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Synthesis of homo- and heterocyclic silanes via intermediates with Si=Si bonds*

Kai Abersfelder and David Scheschkewitz[‡]

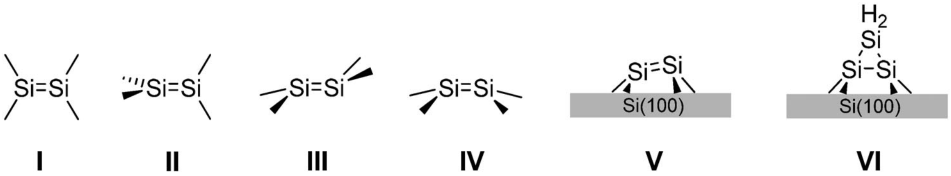
Department of Chemistry, Imperial College London, Exhibition Road, London SW7 2AZ, UK

Abstract: An account is given of our efforts in the synthesis of homo- and heterocyclic silanes via occasionally stable unsymmetrically substituted disilene intermediates of the $A_2Si=Si(A)B$ type that are accessible from a disila analog of a vinyl lithium. This approach is particularly powerful in the preparation of three-membered rings such as cyclotrisilanes with a residual functionality that can be either electro- or nucleophilic in nature and can even give rise to ring-expanded products with preserved Si=Si moiety. The intermediacy of transient silylenes in some of these transformations is discussed as well as the structural effects of the electronic properties of the residual functional group. The relevance of these studies for the understanding of Si(100) surface annealed species during the epitaxial growth of elemental silicon is pointed out, and the potential of the methodology for the synthesis of unusual polycyclic silicon clusters is noted.

Keywords: disilenes; heterocycles; silicon; small rings; tin.

INTRODUCTION

Stable disilenes, i.e., compounds with kinetically or thermodynamically stabilized Si=Si bonds [1], have been intensely studied since the isolation of the first example by West, Michl, and Fink in 1981 [2]. The development was driven by the fundamental interest in the Si=Si bond as well as its physical and chemical properties. As documented by X-ray diffraction studies, the Si=Si bond exhibits a high degree of conformational flexibility (Scheme 1) resulting in planar (**I**) [3], twisted (**II**) [4], *trans*-bent (**III**) [5], and slightly *cis*-bent conformations (**IV**) [6].



Scheme 1 Conformations of disilenes **I** to **IV**, the "buckled dimer" of the Si(001)-2x1 surface **V** and a possible surface intermediate **VI** of CVD of silicon from silanes.

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[‡] Corresponding author: d.scheschkewitz@imperial.ac.uk

Especially the *cis*-bent conformation **IV** has been proposed as a model for the reconstructed Si(001)-2x1 surface and its most prominent feature, the so-called "buckled dimer" **V** [6], which essentially consists of a Si=Si bond with an electrophilic atom pointing downwards and a nucleophilic atom pointing upwards [7]. In principal, however, the mentioned shallow energy profile should render all stable disilenes suitable models for **V**. As such, stable disilenes can exemplify and elucidate fundamental chemical processes taking place on the Si(001) surface by allowing for the direct observation and structural characterization of suitable model compounds for transient or analytically elusive surface-bonded species. Incidentally, the recently reported product of the reaction of a stable trisila allene with acetone [8] plausibly reiterates the proposed mechanism of the chemisorption of the same reagent to the Si(001)-2x1 surface [9].

As concerns the epitaxial growth of elemental silicon from the chemical vapor deposition (CVD) of silanes, the formation of a surface-annulated cyclotrisilane **VI** from the "buckled dimer" **V** and a silylene fragment (:SiH_2) was shown to be a pivotal process by means of a computational study [10]. To the best of our knowledge, however, **VI** has never been observed experimentally. In addition, according to theoretical calculations, cyclic Si_3 motifs are ubiquitous in partially hydrogenated silicon clusters ranging from the molecular level [11a] to the nanometer regime [11b]. Such highly unsaturated clusters have been detected by mass spectroscopy after the flash pyrolysis of silanes and have consequentially been implicated in the formation of elemental silicon by CVD techniques [11c]. Due to their relatively large highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) distances silicon cluster with or without unsaturated valencies are also thought to be the band-gap determining species in amorphous or porous silicon films [11d].

