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Silylenes and disilenes: examples of low coordinated silicon compounds*

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CONTENTS

ABSTRACT

This report summarises some aspects of silicon compounds of coordination numbers two and three. As examples for such molecules, generation and trapping reactions of the sterically encumbered silylenes: dimesitylsilylene, di-tert-butylsilylene, and diadamantylsilylene are discussed. Some more recent results from the chemistry of stable and marginally stable disilenes are also considered.

A. INTRODUCTION

Enormous advances have been made in silicon chemistry since 1980. Many compounds which previously had not been thought to exist or were considered only to exist as reactive intermediates are now accessible as thermally stable molecules.

The first stable compounds with Si–C [1,2], Si–Si [3,4], Si–N [5–7], Si–P [8–10], and Si–As [11] double bonds were isolated and completely characterized, and there is also a well developed chemistry of some of these compounds.

In recent years much interest has been focused on sterically encumbered silylenes which by reaction with multiply bonded compounds afforded novel cyclic and acyclic molecules. In addition, several silylene complexes of transition metals of type 1 have been

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*Dedicated to Professor Dr.Dr. h.c. Ulrich Wannagat on the occasion of his 70th birthday honouring his numerous outstanding contributions to organosilicon chemistry.

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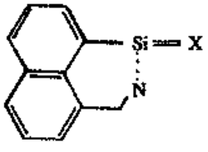
prepared which (with the exception of cationic species) require an additional donor to the silicon atom and, as a consequence, formally belong to four-coordinate silicon compounds [12,13]. The same applies to the intramolecular base stabilized compounds **2** and **3**. The X-ray structure analysis of the silathione **2** verifies the zwitterionic character of this molecule [14] (eqn. (1)).

$$L_nM=\underset{\underset{\mathrm{Do}}{\vdots}}{\mathrm{Si}}R_2$$

1



X = S, **2**; Se, **3**

(1)

The many advances in organosilicon chemistry are documented in the *Proceedings of the Edinburgh Conference on Organosilicon Chemistry* [15] and in particular in the comprehensive two-volume publication, *The Chemistry of Organic Silicon Compounds* from 1989 [16]. More specific reviews are cited at appropriate places in the text.

If the field of low-coordinated silicon compounds is compared with corresponding organic molecules, it becomes clear that there are still large gaps. For example, stable disilynes, compounds with a Si–Si triple bond, are unknown as are molecules in which silicon is part of a stable system of cumulated double bonds. A good example of different stabilities of carbon and silicon compounds is shown by carbenium ions $R_3C^{\oplus}$ and silicenium ions $R_3Si^{\oplus}$. On the one hand, silicenium ions are frequently more stable in the gas phase than their carbon analogues [17], however, in the condensed phase this situation is completely reversed. Whilst carbenium ions often form stable compounds which in individual cases can even be characterized by X-ray structure analyses [18,19], the existence of silicenium ions has not been unambiguously proven. Even though Wannagat et al. were able to show in the middle of the 1950s that trialkylsilyl and triarylsilyl perchlorates are covalent esters of perchloric acid [20,21] as opposed to the corresponding carbon compounds, it is precisely this class of compounds which has been the subject of heated disputes in recent years. Lambert et al. assumed from conductance, molecular weight determinations and NMR studies [22–25] that silicenium ions exist at least in highly diluted solutions of such perchlorates. Olah and his group, on the other hand, have arrived at the conclusion that these molecules are also of covalent nature in diluted solutions [26,27] and that the phenomena observed by Lambert et al. indicate a hydrolysis of the silyl perchlorates by residual water in "dry" solvents to give perchloric acid. In a recent report about this controversy, Lickiss [28] sums up: "... there is no *clear* evidence for their [silyl perchlorates] ionization to give $R_3Si^{\oplus}$ ions in the solvent studied".

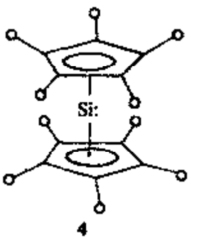
This review article should be considered neither as a short form, nor as a supplement to the monographs mentioned [15,16]. On the contrary, some aspects of silicon compounds of coordination numbers two and three are discussed and the limitations which exist at present are indicated. As examples for such molecules, generation and trapping reactions of sterically encumbered silylenes and some more recent results from the chemistry of stable and marginally stable disilenes are discussed.

B. STERICALLY ENCUMBERED SILYLENES

The contributions made by Gaspar in the series *Reactive Intermediates* [29] have proved to be extremely informative. As this periodical presumably will not be printed in future [30] and as the chapter about silylenes which was to have appeared in the two volumes by Patai/Rappoport could not be realized [16], there is an urgent requirement for an up-to-date, competent and comprehensive review of this class of compounds. In this paper, some bulky substituted silylenes are dealt with, the majority of which have only become available in recent years but have, nevertheless, enabled a quite comprehensive chemistry.

As opposed to carbenes, all silylenes investigated up to now occur exclusively in a singlet ground state. One of the interesting aspects of silylenes with bulky substituents is that by expanding the bond angle, the singlet-triplet energy gap can be reduced to such a degree that reactions from the triplet state become possible. In the case of the parent silylene, $:SiH_2(S)$, there is excellent agreement between experimental and theoretical values for the bond angle; the theoretically calculated [31] and the experimentally observed [32] bond angles are 92.5° and 92.8°, respectively, whilst the angle for $:SiH_2(T)$ was calculated to be 118° and the singlet-triplet energy difference ca. 85 kJ mol^{-1} [31]. In the case of di-tert-butylsilylene, extremely time-consuming calculations were used to give the angles 111.7(S) and 124.7(T) and a singlet-triplet gap of more than 40 kJ mol^{-1} [33]. If the bond angle should exceed 130° by even larger substituents at the silicon atom, then the triplet state may become the ground state [34], a case that has, up to now, not been experimentally realized. For a detailed theoretical review see [35].

These considerations apply, however, only for silylenes which contain divalent and two-coordinate silicon atoms. Hence, although Jutzi's decamethylsilicocene **4** [36] possesses divalent silicon and two ligands in a linear or only weakly angled sandwich structure, the coordination number is 10 and, as a result, this compound as well as **5** [37] does not appear as a typically electron-deficient compound (eqn. (2)).



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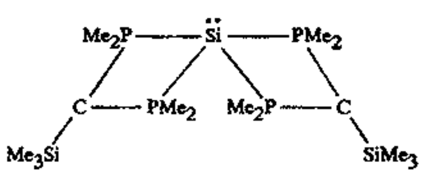
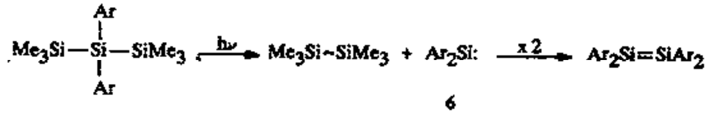


5

(2)

(i) Generation

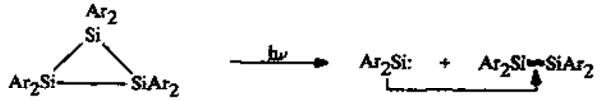
Typical examples of silylenes are, on the other hand, the bulky substituted molecules dimesitylsilylene **6**, di-tert-butylsilylene **18** or the recently described diadamantylsilylene **25**. The best access to **6** as well as to other arylsilylenes is the photolysis of 2-aryltrisilanes [38]. 2,2-Dimesityl-1,1,1,3,3,3-hexamethyltrisilane [39], has been known for some time as a silylene source in solution [40,41], and generates **6** at low temperatures [38]. In the absence of trapping reagents, **6** dimerizes to tetramesityldisilene when the temperature is increased [3] (eqn. (3)).



