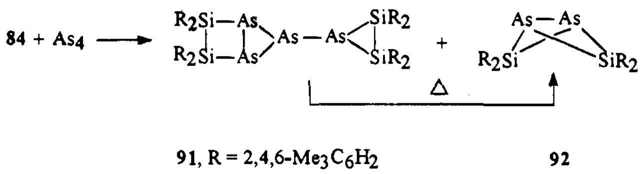
The reaction of tetrachloro-1,2-dimesityldisilane with lithium mesitylamide is also unusual in that the azadisilirane **88** is isolated together with *cis*- and *trans*-cyclodisilazanes.[69]



Photolysis of hexamesitylcyclotrisilane (**26**) in the presence of azobenzene does not proceed by way of the expected [2 + 2]-cycloaddition of **84** to the N=N double bond but rather through a putative diazasilacyclopropane derivative and its reaction with water since the silanol **89** is isolated as the main product. On the other hand, a reaction sequence comprising the initial formation of the disilene **84** from the cyclotrisilane **26** and reaction of the former with azobenzene should proceed smoothly to furnish the target 1,2-diaza-3,4-disilacyclobutane **90**.[70]

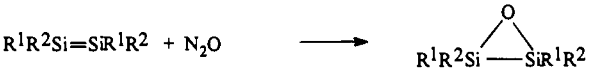


The action of white phosphorus on the disilene **84** yields a 1,3-diphospha-2,4-disilabicyclo[1.1.0]butane derivative through cleavage of both Si–Si bonds,[71] whereas the analogous reaction with arsenic gives, in addition to the corresponding 1,3-diarsa compound **92**, the tricyclic product **91** containing, among others, an arsadisilirane ring.[72]

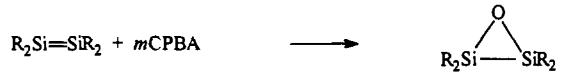


Disiliranes with elements of the sixth main group are mostly accessible by simple reaction of disilenes with the respective element. This method is less advantageous in the case of triplet oxygen since the main products of the reaction are the 1,2-disiladioxetanes **93**, which undergo rearrangements with retention of configuration to the 1,3-cyclodisiloxanes **95**. The concomitantly formed disilaoxirane byproducts **94** are also easily transformed into **95** in the presence of oxygen[73] (Scheme 3).

The disilaoxiranes **94** are available from the corresponding disilenes without the formation of byproducts when dinitrogen monoxide is used as the one-atom source.[74,79] The sterically more encumbered tetrakis(2,4,6-triisopropylphenyl)disilene and tetrakis(2,6-diisopropylphenyl)disilene, however, do not react with dinitrogen monoxide. This suggests that the reaction of, e.g., **84** with dinitrogen monoxide is a [3 + 2]-cycloaddition followed by loss of nitrogen and ring closure. Owing to the increased steric bulk of the 2,6-diisopropylphenyl- and 2,4,6-triisopropylphenyl-substituted disilenes, the [3 + 2] approach of dinitrogen monoxide to the silicon–silicon double bond is less favored. However, with *m*CPBA the disilaoxiranes **94f** and **94g** are smoothly obtained.[75,79]



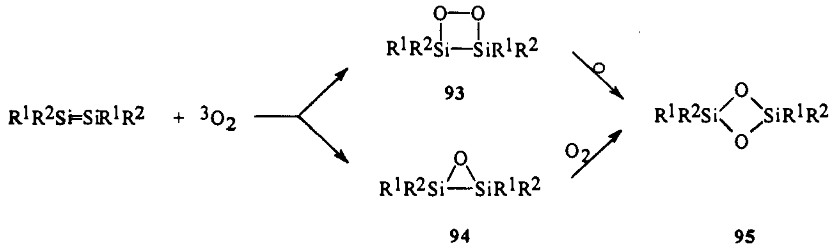
$R^1 = R^2 = 2,6\text{-}Me_2C_6H_3$ (70)	94a
$R^1 = R^2 = 2,4,6\text{-}Me_3C_6H_2$ (84)	94b
$R^1 = R^2 = 2,6\text{-}Et_2C_6H_3$ (71)	94c
$R^1 = R^2 = 2,6\text{-}Me_2\text{-}4\text{-}t BuC_6H_3$	94d
$R^1 = 2,6\text{-}Et_2C_6H_3$; $R^2 = 2,6\text{-}Et_2\text{-}4\text{-}t BuC_6H_2$	*cis*-94e, *trans*-94e