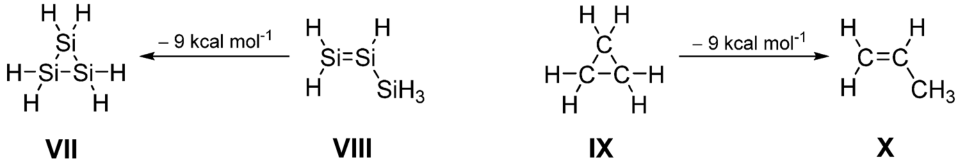
The aim of the present account is to provide the perspective of synthetic preparative chemists on these technologically important processes and species. How can preparative disilene chemistry contribute to the understanding of the structure and formation of preparatively or analytically elusive gas-phase or surface-bound motifs? As will be detailed in the following, the unique reactivity of novel functional disilene derivatives allows for first glimpses into an otherwise largely inaccessible structural realm.

DESYMMETRIZATION STRATEGY

The vast majority of the three-membered cyclic moieties encountered in small silicon clusters or surface annulated species are by virtue of their coordination environments (bulk or cluster bonds vs. Si–H or "dangling" bonds) nonsymmetric to at least some extent. Most conventional synthetic approaches to stable molecular cyclotrisilanes, however, tend to favor symmetrical structures since they employ starting materials that contain only one of the three silicon atoms of the cyclic product, such as monosilanes [12]. The use of two or even three different monosilanes in order to obtain unsymmetrical substitution patterns under these reaction regimes inevitably leads to very low yields and complicated product mixtures. In order to model these gas-phase and surface-bonded species in a preparative fashion, an unsymmetrical synthetic approach was thus desirable.

A closer look at the potential energy surface, i.e., the thermodynamic stability, of the parent cyclotrisilane **VII** is instructive in this regard. Notably, cyclotrisilane **VII** is about 9 kcal mol^{-1} lower in energy than silyl disilene **VIII**, thus reversing the thermodynamics of the analogous carbon case with cyclopropane **IX** being by approximately the same amount less stable than propene **X** (Scheme 2) [13].

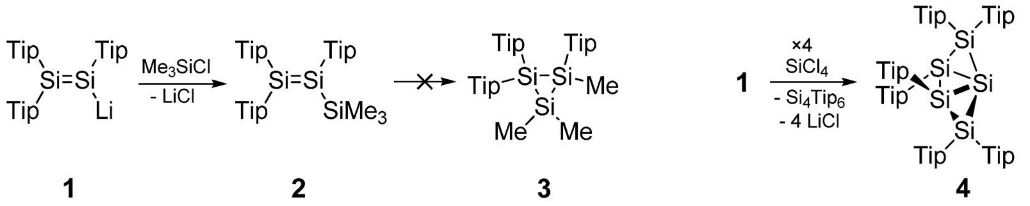
The recently reported functional disilenes with either a nucleophilic [14] or an electrophilic sp^2 silicon atom [15] offered a retro-synthetic handle on substituted derivatives of **VIII** that on grounds of the respective stabilities of the parent compounds could reasonably be expected to isomerize to the corresponding cyclotrisilanes. They were thus granting an access to the desired three-membered ring motifs that clearly held the potential to sustain a symmetry-breaking substitution pattern in the cyclotrisilanes, because of the consecutive expansion of the silicon framework. The starting point of our investigations was therefore our triaryl-substituted disilenide **1** [14a], the first structurally characterized



Scheme 2 Approximate energy difference between unsaturated and cyclic derivatives of the general formula E_3H_6 with E = C, Si (a negative sign denotes an exothermic process) [13].

disila analog of a vinyl lithium, the reactivity of which we recently reviewed in the broader context of other anionic reagents with silicon containing double bonds [16].

Initially, we reacted **1** with Me_3SiCl affording the trimethylsilyl-substituted disilene **2** in near quantitative yield (Scheme 3) [14a]. As it turned out, however, a rearrangement to the envisaged isomeric cyclotrisilanes, e.g., **3**, did not occur. Our later report on the preparation of the stable silicon cluster **4** with a substituent-free vertex, prepared by reaction of disilenide **1** with tetrachlorosilane [17], provided a hint toward the reason for the failure of **2** to isomerize by indicating that the presence of residual functionality may be crucial to effect the cyclization of the $A_2Si{=}Si(A)B$ disilene species. Notably, **4** constitutes a tricyclic system based on Si_3 motifs, which bears a certain resemblance to partially hydrogenated silicon clusters in that it features vertices with either one, two, or no substituent at all [11]. Preparative results on the formal expansion on the silicon framework have just been published elsewhere [18].