$$\mathrm{Me_3Si{-}\overset{Ar}{\underset{Ar}{Si}}{-}SiMe_3 \xrightarrow{h\nu} Me_3Si{-}SiMe_3 + \underset{\mathbf{6}}{Ar_2Si:} \xrightarrow{\times 2} Ar_2Si{=}SiAr_2} \qquad (3)$$

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

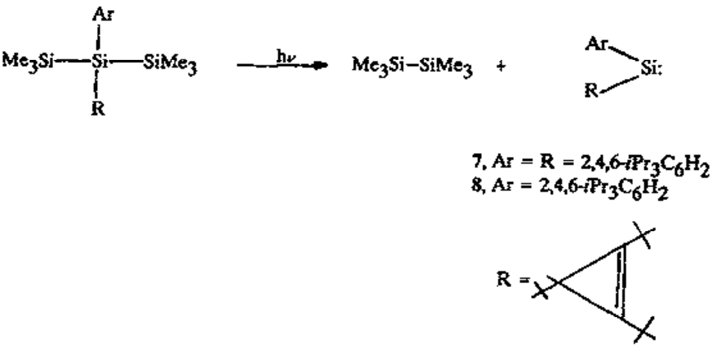
An alternative route to aryl-substituted silylenes is the photolysis of hexaarylcyclotrisilanes which proceeds by cleavage of two Si–Si bonds to produce the disilene and the silylene, with the latter undergoing dimerization to give more disilene (see below) [4] (eqn. (4)).



(4)

Ar = $2,6\text{-}Me_2C_6H_3$

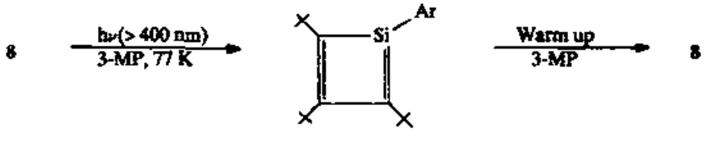
The general applicability of the acyclic trisilane method for the generation of arylsilylenes is shown by the formation of the sterically congested silylenes bis(2,4,6-triisopropylphenyl)silylene **7** [42] and 2,4,6-triisopropylphenyl(1,2,3-tri-tert-butylcyclopropenyl)silylene **8** [43] (eqn. (5)).



7, Ar = R = $2,4,6\text{-}i\mathrm{Pr}_3C_6H_2$
8, Ar = $2,4,6\text{-}i\mathrm{Pr}_3C_6H_2$

(5)

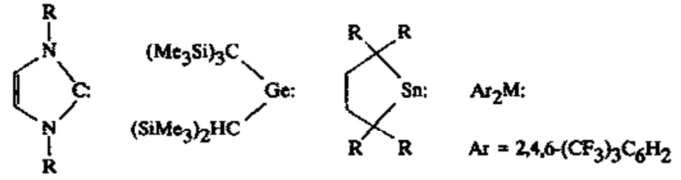
Silylene **8** is unusual in two respects. Irradiation of **8** with visible light in a 3-methylpentane glass at 77 K gives the silacyclobutadiene derivative **9**, which is converted into **8** when the temperature is raised. Obviously, **8** is thermally more stable than cyclobutadiene **9** and appears to be the most stable of all previously investigated silylenes decomposing only above 200 K [43] (eqn. (6)).



9

(6)

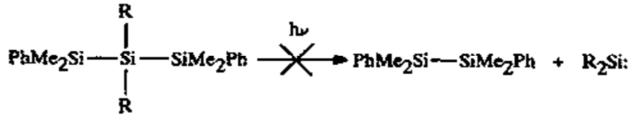
There are, however, notable differences in the stabilities of the analogous room temperature stable germylenes [44], stannylenes and plumbylenes [45] known from the work of Lappert and co-workers [46]. More recently, the crystalline carbene **10** has been isolated and completely characterized [47]. The structure of **10** together with some more recent examples of thermally stable germylenes **11** [48], stannylenes **12**, **13** [49,50] and plumbylenes **14** [51] is summarized in the following formulae. It would be extremely useful if, similar to the accidental discovery of **10**, a silylene, stable at room temperature, could be isolated (eqn. (7)).



10, R = Adamantyl **11** **12**, R = $SiMe_3$ **13**, M = Sn; **14**, M = Pb

(7)

In contrast to the arylsilylenes, alkyl-substituted silylenes are hardly accessible from acyclic trisilanes. Photolysis of 2,2-di-tert-butyl-1,1,3,3-tetramethyl-1,3-diphenyltrisilane **15** [52] or of the corresponding 2,2-diadamantyltrisilane derivative **16** [53] does not proceed by simultaneous cleavage of two Si–Si bonds to give the corresponding silylenes. Instead, Si–Si bond homolysis dominates as an important primary step in the photoreaction (eqn. (8)).

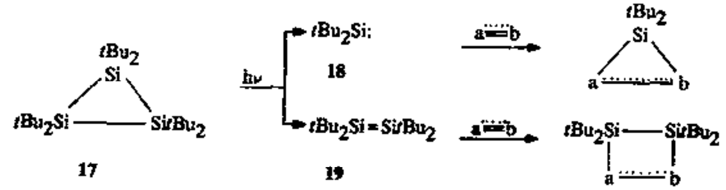


$$\mathrm{PhMe_2Si{-}SiR_2{-}SiMe_2Ph} \overset{h\nu}{\not\longrightarrow} \mathrm{PhMe_2Si{-}SiMe_2Ph} + \mathrm{R_2Si:}$$

(8)

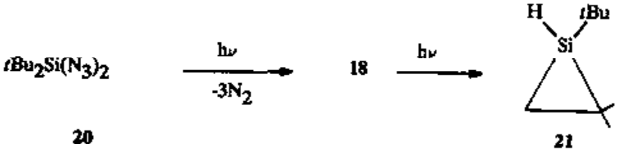
15, R = *t*Bu; **16**, R = Adamantyl

Di-tert-butylsilylene **18**, which is not accessible via the trisilane route, can, however, be generated by a number of different methods. One possibility is the photolysis of hexa-tert-butylcyclotrisilane **17** [54], which also produces tetra-tert-butyldisilene **19**. In contrast to hexaarylcyclotrisilanes, which upon photolysis are completely converted into tetraaryldisilenes, **17** gives the short-lived **18** and the marginally stable **19** together in a sort of cage and they do not separate until reaction occurs with a trapping reagent [55]. If **17** is subjected to irradiation in the absence of trapping reagents, the three-membered ring **17** is quantitatively recovered after irradiation (eqn. (9)).



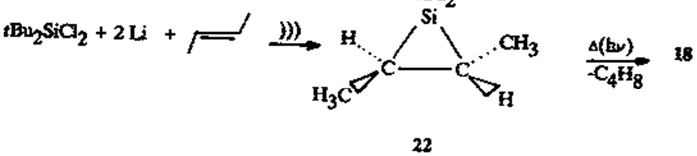
(9)

The major product from 254-nm irradiation of matrix-isolated diazidodi-tert-butylsilane **20** is also **18**, which undergoes a subsequent photochemical C–H insertion to give isolable 1-tert-butyl-2,2-dimethyl-1-silacyclopropane **21**[56] (eqn. (10)).