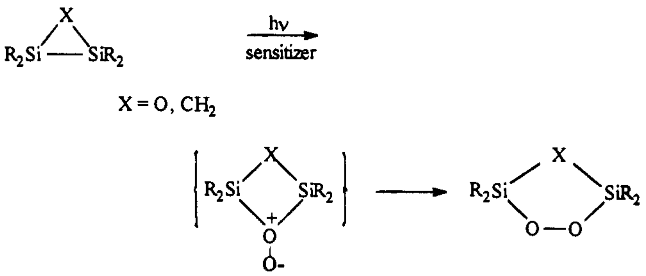


R = 2,4,6-$i Pr_3C_6H_2$ (13)	94f
R = 2,6-$i Pr_2C_6H_3$	94g

The Si–Si bond in the silaoxiranes **94**, as well as that in hexamesityldisilirane, has proved to be a good electron donor toward singlet oxygen. Thus, photooxygenation of these molecules in the presence of a sensitizer result in the formation of the 1,2,3,5-dioxadisilolanes and 1,2,4,3,5-trioxadisilolanes **97**, presumably through the *exo*-peroxide intermediate **96**.[76-80]

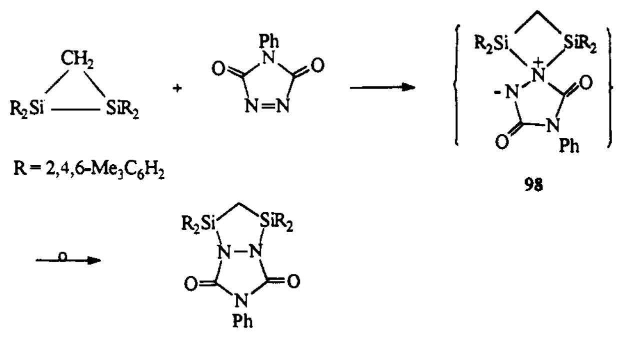
Scheme 3





96 97

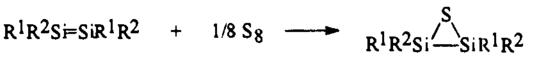
Indirect evidence for the course of the photooxygenation is provided by the reaction of tetramesityldisilirane with 4-phenyl-1,2,4-triazoline-3,5-dione. Low-temperature NMR spectroscopic studies have demonstrated that this reaction proceeds through the detectable azetidinium imide **98** and finally yields the 1,2,3,5-diazadisilolidene derivative **99** as product.[81]



98

99

The reactions of the disilenes **84** and **100** with sulfur proceed more simply than those with oxygen: even in the presence of a large excess of sulfur the disilathiiranes **101** and **102** are formed exclusively.[82] A second approach to **101** is provided by the reaction of **84** with cyclohexene sulfide which also smoothly leads to the three-membered ring product.[83]



$R^1R^2Si{=}SiR^1R^2 + 1/8\ S_8 \longrightarrow R^1R^2Si(S)SiR^1R^2$

84 101

100, $R^1 = 2,4,6\text{-}Me_3C_6H_2$, $R^2 = t\text{Bu}$ 102

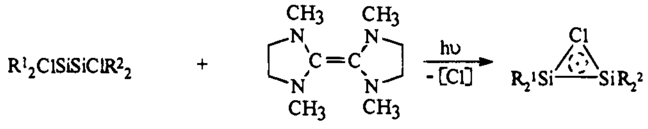
Like sulfur, selenium and tellurium also react with the disilene **84** to yield the disilaselenirane **103** and the disilatellurirane **104**, respectively.[84]