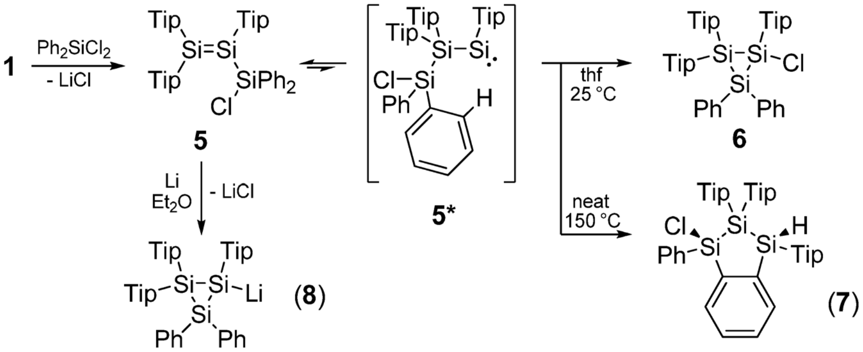
Scheme 3 Synthesis of monosilyl disilene **2** [14a], its failure to rearrange to cyclotrisilane **3**, and preparation of tricyclic Si_5-cluster with an unsubstituted vertex **4** [17] (right, Tip = 2,4,6-$^{i}Pr_3C_6H_2$).

In view of these preparative findings and keeping in mind that halogene functions can usually be readily removed by means of reduction (e.g., with alkaline and earth alkaline metals), we then focused on the reactivity of **1** toward chlorosilanes with at least one residual functionality, in general, an additional chloro group. In the following, we give an account of our published results in this regard including those concerning unsaturated heterocyclic silanes as well as tin-containing species.

CYCLOTRISILANES FROM SILYL DISILENES

The reaction of disilenide **1** with one equivalent of Ph_2SiCl_2 affords the orange chlorosilyl disilene **5** in quantitative yield [19]. While **5** is indefinitely stable in the solid state as well as in solution in non-donating solvents at room temperature, it isomerizes in the presence of tetrahydrofuran (THF) at 25 °C to the corresponding pale yellow chloro cyclotrisilane **6** (Scheme 4). Conversely, keeping neat **5** for 30 min above its melting point (150 °C) results in the essentially quantitative formation of the colorless 1,2,3-trisilaindane **7**.

The apparent changes in substitution pattern between the two products **5** and **7** (the $SiTip_2$ moiety in **7** is situated between the two remaining silicon atoms rather than being in a terminal position as



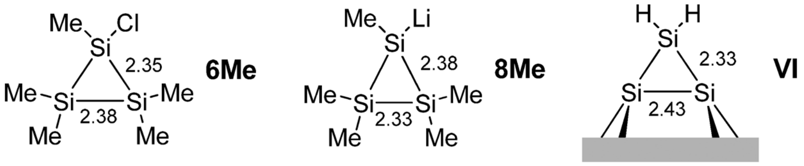
Scheme 4 Synthesis and reactivity of chlorosilyl disilene **5**: rearrangements affording cyclotrisilane **6** and 1,2,3-trisilaindane **7**, respectively; reduction with lithium to cyclotrisilanide **8** (Tip = 2,4,6-$^i Pr_3C_6H_2$) [19].

in **5**) lead us to suggest the intermediacy of a disilanyl silylene **5***, which we postulated would be generated from **5** in small quantities by a presumably reversible 1,2-silyl shift (Scheme 4).

In fact, the hydrogen-substituted parent of **5*** has been calculated to be only about 10 kcal mol^{-1} higher in energy than **VII** (see Scheme 2) [20]. Incidentally, a high-level computational study of the cyclopropane–propene interconversion, i.e., the corresponding carbon case, predicted the kinetic competitiveness of an analogous pathway involving propylidene [13b]; a prediction that was recently confirmed by isotopic marking experiments [21]. In case of the rearrangements of silyl disilene **5**, the taming of the postulated transient silylene **5*** by THF coordination to the vacant p_z orbital would nicely explain the preference of Si–Cl over C–H insertion, yielding **6** under the indicated milder conditions.