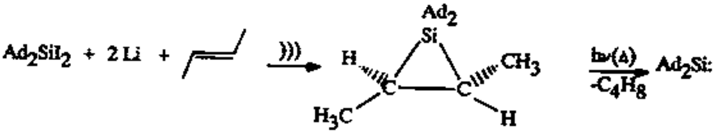
(10)

A number of years ago, Seyferth and co-workers showed that the thermolysis of hexamethylsilirane is an elegant method to generate dimethylsilylene [57]. Recently, Boudjouk and co-workers have shown that treatment of di-tert-butyldichlorosilane with lithium in the presence of *cis*- and *trans*-butene under ultrasonic irradiation led to the stereospecific formation of 1,1-di-tert-butyl-*cis*(*trans*)-2,3-dimethylsiliranes, for example **22** [58]. Photolysis or thermolysis of both siliranes produces **18** along with the less reactive *cis*- or *trans*-butene (eqn. (11)).



(11)

In a similar manner, Gaspar and co-workers have recently succeeded in obtaining several 1,1-diadamantylsiliranes and 1,1-diadamantylsilirenes [53]. The siliranes are effective precursors for the thermal or photochemical generation of diadamantylsilylene **25**. Very original in this respect was the synthesis of diadamantyldiiodosilane **23** which was obtained by hydrosilylation of 2 equiv. of dehydroadamantene [59,60] with diiodosilane. The following formula shows the generation of **25** via silirane **24** [53] (eqn. (12)).

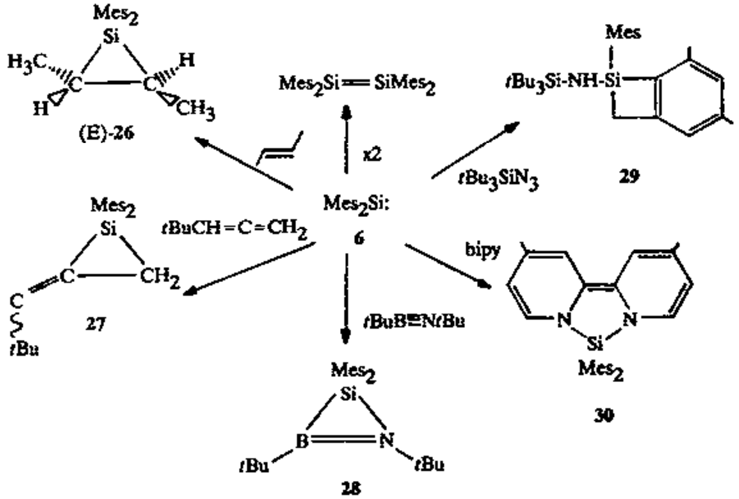


23 **24** **25** (12)

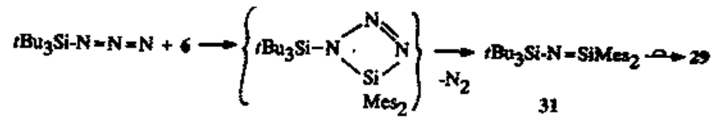
(ii) Addition and cycloaddition reactions

Whilst addition or cycloaddition reactions of sterically less crowded silylenes are frequently accompanied by rearrangements or other consecutive reactions [29], corresponding reactions of the bulky substituted silylenes **6**, **18** and **25** lead to considerably more stable products. Scheme 1 summarizes selected reactions of silylene **6**.

The most important reaction of **6** is certainly the dimerization to tetramesityldisilene, the very first isolated disilene [3]. In addition, several cycloaddition reactions of **6** are also interesting which mainly result in stable ring systems without any rearrangement. For example, **6** reacts with *trans*-2-butene to form silirane **26** which is isolated along with its (*Z*)-isomer [42]. With tert-butylallene, **6** forms several products of which the (*E*)- and (*Z*)-isomeric alkylidensiliranes **27** are mentioned here [61]. Furthermore, [2+1]-cycloaddition also takes place with iminoboranes which, for example, produce the azasilaboriridene derivative **28** [62]. The attempted [3+1]-cycloaddition of **6** to a sterically overcrowded silyl azide was more complicated and the silacyclobutene derivative **29** was isolated. The formation of **29** is most easily explained when it is assumed that the [3+1]-cycloaddition of **6** to the silyl azide followed by a loss of nitrogen gives **31** which rearranges by a [1,5]-sigmatropic shift of hydrogen from one of the *ortho*-methyl groups to the nitrogen atom, followed by conrotatory ring closure [63] (eqn. (13)).

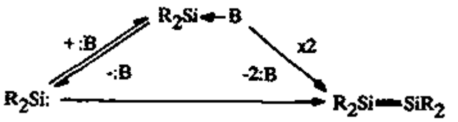


Scheme 1. Selected reactions of silylene **6**.

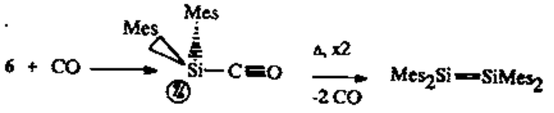

(13)

Silylene **6** reacts with 2,2'-bipyridyl and its derivatives in a [4+1]-fashion to provide the violet dimesityl-2,2'-bipyridyl-(*N,N'*)silanes **30** [64] in which the heteroaromatic rings of bipyridyl were converted into *ortho*-quinoid systems.

Due to their electron deficiency, silylenes like **6** should behave as typical Lewis acids and form corresponding adducts with Lewis bases. West and co-workers [65] have been able to show in a comprehensive study that free silylenes, generated photolytically at 77 K in 3-methylpentane matrices, react upon annealing of the matrix with ethers, amines, sulfides and phosphines to give the corresponding acid-base complexes. In the case of some adducts of **6**, further warming of the matrix leads to tetramesityldisilene (eqn. (14)).


(14)

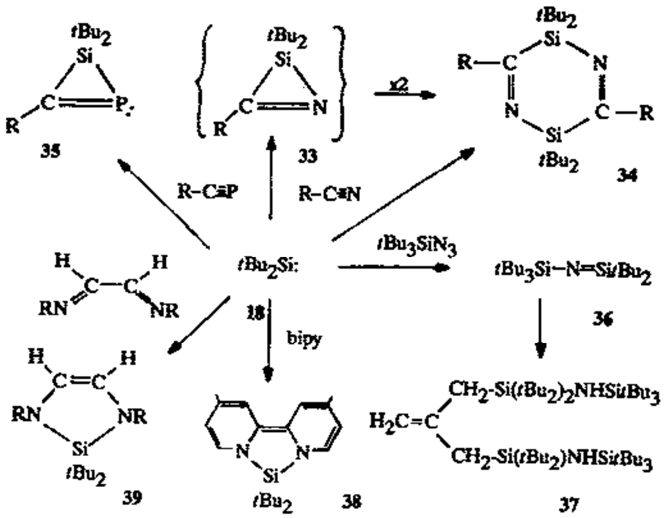
In the presence of branched alcohols the same reaction leads to silylene insertion into the O–H bond [65]. A Lewis acid-base adduct is also formed with carbon monoxide which, according to the spectroscopic data as well as the reaction behaviour, should correspond to the structure of the non-planar complex **32** [66]. Theoretical calculations on the hydrogen compound H_2SiCO predict that the energy of the non-planar form **32** is appreciably lower than that of a planar geometry [67] (eqn. (15)).