$84 + E \longrightarrow R_2Si(E)SiR_2$

103, E = Se

104, E = Te

The chlorine-bridged, neutral radicals **108** and **109** belong formally to the series of disiliranes; these products are obtained by elimination of chlorine from the dichlorodisilanes **105** and **106** with the electron-rich olefins **107**; their constitutions were substantiated by EPR spectroscopy.[85,86]

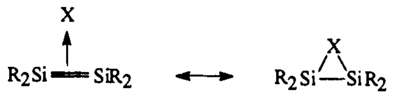


105, $R^1 = R^2 = 2,4,6\text{-}Me_3C_6H_2$ 108

106, $R^1 = 2,4,6\text{-}Me_3C_6H_2$, $R^2 = t\text{Bu}$ 107 109

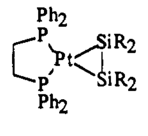
The structures of the disiliranes (Table 3), especially those containing heteroatoms that are both electronegative and relatively small, exhibit some special features.

In spite of the presence of the usually bulky substituents at the silicon atoms, some of the Si–Si bond lengths are dramatically shortened in comparison to the normal value of approximately 234 pm. Thus, the disiliranes differ markedly from the cyclotrisilanes (Table 1) which all possess lengthened Si–Si bonds. This bond shortening is accompanied by a planar or almost planar arrangement of the two *ipso* carbon atoms and the second silicon atom about each silicon atom. Such a geometric arrangement resembles the bonding situation in transition metal–olefin complexes which, according to the model of Dewar and Chatt and Duncanson,[87,88] exist in a continuum between three-membered rings and π-complexes. In harmony with this model, short Si–Si bond lengths and an almost planar environment of the silicon atoms should reflect the bonding state of **110** while longer Si–Si bonds and a pyramidalization of the substituents represent more the classical three-membered ring structure **111**.



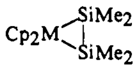
110 111

Indirect evidence for the validity of this assumption is provided by the recently discovered disilene complexes of transition metals such as, for example, the platinum complexes **112** and **113**[89] or the molybdenum and tungsten complexes **114** and **115**.[90]



112, R = *i*Pr

113, R = Ph



114, M = Mo

115, M = W

The short Si–Si separation in **115** (Table 3) is indicative of a partial double-bond character; however, the silicon atoms in this complex exhibit a more pronounced pyramidalization than disiliranes with comparable bond lengths.[90] Irrespective of whether

Table 3. Selected Structural Parameters for the Disiliranes $(R^1R^2Si)_2X$

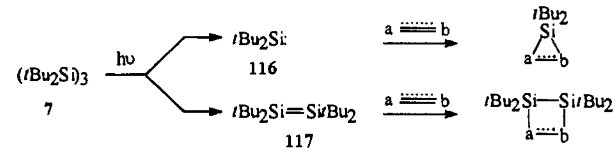
compd	R^1	R^2	X	d(Si–Si), pm	$\Sigma\angle$,[a] deg	ref
77	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$	C=C<	232.7		56
78	2,6-$Me_2C_6H_3$	2,6-$Me_2C_6H_3$	CH_2	227.2	357.5	58
79	2,6-$Me_2C_6H_3$	2,6-$Me_2C_6H_3$	C=NR	232.8		59
83	Me_3Si	Me_3Si	$Ge(SiMe_3)_2$	237.7(14)		63
87	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$	$NSiMe_3$	223.2	358.0	68
88	2,4,6-$Me_3C_6H_2$	NH-2,4,6-$Me_3C_6H_2$	NR	228.8	359.4	69
91	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$	As-As<	231.5		72
94b	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$	O	222.7	360	74
trans-**94e**	2,6-$Et_2C_6H_3$	2,6-Et_2-4-*t*BuC_6H_2	O	221.4	359.8	79
94f	2,4,6-*i*$Pr_3C_6H_2$	2,4,6-*i*$Pr_3C_6H_2$	O	225.4	359.7	75
101	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$	S	228.9	357.4	82
103	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$	Se	230.3	355.8[b]	84
104	2,4,6-$Me_3C_6H_2$	2,4,6-$Me_3C_6H_2$	Te	233.7	355.5[b]	84
115	Me	Me	Wcp_2	226.0	348.3	90

[a] $\Sigma\angle = R^1{-}Si{-}R^2 + R^1{-}Si{-}Si + R^2{-}Si{-}Si$. [b] Average value.

the bond situation in the disiliranes is best represented by a partial π-complex character,[91,92] as indicated in **110**, or rather by an extremely arched Si–Si bond,[93] the disiliranes constitute an interesting class of compounds with unusual properties.