It is interesting to note that upon reduction of **5** with elemental lithium no evidence for the intermediacy of an open-chained trisila analog of allyl anions could be obtained and the lithio cyclotrisilane **8** was isolated as the only detectable product. The comparison of the solid-state structures of chlorinated **6** with that of its lithiated counterpart **8** revealed a strong structural influence of the functional group [19]. While the electropositive lithium in **8** considerably shortens the opposing Si–Si bond of the cyclotrisilane motif, the electronegative chlorine lengthens the corresponding bond in **6**. Conversely, the effect on the Si–Si bonds adjacent to the functional group follows the opposing trend: the bond distance is shortened with increasing electronegativity of the group. This observation is in line with Bent's rule that the s-character of a bond decreases with increasing electronegativity [22]. A lower s-character of the bond to the functional group allows for higher s-contributions within the ring and therefore less bent and thus shorter endocyclic bonds.

These findings were reproduced by density functional theory (DFT) calculations on permethylated model systems **6Me** and **8Me** (Scheme 5) and rationalized on grounds of simple MO considerations as well as analysis of Wiberg bond indices [19]. Although other contributing factors such as large angular strain are without doubt contributing as well to some extent, the structure of the Si(100) surface annulated cyclotrisilane **VI** with its two strongly differing Si–Si bond distances calculated by



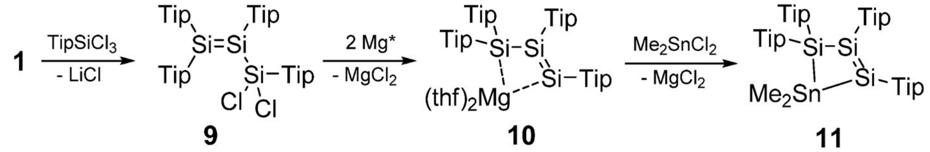
Scheme 5 DFT-calculated endocyclic bond lengths in Å of methylated model compound **6Me** and **8Me** [19] in comparison with Si(100) surface annulated cyclotrisilane **VI** [10].

Hong and Chou fits nicely into this explanation in view of the higher electronegativity of hydrogen compared to silicon [10].

It should be noted that a series of compounds analogous to **5**, **6**, and **8** was also synthesized starting from **1** and Me_2SiCl_2, thus hinting at the potentially general importance of these transformations [19]. In fact, the relevant compounds **VII**, **VIII**, as well as the hydrogen-substituted parent of the transient silylene intermediate **5*** have been implied in the gas-phase particle nucleation during the CVD of silanes by Swihart and Girshick [23].

A DICHLOROSILYL DISILENE AND A TRISILENDIIDE

Residual functional groups are pivotal to our research program in both the unsaturated and cyclic homonuclear silicon compounds, because of the thus conferred potential to extend the silicon backbone by standard preparative manipulations. To increase the number of functional groups available to this end, we investigated the reactivity of **1** toward trichloro silanes. Indeed, reaction of **1** with $TipSiCl_3$ afforded the dichlorosilyl disilene **9** (Scheme 6) [24].



Scheme 6 Synthesis of dichlorosilyl disilene **9**, its reduction to the magnesium salt of a trisilendiide **10** and derivatization of **10** to the tin-containing unsaturated heterocyclic silane **11** (Tip = 2,4,6-$^iPr_3C_6H_2$) [24].

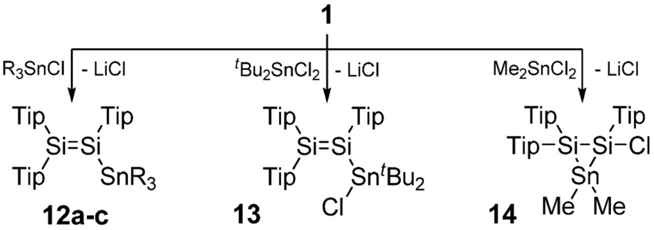
Presumably due to the bulkiness of the additional Tip group, **9** failed to undergo cyclization to the corresponding dichloro cyclotrisilane, which prompted us to subject it to an excess of activated magnesium [25] in THF in order to induce cyclization reductively (cf. the ease of cyclization of **5** to **8** upon reduction with lithium). The only reaction product detectable by NMR was the magnesium trisilendiide **10**, which could be isolated as red–orange crystals suitable for X-ray analysis. The unperturbed Si=Si bond length of 219.8 pm and the absence of a red-shift of the longest wavelength UV–vis absorption at 415 nm in comparison to **1** implies that no significant charge delocalization is active in **10**. The formal presence of two negative charges in the trisilendiide moiety of **10** and the resulting Coulomb repulsion served as rationalization of these findings [24].