(15)

32

Silylene **6**, generated photochemically in an oxygen matrix at 16 K, reacts smoothly with the oxygen to form a product which, on the basis of its IR spectrum and calculations of the parent compound H_2SiO_2, has the structure of a silanone O-oxide [68].

Now that sterically encumbered diarylsilylenes are readily available, it is interesting to compare their properties with those of dialkylsilylenes like di-tert-butylsilylene **18**. However, this should be considered with caution as comparable investigations are not available in most cases. Silylene **18** is formed mainly by photolysis of the cyclotrisilane **17** or, less frequently, by photolysis or thermolysis of silirane **22**. Some addition reactions of **18** are summarized in Scheme 2 [69].



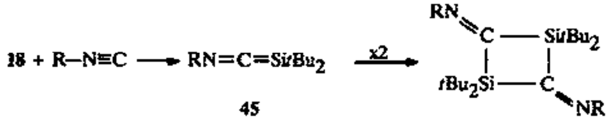
Scheme 2. Selected reactions of silylene **18**.

Silylene **18** undergoes [2+1]-additions to the triple bonds of several nitriles to give silaazirines **33**, which undergo spontaneous σ-dimerization to give 1,4-(**34**) or 1,3-diaza-2,5-disila-1(6),3-cyclohexadienes, presumably owing to the high ring strain. Formation of the silaazirine intermediates could be confirmed indirectly by the analogous reaction of **18** with phosphaalkynes, from which stable phosphasilirenes **35** are isolable. The molecules **35** ($R = {}^{t}Bu$, adamantyl) were the first three-membered rings containing a P–C double bond [71]. The structure of the adamantyl derivative has been confirmed by X-ray crystallography of its end-on coordinated complex with tungsten pentacarbonyl [71].

Reaction of **18** with tri-tert-butylsilyl azide gives two compounds, both of which have been previously obtained by independent routes [72]. The 1,7-diaza-2,6- disilaheptane **37** is the major product of this reaction. The proposed primary intermediate, the silanimine **36**, is also isolated in minor amounts [63]. It is believed that the reaction sequence initially gives the silanimine **36** which by an ene reaction with photochemically formed isobutylene produces the final product **37** [63]. When 2,2'-bipyridyl or 4,4'-dimethyl-2,2'-bipyridyl are allowed to react with **18**, only the [4+1]-cycloaddition products **38** are obtained, in which the heteroaromatic rings are converted into *ortho*-quinoid ring systems, as in the case of **30**. Compound **38** has a dark violet colour and shows absorptions at ca. 560 nm [73]. Photolysis of **18** in the presence of 1,4-dialkyl-1,4-diaza-1,3-butadienes or reaction of these butadienes with lithium and di-tert-butyldichlorosilane gives the colourless cyclopentenes **39**, which possess the same C_2N_2Si-framework as the bipyridyl adducts **38** [74].

In contrast to the numerous cycloaddition reactions of **18** to multiple bonded compounds, co-photolysis of **17** and several isocyanides seem to follow an alternative route. Assuming the branching of the substituents is not too great, the disilacyclobutane-1,3-

diimines **40**–**44** are formed, whose colours in the crystal vary betweeen bright yellow and red [75–77]. A plausible explanation for the formation of these rings is the addition of silylene **18** to the carbene-like carbon atom of the isocyanide to give a ketenimine **45**, or a Lewis-acid-base adduct between **18** and the isocyanide, whose cyclodimerization should result in the isolated rings (eqn. (16)).



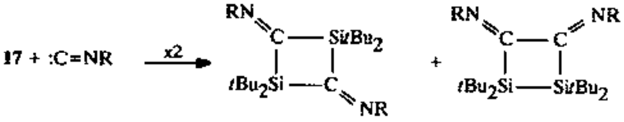
(16)

40 - **44**

40, R = CF_3; **41**, R = C_6H_5; **42**, R = C_6F_5; **43**, R = 3,5-$(CF_3)_2C_6H_3$; **44**, R = 2,4,6-$Me_3C_6H_2$

Another possibility is a twofold addition of the respective isocyanides to the two Si–Si bonds of tetra-tert-butyldisilene, which is formed simultaneously with **18** upon photolysis of **17**. Indeed, West et al. [78] have isolated a disilacyclopropanimine by isocyanide addition to a stable disilene.

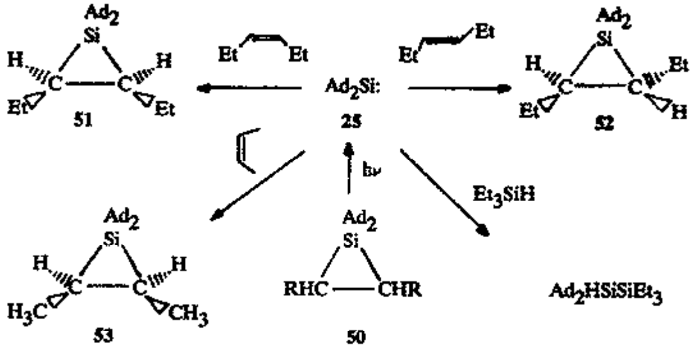
A little more clarity in the process of the photolysis of **17** with isocyanides is achieved by aryl groups bearing highly branched *ortho*-substituents. Thus, the irradiation of **17** in the presence of 2,6-diisopropylphenyl isocyanide results in a dark-green solution, from which violet crystals of **46** are first isolated. Prolonged cooling of the solution at –30°C results in a small amount of green crystals of **47**. The molecules **46** and **47**, whose structure is confirmed unambiguously by X-ray crystallography, are always isolated in a ratio of ca. 10:1, regardless of the reaction conditions. They are not photochemically interconverted into one another [76] (eqn. (17)).



(17)

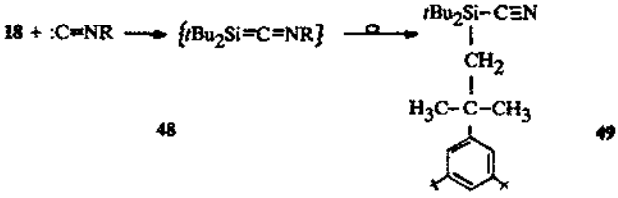
R = 2,6-$iPr_2C_6H_3$ **46** **47**

It is possible that they arise from a common intermediate, such as a silaketenimine of the type $^tBu_2Si{=}C{=}NR$. Head-to-tail dimerization then should give the four-membered ring **46**, whereas head to head dimerization should yield the isomer **47**. In the absence of trapping reagents, some short-lived silaethylenes [1] and silapropadienes [79] bearing bulky substituents also undergo head-to-head dimerization yielding 3,4-disilacyclobutanes. To verify that **46** and **47** result from dimerization of the suggested silaketenimine **45** and not from a twofold addition of aryl isocyanide to the disilene **19**, we allowed **17** to react with 2,4,6-tri-tert-butylphenyl isocyanide, whose bulky *ortho*-tert-butyl groups should disfavour both cyclodimerization and insertion into the Si–Si bond of a possible disilacyclopropanimine intermediate.