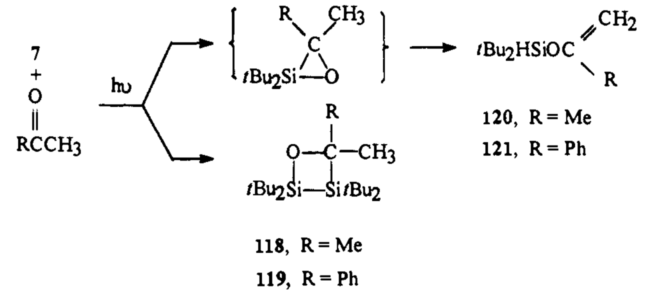
C. Photolyses of Hexa-*tert*-butylcyclotrisilane

Similar to the photolyses of aryl-substituted cyclotrisilanes, irradiation of hexa-*tert*-butylcyclotrisilane (**7**) leads to the silylene **116** and the disilene **117** under simultaneous cleavage of two Si–Si bonds. However, while the aryl-substituted silylenes undergo dimerization to furnish further disilene, the short-lived silylene **116** and the disilene **117**, which is stable for a few hours,[11,94] remain together in the form of a cage[95] and only separate when appropriate trapping reagents are available.



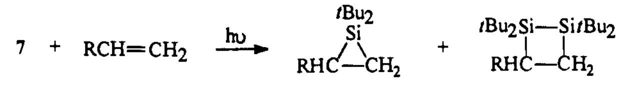
The formation of two reactive intermediates in the photolysis of **7** offers the advantage that most trapping reactions with unsaturated compounds produce at least one isolable product. On the other hand, it cannot always be distinguished unequivocally if the product obtained is formed by a single addition of **117** or by a 2-fold addition of **116**. In spite of these occasional uncertainties, both **116** and **117** possess a high synthetic potential that has already led to a series of novel compounds.[96]

The rare cases where **116** and **117** both react with the same substrate are illustrated by the reaction of **7** with phenylacetylene which gives rise to the 1-silacyclopentadiene and 1,2-disilacyclobutadiene derivatives and by the photolysis of **7** in the presence of various ketones which are also initiated by [2 + 2]- and [2 + 1]-cycloadditions. While the 2,3-disiloxetanes **118** and **119** are stable in the solid state, the putative silaoxirane intermediates undergo spontaneous isomerization to the silyl enol ethers **120** and **121**.[97]



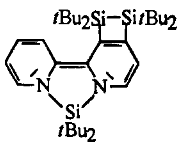
118, R = Me
119, R = Ph

On the other hand, the silirane **122** as well as the 1,2-disilacyclobutane **123** obtained from the photolysis of **7** in the presence of 2-methylstyrene are thermally stable.[98] Surprisingly, the [2 + 2]-cycloadducts from aryldisilenes to olefinic double bond systems were previously unknown so that **123** represents the first completely characterized addition product of a disilene to an alkene.



R = 2-MeC_6H_4 122 123

Particularly instructive for clarifying the course of the photolysis of **7** are its reactions with 2,2′-bipyridyl[99] or pyridine-2-carbaldimines[100] since, in **124** and **126**, both cleavage products of the three-membered ring have undergone addition to the same molecule.