Reaction of **10** with Me_2SnCl_2 afforded the four-membered unsaturated heterocyclic silane **11**, which, in the absence of information on its solid-state structure, was identified by multinuclear NMR spectroscopy, taking particular advantage of its diagnostic $^{117/119}Sn/^{29}Si$ coupling patterns [24]. Formation of **11** can be regarded as proof-of-principle for the suitability of **10** for the expansion of the unsaturated scaffold based on heavier group 14 elements by employment of the residual functionality. Future investigations involving **11** will aim at the homonuclear expansion of the silicon scaffold, e.g., by its reaction with silicon tetrachloride.

STANNYL DISILENES AND A DISILASTANNIRANE

The synthesis of **11** demonstrated that at least one tin atom is readily tolerated directly adjacent to a Si=Si double bond. Therefore, we included the preparation of simple monostannyl-substituted disilenes into our investigations in order to extend the concepts established for the homonuclear case to heterocyclic examples. It was anticipated that the presence of the tin atom may actually increase the tendency to isomerize to the corresponding heteronuclear three-membered rings, namely, disilastanniranes, which, much like their designated precursors, had not been reported previously.

Indeed, the reactions of **1** with a range of selected chlorostannanes R_3SnCl generally proceeded in a quantitative manner, affording thermally stable stannyl-substituted disilenes **12a–c**. Similar to the case of the nonfunctional silyl disilene **2**, no traces of any rearrangement products were observed even upon melting of **12a–c** (Scheme 7) [26].



Scheme 7 Reactivity of disilenide **1** toward R_3SnCl, ${}^tBu_2SnCl_2$, and Me_2SnCl_2 (R = Me (**12a**), Bu (**12b**), Ph (**12c**); Tip = 2,4,6-${}^iPr_3C_6H_2$) [26].

As concerns the use of dichloro stannanes as electrophiles toward **1**, we abstained from a more excessive variation of the substituent R and limited the study to one bulky and one sterically innocent group. Reaction of **1** with ${}^tBu_2SnCl_2$ thus afforded the red–orange chlorostannyl disilene **13** in 59 % isolated yield. Conversely, treatment of a 1.8-fold excess of Me_2SnCl_2 with **1** gave the disilastannirane **14** as a colorless crystalline solid in 21 % yield [26].

Even though a number of unidentified side products were formed in the case of **14**, its formation serves as proof-of-principle and future investigations aim at the study of the reactivity of **1** toward trichlorostannanes and tetrachlorostannane.

CONCLUSION

Aside from their possibly most important application as transfer reagents for Si=Si double bonds to organic substrates [14h,27], which is, however, outside the scope of this overview, the unique reactivity of disilenides such as **1** offers considerable potential for the synthesis of stable model compounds for otherwise elusive gas-phase and surface-bound species. The structural characterization of symmetry-broken functional cyclotrisilanes thus obtained neatly demonstrates the strong dependence of geometrical parameters on the electronic nature of the substitution pattern (or coordination environment) of cyclic Si_3 motifs. Applying the same synthetic principles, heteroatoms such as tin are readily incorporated into the silicon scaffold. The study of the reactivity of **1** and other disilenides as well as the elucidation of reaction mechanisms by the isolation of intermediates provides corroboration for the corresponding processes in the gas phase and may well serve as inspiration for modified mechanistic views.

By increasing the degree of residual functionality in the substituent B of the transient or stable disilenes of the $A_2Si{=}Si(A)B$ type, an extension of the concept toward expanded unsaturated rings and polycyclic silicon clusters is readily possible. The latter compounds exhibit structural features that strongly resemble those of calculated species relevant to the formation and structure of amorphous or porous silicon.

In conclusion, the scope of functional disilenes as preparative model systems in the context of silicon materials is considerable at this early stage of developments already and without doubt will be further extended in the near future.

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