Scheme 3. Thermally induced generation and trapping of silylene **25**.

In fact, a monomeric compound consisting of **18** and the aryl isocyanide in a ratio of 1:1 was isolated. The spectroscopic data indicated, however, that the expected intermediate **48** had rearranged to the colourless trialkylsilyl cyanide **49** (eqn. (18)).



(18)

Investigations dealing with diadamantylsilylene **25** are still very much in their initial phase in spite of numerous insertion and addition reactions [53] (Scheme 3). The addition of thermally generated **25** (derived from various precursors **50**) to *cis*-butene and *cis*- and *trans*-hexene is totally stereospecific. The stereospecific formation of the addition products **51**–**53** implies a singlet electronic state of **25**. Generation of **25** by photochemically induced bond cleavage, however, is complicated by photoisomerization of *cis*- and *trans*-1,1-diadamantylsiliranes **50**, but again a high degree of stereospecificity is observed [53].

The reactions of sterically encumbered silylenes described briefly here not only indicate their synthetic potential, but also give reason to expect that there are additional reactions of this type. Long-term aims are still the generation of silylenes with an electronic triplet ground state which might be possible by other substitution patterns and the synthesis of the first room temperature stable silylene.

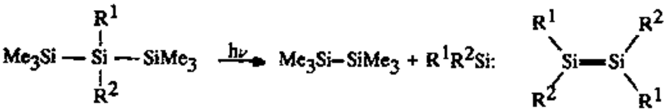
C. STABLE AND NEARLY STABLE DISILENES

The synthesis and chemistry of unsaturated silicon compounds and particularly of disilenes have already been the subject of reviews such as *The Chemistry of Disilenes*, by R. West [80], *Multiple Bonding to Silicon*, by Raabe and Michl [81], *Novel Silicon Ring*

Compounds, by R. West [82], and the comprehensive review article by Masamune et al., *Strained Ring and Double Bond Systems Consisting of Group 14 Elements Si Ge, Sn* [83]. Hence, in order to avoid unnecessary repetition, particularly with [82,83], this paper is restricted to some fundamental principles of disilene chemistry, together with more recent reactions of this class of compounds.

(i) Synthesis

Since the report on tetramesityldisilene **54** in 1981 [3], the first molecule with a Si–Si double bond stable at room temperature, a number of different methods have been used to synthesize disilenes. The oldest of these has been applied most frequently and involves the photolysis of acyclic 1,1,1,3,3,3-hexamethyltrisilanes at low temperatures. Simultaneous cleavage of two Si–Si bonds gives hexamethyldisilane and a silylene which results in the corresponding disilene upon dimerization. This method, mainly used by West et al.,. has enabled the isolation of a number of disilenes, some of which are listed below [3,84,87] (eqn. (19)).

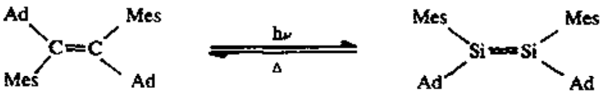


$R^1 = R^2 = Mes$, **54**
$R^1 = Mes, R^2 = t$Bu, **55**
$R^1 = Mes, R^2 = Xyl$, **56**
$R^1 = Mes, R^2 = 1\text{-}Ad$, **57**
$R^1 = Mes, R^2 = N(SiMe_3)_2)$ **58**

(19)

Mes = 2,4,6-$Me_3C_6H_2$; Xyl = 2,6-$Me_2C_6H_3$, 1-Ad = 1-Adamantyl

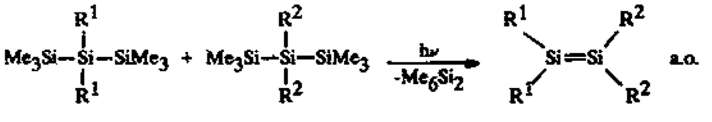
The presence of an aryl group on the central silicon atom of the trisilane is obviously the necessary condition for preference given to the silylene extrusion instead of bond homolysis and formation of radicals. The disilenes **55–58** having two different substituents per silicon atom occur mainly as the thermodynamically favoured *E* isomers. However, they can often be converted into the *Z* isomer by irradiation, or be enriched in this form as shown in eqn. (20) [86]:



(*E*) - **57** (*Z*) - **57**

(20)

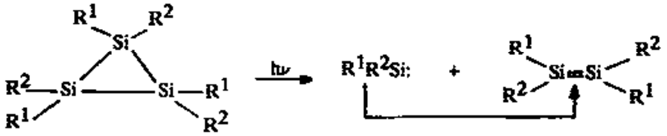
Co-photolysis of two trisilanes having different substitution patterns on the central silicon atoms enables not only isolation of the compounds $R^1_4Si_2$ and $R^2_4Si_2$ but also of the asymmetrical substituted compounds **59** [85] which are necessary for the determination of the ^1J(SiSi) coupling constants [88] (eqn. (21)).



59

(21)

The photochemically induced cleavage of cyclotrisilanes is also a frequently used procedure for the formation of disilenes [4]. This method was subsequently used for the synthesis of digermenes and of a marginally stable distannene [83]. Examples of some disilenes synthesized in this manner are shown below [4, 89–90] (eqn. (22)).



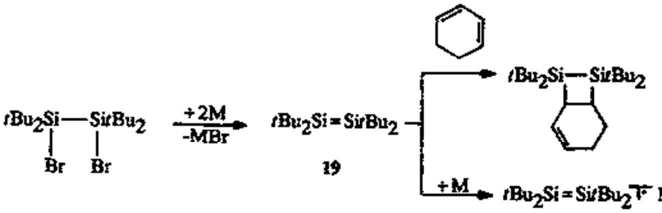
R^1, R^2 = Xyl **60**
R^1, R^2 = Dep **61**
(*E*)- and (*Z*)- **55**

Xyl = 2,6-$Me_2C_6H_3$; Dep = 2,6-$Et_2C_6H_3$

(22)

The above photolysis proceeds by simultaneous cleavage of two Si–Si bonds to form disilene and silylene, with the latter undergoing dimerization to give more disilene. The occurrence of silylene during photolysis was shown by the trapping reaction with 2,3-dimethyl-1,3-butadiene from which the [4+1]-cycloadduct was isolated [91]. A disadvantage of this method is the fact that aryl-substituted cyclotrisilanes can usually only be obtained in low yields [83]. On the other hand, an advantage is that alkyl-substituted disilenes are also accessible. For example, the marginally stable tetra-tert-butyldisilene **19** is obtained by photofragmentation of cyclotrisilane **17** [54].

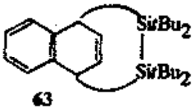
The most obvious method for the synthesis of disilenes is supposed to be the reductive halide elimination from sterically crowded dihalosilanes or 1,2-dihalodisilanes. However, this is only occasionally successful. The attempted synthesis of **19** by reductive halide elimination from, for instance, 1,2-dibromo-1,1,2,2-tetra-tert-butyldisilane resulted in an impure **19** which was trapped with 1,3-dienes to give the [2+2]-cycloaddition product [92] (eqn. (23)).



62

(23)

Later we were able to prove that this reaction did not stop at the disilene **19** stage; instead the persistent disilenyl radical anions **62** were formed by an additional electron transfer [93]. By photochemical retro Diels–Alder reaction of **63**, Masamune et al. also obtained disilene **19**, which is rather unstable at room temperature and has a half-life of only several hours [94] (eqn. (24)).