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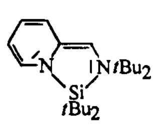

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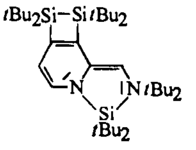

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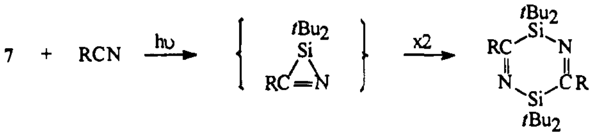
In the course of the [4 + 1]-cycloaddition of **116** to the two nitrogen atoms, the heteroaromatic rings of the starting compounds have been converted into systems with alternating single and double bonds. The unusual bonding situations in the polycyclic compounds **124** and **125** are reflected in their darkred to violet colorations which can presumably be attributed to the *o*-quinone ring together with the silicon substitution. The *o*-quinone structure is destroyed by the further [2 + 2]-cycloaddition of **117** to one of the double bonds in **125** and the colorless product **126** is formed.

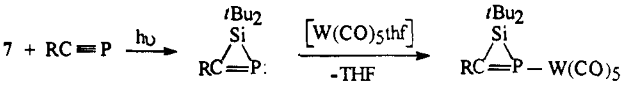
To date, only a few cases are known in which the addition reactions of silylene **116** are preferred over the competing disilene additions. For example, cophotolyses of **7** with acetonitrile or benzonitrile finally furnish the 1,4-diaza-2,5-disila-1,3-cyclohexadienes **129** and **130**, presumably via σ-dimerization of the silaazirines **127** and **128**. When pivalonitrile is employed the isomeric 1,3-diaza-2,5-disila-3,6-cyclohexadiene derivative is obtained unexpectedly; this compound contains four bulky *tert*-butyl groups in direct proximity and, accordingly, exhibits widened endocyclic Si–C bonds.[101]



127, R = CH_3 129

128, R = C_6H_5 130

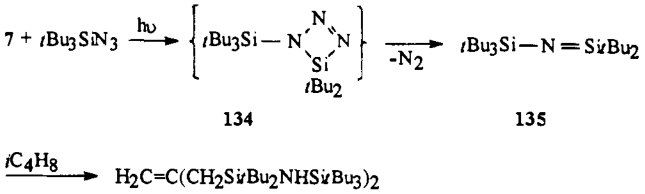
The formation of the putative silaazirines **127** and **128** is substantiated indirectly by the analogous reactions of **7** with phosphaalkynes which give rise to the stable and isolable silaphosphirenes **131** and **132**. Compounds **131** and **132** are the first three-membered ring compounds known to contain an endocyclic P=C double bond.[102] This structure was confirmed by an X-ray crystallographic analysis of the tungsten pentacarbonyl complex, **133**, of **132**.



131, R = *t*Bu 133, R = 1-adamantyl

132, R = 1-adamantyl

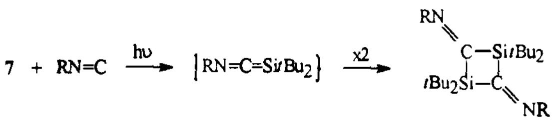
Even rarer than the [2 + 1]-cycloadditions of photochemically generated **116** are the corresponding [3 + 1]-reactions. Cophotolysis of **7** with the sterically overloaded tri-*tert*-butylsilyl azide furnishes two products which had previously been prepared by other routes.[103] The main product of the reaction is the 1,7-diaza-2,6-disilaheptane **136** which is probably formed by an ene reaction of photochemically generated isobutene with the silanimine **135**; the latter compound can be isolated as the minor product.[104]



134 135

136

While the thermal reactions of **7** with aryl isocyanides proceed via ring expansion to give trisilacyclobutanimines,[53,54] photolyses of the same starting materials furnish the yellow to red 2,4-disilacyclobutane-1,3-diimines **137–141**. A feasible explanation for the formation of this novel ring system is the addition of **116** to the carbene-like carbon atom of the respective isocyanide to give silaketenimines and subsequent head-to-tail cyclodimerization of the latter to the ring products isolated.[105–107]

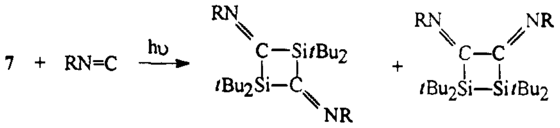


137 - 141

137, R = CF_3, 138, R = C_6F_5, 139, R = C_6H_5,

140, R = 3,5-$(CF_3)_2C_6H_3$, 141, R = 2,4,6-$Me_3C_6H_2$

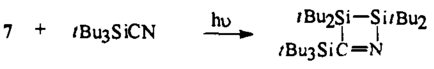
Since West et al.[59] had already shown that the addition of isocyanide to the disilene **70** proceeded smoothly to give the disilacyclopropanimine **79**, the formation of the cyclic products **137–141** by a 2-fold addition of isocyanide to the Si=Si double bond of the photolytically generated species **117** cannot be discounted. The cophotolysis of **7** with the branched aryl isocyanide **142**, which produces isolable, violet crystals of **143** together with a small amount of the isolable, green crystalline **144**, provides more information about the course of the reaction.[106]



142, R = 2,6-$iPr_2C_6H_3$ 143 144

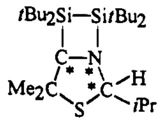
The putative silaketenimine can be considered as a common intermediate of the two disilacyclobutanediimines; head-to-tail dimerization of this species yields **143** and head-to-head dimerization **144**.

Although [1 + *n*]-cycloadditions of the photolytically-generated silylene **116** are still rare, the disilene **117**, formed under the same conditions, undergoes numerous additions to various substrates. In addition to the already-mentioned [2 + 2]-cycloadditions to the multiple bonds of alkynes, alkenes, and ketones, reactions at the Si=Si double bond of **117** are also possible which are not or are only difficulty realizable with the C=C double bonds in simple alkenes. For example, the photolysis of **7** in the presence of the sterically overloaded cyanide **145** is unusual; this reaction furnishes the 2,3-disila-1-azetine derivative **146** by cycloaddition of **117** to the C≡N triple bond.[108]



145 146

Also atypical for the C=C double bonds of simple alkenes are the reactions of **117** with the C–N multiple bond of a racemic 3-thiazoline or of isoquinoline which give rise to the 2,3-disila-1-azetidine derivative **147**[109] stereoselectively and the tricyclic product **148**[110] regioselectively.



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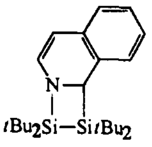
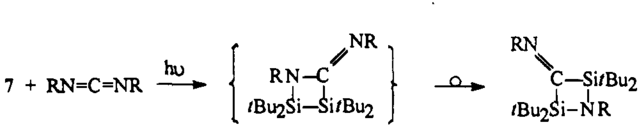


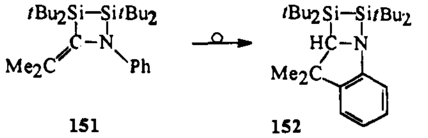
148

The cycloadditions of **117** are occasionally accompanied by rearrangements. Thus, the reaction of this disilene with *N,N*-dicyclohexylcarbodiimide ultimately yields the 2,4-disila-1-azacyclobutanimine **150**. The formation of this product is best explained by addition of **117** to one of the C=N double bonds to give **149** and subsequent rearrangement with formal insertion of a nitrogen atom in the Si–Si bond of **149**.[110]



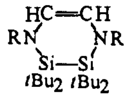
149, R = c-C_6H_{11} 150

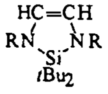
Indirect confirmation for the postulated product **149** is provided by the replacement of one of the electronegative NR groups in the carbodiimide by a CR_2 group which is considered to have a low tendency for insertion into Si–Si bonds. In fact, the photolysis of **7** in the presence of dimethyl-*N*-phenylketenimine does yield the product **152** in which, in contrast to **150**, the Si–Si bond remains intact. However, an X-ray crystallographic analysis reveals that the primary product **151** of the cycloaddition had rearranged by 1,4-hydrogen shift and subsequent ring closure to yield the tricyclic compound **152**.[111]



151 152

In comparison to the numerous additions of stable or marginally stable disilenes to C–X multiple bonds, information on the corresponding reactions of the Diels–Alder type is extremely scarce at present. Solely the reaction of **117** with 2,3-dimethylbutadiene proceeds as a typical [4 + 2]-cycloaddition together with other competing reactions.[11,98] Photolysis of **7** in the presence of heterodienes,[112] on the other hand, yields the [4 + 2]-cycloadducts smoothly. For example, reactions of **7** with 1,4-diazabutadienes furnish the highly strained six-membered ring products **153** and **154** and not the almost strain-free five-membered ring compounds **155** and **156** which must be prepared by other routes.[113]