63

$$\xrightarrow{h\nu} \mathbf{19} + C_{10}H_8 \qquad (24)$$

Up to now, only a few cases are known where stable disilenes are produced by halide elimination reactions. Masamune et al. succeeded in obtaining the first, and up to now only, stable tetraalkyldisilene **64** by reaction of diiodobis(trimethylsilylmethyl)silane with lithium naphthalenide [95] (eqn. (25)).

$$2[(Me_3Si)_2CH]_2SiI_2 + 4Li/C_{10}H_8 \longrightarrow \underset{\mathbf{64}}{[(Me_3Si)_2CH]_2Si{=}Si[HC(SiMe_3)_2]_2} \qquad (25)$$

Watanabe and Nagai et al. found independently that either reductive coupling of dichlorobis(2,4,6-triisopropylphenyl)silane or reductive chloride elimination from the corresponding 1,2-dichlorodisilane provides the sterically extremely congested disilene **65** [96] (eqn. (26)).

$$R_2SiCl_2 + Li/C_{10}H_8 \longrightarrow \underset{\mathbf{65}}{R_2Si{=}SiR_2} \longleftarrow R_2ClSi{-}SiClR_2 + Li/C_{10}H_8 \qquad (26)$$

$R = 2,4,6\text{-}iPr_3C_6H_2$

(*Z*)- and (*E*)-disilenes **66** have been prepared by Masamune et al. by a similar route [97] (eqn. (27)).

$$R^1R^2SiCl_2 + Li/C_{10}H_8 \longrightarrow R^1R^2Si{=}SiR^1R^2 \qquad (27)$$

$R^1 = 2,4,6\text{-}Me_3C_6H_2$;
$R^2 = 2,6\text{-}iPr_2C_6H_3$ (*E*)-, (*Z*)-**66**

The method of reductive coupling appears to be very promising for the synthesis of additional disilenes, especially in the case of very bulky substituted dihalosilanes which cannot be converted into cyclotrisilanes.

(ii) Chemical properties

As mentioned above, synthesis and reactivity of disilenes has been the subject of several leading review articles [80–83]. Consequently, only some principles and examples for the reactivities of disilenes are described here. Inspite of shielding by bulky substituents, disilenes are often the subject of many unusual reactions. The majority of reactions described here refer to the stable disilene **54** and nearly stable disilene **19** and, therefore, illustrate the differences and similarities in the reactivity of tetraaryl- and tetraalkyldisilenes. The oxidation of disilenes by air are discussed first. Although one of the first reactions to be investigated, they have only very recently been clarified.

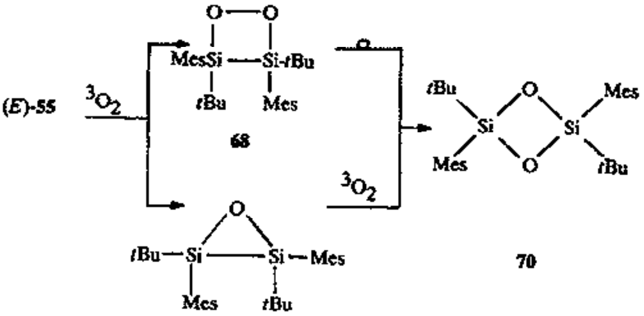
In contrast to most alkenes, which do not react with triplet dioxygen ($^3O_2$) at low temperatures, treatment of **54** with $^3O_2$ eventually gives the 1,3-cyclodisiloxane **67** [98] (eqn. (28)).

67 (*A*) **67** (*B*)

(28)

A striking feature of the structure of **67** is the silicon–silicon distance of 231 pm, somewhat shorter than the normal Si–Si single-bond length of ca. 234 pm [98]. From a ^{29}Si NMR study of cyclodisiloxanes with different substitution patterns at the silicon atoms, West and co-workers have concluded, that despite the short intramolecular Si–Si contact, there is probably no bonding between the silicon atoms. Typical ^2J(SiOSi) values range from 1 to 4 Hz. The measured values of 3.85–4 Hz for the disiloxanes are consistent with structure *A* [88].

The mechanism for air oxidation of disilenes is described below. For instance, disilene (*E*)-**55** reacts in solution with $^3O_2$ to give 1,2-disiladioxetane **68** as the major product along with smaller amounts of disilaoxirane **69**. Compound **68** rearranges either in the solid state or in solution to give 1,3-cyclodisiloxane **70** [99] (eqn. (29)).

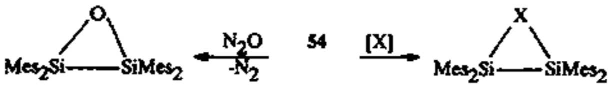


68 **69** **70**

(29)

Both, air oxidation of (*E*)-**55** and rearrangement of **68** to 1,3-cyclodisiloxane **70** take place with retention of configuration at silicon [99,100]. Crossover experiments with unlabeled **68** and doubly ^{18}O-labeled **68** as well as crystallographic data indicate that the rearrangement **68** → **70** is intramolecular both in the solid state and in solution [100].

Treatment of disilene **54** with dinitrogen oxide or with the heavier chalcogens sulfur, selenium and tellurium gives the novel ring systems of oxa- [101], thia- [102], selena- and telluradisiliranes [103] **71–74**, which are hardly accessible by other routes (eqn. (30)).

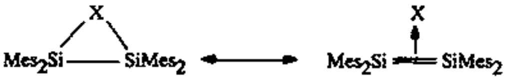


71

X = S, **72**; Se, **73**, Te, **74**

(30)

An interesting feature of these rings is the decrease in the Si–Si bond distances with increasing electronegativity of the chalcogen atom. Thus, for **71** the Si–Si bond distance of ca. 223 pm [101] is closer to the double bond length of ca. 215 pm than to the single bond distance of ca. 235 pm. In **71**, the arrangement of silicon and the two ipso-carbon atoms of the aryl groups at both silicon atoms is strictly planar (sum of angles at Si 360°) and nearly planar in **72–74**. The bonding in these rings may, therefore, be regarded to exist in the continuum between the three-membered ring structures and that of π-complexes **75** (eqn. (31)).

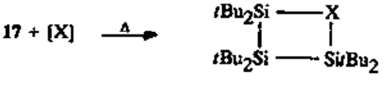


75

(31)

A similar phenomenon has been observed for the corresponding thia- [104], selena- [104, 105], and telluradigermiranes [106] and for 1,2-dithiadistannetane [107] and telluradistannirane [108] which also reveal a nearly planar arrangement at the germanium and tin atoms. The π-complex model **75** can probably be ruled out for these molecules, since the Ge–Ge and Sn–Sn bond distances are not markedly shorter than the normal single bond lengths.

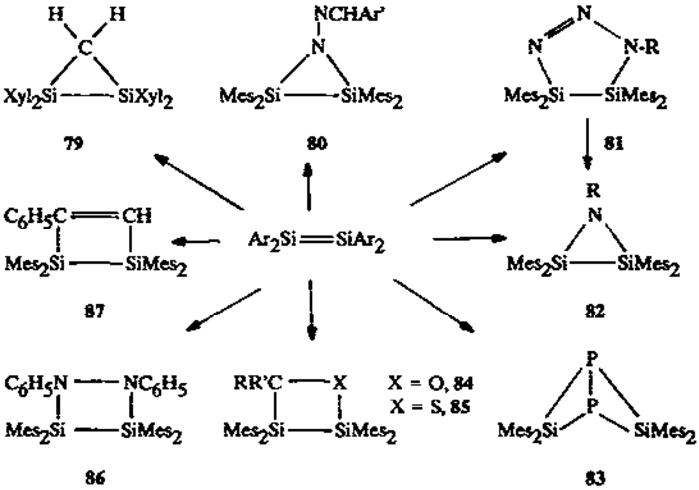
In contrast to the reactions of **54** with chalcogens, thermolysis of **17** in the presence of oxygen, sulfur or selenium results in the ring-enlarged molecules **76–78** [109] (eqn. (32)).



X = O, **76**
= S, **77**
= Se, **78**

(32)

Several cycloaddition reactions of stable tetraaryldisilenes (in particular **54**) are summarized in Scheme 4. Treatment of disilene **60** with diazomethane gives the disilirane **79** whose X-structure analysis reveals a remarkably short Si–Si bond distance of

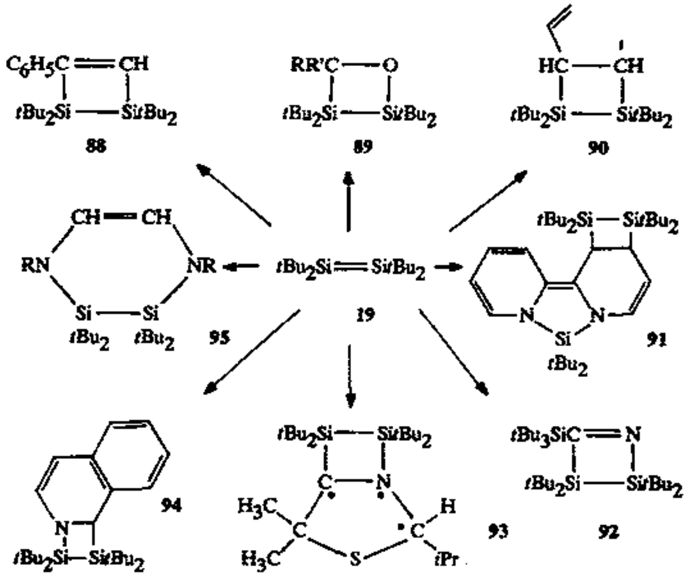


Scheme 4. Addition reactions of tetraaryldisilenes.

227.2 pm [90]. On the other hand, disilene **54** reacts with *para*-tolyldiazomethane in a [2+1]-fashion without losing N_2 to give the adduct **80** [110]. The reactions of azides with **54** are strongly dependent on the group R in RN_3. Aryl substituted azides give two products, disilatriazolines **81** and disilaaziridines **82**. When R = $PhCH_2$ or Me_3SiCH_2, intermediate three-membered rings are formed which upon thermolysis yield the corresponding disilaaziridines. For R = Me_3Si, only compound **82** was formed, the structure of which was found to have a short Si–Si bond length of 223 pm [111]. Treatment of **54** with white phosphorus proceeds by cleavage of the two Si–Si bonds in **54** to give the disiladiphosphane **83** having a butterfly-like bicyclo[1.1.0]butane structure [112]. Disilene **54** also reacts with several aldehydes and ketones [113,114] by [2+2]-cycloaddition to the carbonyl group, yielding oxadisiletanes of type **84**. The reaction of **54** with thiobenzophenone proceeds similarly to give the first thiadisiletane **85** (R, R' = C_6H_5) [115]. Recently, the 1,2-diaza-3,4-disilacyclobutane derivative **86** was isolated from the reaction of **54** with azobenzene in low yield [116]. Although disilene **54** is unreactive towards dienes and several acetylenes, it undergoes [2+2]-cycloaddition to phenylacetylene to give the 1,2-disilacyclobutene **87** in good yield [113].

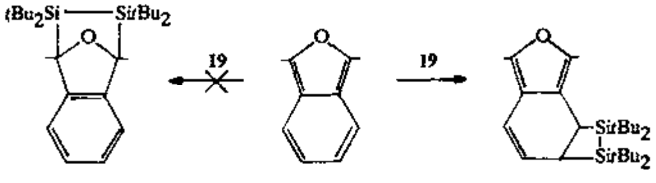
Many of the reactions of **54** and other tetraaryldisilenes mentioned here underline that these disilenes behave as electron-rich olefins. This is also true for tetraalkyldisilene **19**, some reactions of which are summarized in Scheme 5.

Consistent with **54**, disilene **19** undergoes [2+2]-cycloadditions to the C–C triple bond of phenylacetylene and to the carbonyl bond of several ketones to give the 1,2-disilacyclobutene derivative **88** and the addition products **89** [117]. Whereas **54** does not react with alkenes and conjugated dienes [118], **19** is found to be reactive towards 1,3-



Scheme 5. Cycloaddition reactions of disilene **19**.

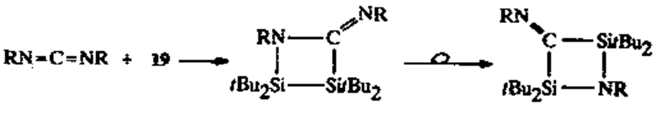
dienes including 1,3-cyclohexadiene (see above) [91] or with the (*N*,*N'*)-bipyridylsilane **38** to give the [2+2]- rather than the [2+4]-cycloadducts **90** and **91** [119]. Interestingly, **19** adds to 1,3-diphenylisobenzofuran exclusively in a [2+2]-fashion to provide the adduct **96** [119]. From a thermodynamic point of view, formation of the aromatic compound **97** by a Diels–Alder reaction should be expected rather than the formation of its isomer **96** (eqn. (33)).



(33)

The sterically congested tri-tert-butylsilylnitrile reacts smoothly with **19** to give the 2,3-disila-1-azetine derivative **92** [120] while alkenes do not undergo [2+2]-cycloadditions with nitriles. Despite bulky ligands, which are necessary for the stabilization of the Si–Si double bond, stable or nearly stable disilenes are often more reactive than alkenes bearing sterically less demanding substituents, and, in some cases undergo reactions atypical for C–C double bonds [80]. The unusual reactivity of **19** is further demonstrated in its addition reaction to a racemic 3-thiazoline which proceeds diastereoselectively to yield the 2,3-disila-1-azetidine derivative **93** [121]. The addition reactions of **19** to C–N multiple bonds have also been extended to isoquinoline which gives the tricyclic system **94** [122].

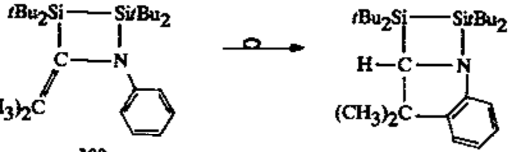
Whilst disilene **19** does not undergo [4+2]-cycloadditions with 1,3-dienes, the Diels–Alder adducts **95** are formed with heterodienes, e.g. 1,4-diazabutadienes [74]. It can be deduced that the electron deficient properties of 1,4-diazabutadienes favour hetero-Diels–Alder reactions operating by inverse electron demand [123]. This is corroborated by theoretical calculations which indicate that the Si–Si double bond is strongly electron donating [124] and therefore should add predominantly to electron poor dienes like 1,4-diazabutadienes [74] or benzil [92,125]. In addition to these cycloadditions, disilene **19** undergoes several reactions from which rearranged products are isolated. Treatment of *N,N'*-dicyclohexylcarbodiimide with photochemically generated **19** seems to proceed by [2+2]-addition to one of the C–N double bonds, followed by formal insertion of the NR groups into the Si–Si bond to provide the rearranged 2,4-disila-1-azacyclobutanimine **99** [122] (eqn. (34)).