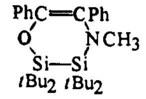


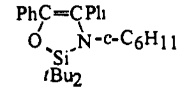


153, R = *i*Pr 155

154, R = c-C_6H_{11} 156

Electron-rich disilenes such as **117** apparently prefer to participate in Diels-Alder reactions with inverse electron demand[114] in spite of the resultant ring strain such as that manifested in **154** by a highly stretched Si–Si bond length of 246.9 pm and a distortion of the six-membered ring.[113] Cophotolyses of **7** and α-ketoimines with sterically undemanding substituents at the nitrogen atom preferentially furnish six-membered ring products such as **157**; with larger substituents, however, five-membered ring products of the type **158** dominate.[101,115]



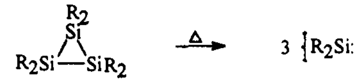


157 158

The examples presented here illustrate the wide reaction possibilities of the photolytically generated disilene **117** which, in part, extend beyond those of the stable disilenes.[3] On the other hand, many other reactions are possible with the stable disilenes but not with **117**.

D. Reactions with Cleavage of All Si–Si Bonds

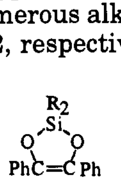
Whereas all other cyclotrisilanes react with cleavage of at most two Si–Si bonds, the thermolysis of **6** furnishes the silylene **159** via cleavage of all three Si–Si bonds. Like **116**, the species **159** can be trapped by numerous unsaturated compounds.[9] The

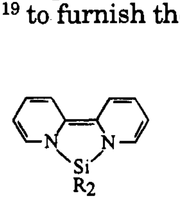


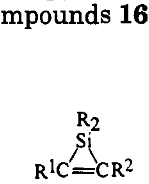
6, R = 2-(Me_2NCH_2)C_6H_4 159

o-bis(dimethylamino)methyl groups are assumed to be responsible for this unusual decomposition. Although these groups are oriented away from the tetracoordinated silicon atom in **6**, in the stepwise cleavage of **6** into silylenes and disilenes, they are able to stabilize the low-coordinated silicon atoms by way of intramolecular Lewis acid–base adducts.

According to recent calculations,[116–118] however, amino groups should rather favor silylenes than disilenes and thus the decomposition of **6** into three molecules of **159** is plausible. This species can be trapped with, for example, benzil, 2,2′-bipyridyl,[9] or numerous alkynes[119] to furnish the compounds **160**–**162**, respectively.

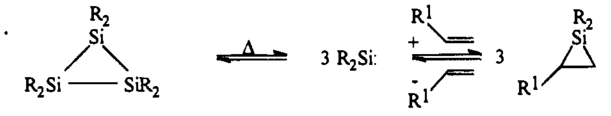






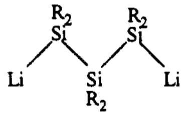
160 161 162

Further evidence in support of the cleavage of all three Si–Si bonds in **6** with formation of the silylene **159** is provided by the formation of the siliranes **163** in its reactions with alkenes under mild thermal conditions. When the temperature is increased, the cyclotrisilane and the respective alkene are reformed.[120]



R = 2-(Me$_2$NCH$_2$)C$_6$H$_4$)

The reaction of **6** with lithium proceeds differently: only one Si−Si bond is cleaved to furnish the 1,3-dilithiated trisilane **164**; the crystal structure of the dioxane adduct of this species has been determined. On the other hand, the reaction of **6** with excess lithium furnishes the 1,2-dilithiodisilane **165** which has been structurally characterized by X-ray analysis as its adduct with tetrahydrofuran.[121]



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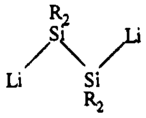

165

R = 2-(Me$_2$NCH$_2$)C$_6$H$_4$

V. Acknowledgments

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