(34)

98 **99**

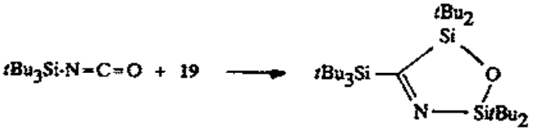
In order to suppress the rearrangement of the probable intermediate **98**, the generation of **19** was carried out in the presence of ketenimines in which one of the NR groups of carbodiimides was replaced by the CR_2 group. Due to the low electronegativity of carbon compared to nitrogen, a rearrangement such as observed for **98** ought not to occur. Actually, the reaction of dimethyl-*N*-phenylketenimine with **19** gives a product, which in contrast to **99** has a Si–Si bond in the four-membered ring. However, the NMR data as well as the X-ray structure analysis show clearly that the originally formed product of the presumed cycloaddition, **100**, undergoes a 1,4-hydrogen shift and eventually ring closure into the tricyclic system **101** [126] (eqn. (35)).



(35)

100 **101**

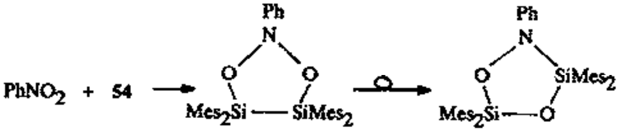
An interesting type of rearrangement has been observed in the addition of a bulky substituted isocyanate to **19**. This reaction is thought to proceed by a [3+2]-cycloaddition of **19** to the isocyanate. By migration of the silyl group from nitrogen to carbon and by formal insertion of the oxygen atom into the Si–Si bond, the five-membered heterocycle **102** was finally isolated [120] (eqn. (36)).



102

(36)

A similar type of rearrangement has been observed in the addition of disilene **54** to nitrobenzene, providing the five-membered 1,3,2-dioxaazadisilolidene **104**. This compound may be produced by rearrangement of the initially formed [3+2]-cycloaddition product **103** [127] (eqn. (37)).



103 104

(37)

Although disilene chemistry is hardly 10 years old, it has borne many fruits, some of which are described here. Nevertheless, numerous questions still remain unanswered. Inspite of the larger bulk of the tert-butyl groups compared to the mesityl groups [128], disilene **54** is a stable molecule at room temperature, whilst alkyl-substituted disilene **19** only has a half-life of some hours. This phenomenon, as well as the absence of other stable tetraalkyldisilenes (with the exception of **64**) is perhaps due to the different shape of the substituents. Aryl groups can be approximated as disc-shaped and can be arranged around the Si–Si double bond without causing substantial twist. The more spherical-shaped tert-butyl groups can lead to an elongation and twisting of the Si–Si double bond and, therefore, result in the proven high reactivity.

ACKNOWLEDGEMENTS

Financial support of our work from the Deutsche Forschungsgemeinschaft, the Volkswagen-Stiftung, and the Fonds der Chemischen Industrie is gratefully acknowledged. The author is greatly indebted to all collaborators and co-workers, whose names are given in the references, and also to Manuela Rathkamp, for the preparation of the manuscript.

ADDENDUM (September, 1993)

Several pertinent results have appeared since submission of this article. They are listed under the headings where they should be presented in this review.

A. INTRODUCTION

An NMR study of the formation of silyloxonium ions by using tetrakis[3,5-bis(trifluoromethyl)phenyl]borate as a counteranion: M. Kira, T. Hino and H. Sakurai, J. Am. Chem. Soc., 114 (1992) 6697.

Continued search for elusive persistent trivalent organosilyl cations: the claimed trimethylsilyl cation revisited. Attempted preparations of cyclic and halogen-bridged organosilicenium ions: G.A. Olah, G. Rasul, L. Heiliger, J. Bausch, and G.K.S. Prakash, J. Am. Chem. Soc., 114 (1992) 7737.

$[(\pi\text{-Me}_5C_5)_2SiH]^+$ – a novel silyl cation: P. Jutzi and E.A. Bunte, Angew. Chem., 104 (1992) 1636; Angew. Chem. Int. Ed. Engl., 31 (1992) 1605.

Tetrakis(pentafluorophenyl)borate: a new anion for silylium cations in the condensed phase: J.B. Lambert and S. Zang, J. Chem. Soc., Chem. Commun., (1993) 383.

A new weakly coordinating anion: approaching to silylium (silicenium) ion: Z. Xie, D.J. Liston, T. Jelinek, V. Mitro, R. Bau and C.A. Reed, J. Chem. Soc., Chem. Commun., (1993) 384.

The crystal structure of $[Et_3Si^+][B(C_6F_5)_4^-]\cdot 2$ toluene has been determined. The shortest Si–C bond distance between the presumed cation and one of the toluene molecules is 218 pm, but the toluene ring is not distorted and is close to planar. The average C–Si–C angle within the "cation" is 114°, rather than 120°: J.B. Lambert, S. Zhang, C.L. Stern and J.C. Huffman, Science, 260 (1993) 1917. On the basis of the structural data, the molecule is viewed as a σ-complex between the triethylsilyl unit and the toluene molecule: Y. Apeloig, Xth International Conference on Organosilicon Chemistry, Poznan, Poland, August 1993.

B. SILYLENES

(i) Synthesis

The first stable silylene, 1,3-di-tert-butyl-1,3-diaza-2-sila-cyclo-4-pentene has been obtained: M. Denk, R. Lennon, R. West, P. Kiprof and M. Wagner, Xth International Conference on Organosilicon Chemistry, Poznan, Poland, August 1993, using a route that had been successfully employed for the synthesis of stable germylenes: W.A. Hermann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock and M. Wagner, Angew. Chem., 104 (1992) 1489; Angew. Chem. Int. Ed. Engl., 31 (1992) 1485.

(ii) Addition and cycloaddition reactions

Photolysis of hexamethyl-2,2-dimesityltrisilane in the presence of *N*-arylpyridine-2-aldimines (aryl = mesityl, 2,4,6-triisopropylphenyl) results in insertion of a silylene into the C–H bond of the acyclic C–N group together with the [4+1]-cycloaddition products: M. Weidenbruch, H. Piel, A. Lesch, K. Peters and H.G. von Schnering, J. Organomet. Chem. 454 (1993) 35; M. Weidenbruch, H. Piel, K. Peters and H.G. von Schnering, Organometallics, 12 (1993) 2881. With heating, the insertion products rearrange into the unexpected 1,3-diaza-2-sila-cyclo-4-pentene derivatives.

C. STABLE AND NEARLY STABLE DISILENES

(i) Synthesis

New 2,4,6-triisopropylphenyl-substituted disilenes (including the first silyl-substituted disilenes): R.S. Archibald, Y. van den Winkel, J. Millevolte, J.M. Desper and R. West, Organometallics, 11 (1992) 3276.

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(ii) Chemical properties

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