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Account

The quest for triplet ground state silylenes

Peter P. Gaspar *, Manchao Xiao, Dong Ho Pae, Daniel J. Berger, Tesfamichael Haile, Tongqian Chen, Deqing Lei, William R. Winchester, Ping Jiang

Department of Chemistry, Washington University, One Brookings Drive, Campus Box 1034, St. Louis, MO 63130-4899, USA

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Abstract

The scarcity of triplet silylenes compared with triplet carbenes can be understood in terms of the sizes of the valence orbitals. The larger size of the silicon orbitals leads to a decrease in the repulsion of the nonbonding electrons in the singlet state and hence their energy-lowering separation in the triplet state is less capable of compensating an attendant promotion energy. Calculations suggested that the effect of bulky substituents must be supplemented by a reduction of their electronegativity in order to reduce the promotion energy to the point that a triplet ground state can be achieved at an attainable bond angle. The culmination of this approach has been the generation of a silylene $(t\text{-Bu})_3$Si–Si–Si$(i\text{Pr})_3$ that appears to react from its triplet ground state. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silylene; Triplet ground state; Reaction mechanisms; Photochemistry; Organosilicon chemistry

Mechanistic differences between the lighter elements of organic chemistry and the heavier elements that are the province of main-group chemistry have long interested the Gaspar group. The study of reactive intermediates like carbenes and their analogs has played an important role in this work. The reactions of these short-lived species are so distinctive that gross differences in mechanisms and reactivity can be deduced from product studies even before formal mechanistic investigations have begun. Here, we examine a dramatic difference between carbenes and silylenes. Carbenes are found with both singlet and triplet ground electronic states, each with a distinctive chemistry [1]. The novelty of such 'electronic isomers' that are nearly degenerate while differing in geometric and electronic structure as well as in their reactivity has attracted many chemists to the study of carbenes since the 1950s. But only singlet silylenes are well-documented.

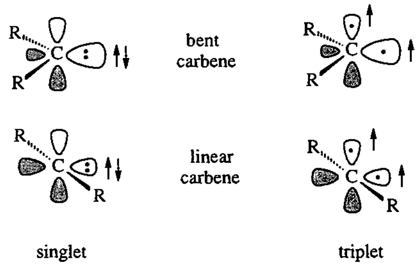

Fig. 1. Schematic representations of the lowest energy singlet and triplet electronic states of carbenes.

A brief review of carbene structures, Fig. 1, is important background for our story.

It has been known for nearly half a century that the lowest singlet and triplet states of carbenes can have nearly equal energies [1]. This is quite understandable for bent carbenes, since separation of the nonbonding electrons requires promotion of an electron from an s-weighted hybrid orbital to a pure 2p atomic orbital. But this one-electron promotion energy is counteracted by a decrease in the electron–electron repulsion of the nonbonding electrons when they are placed in separate orbitals. For the majority of carbenes that are bent, the energy lowering associated with separating the lone-pair electrons can outweigh the one-electron energy increase that attends its movement from an s-weighted orbital to one that is pure p.

Clearly, the geometry of a carbene makes a difference. For a linear carbene the nonbonding orbitals would be degenerate and the triplet state lower in

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* Corresponding author. Tel.: +1-314-935-6568; fax: +1-314-935-4481.

E-mail address: gaspar@wuchem.wustl.edu (P.P. Gaspar).

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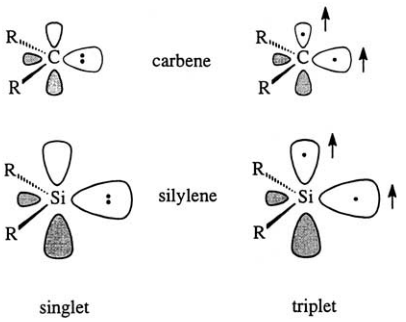


Fig. 2. Schematic comparison of the sizes of the nonbonding orbitals.

energy than the singlet, since there is no energetic price to be paid for the separation of the unshared electrons.

Given the diradical nature of triplet carbenes, with single electrons inhabiting orthogonal orbitals, it is not surprising that their chemistry is quite different from that of their singlet siblings [1]. Singlet carbenes undergo concerted insertion into C–H bonds and concerted addition to the lone pairs of hetero-atoms and to π-bonds. Triplet carbenes undergo free radical-like atom abstraction and π-bond addition processes. Even when similar products are formed, different mechanisms operate [1]. CIDNP signals revealed that formation of a product of formal insertion by triplet CH_2 into a benzylic C–H bond of toluene occurs in a stepwise manner, radical coupling following hydrogen abstraction [2]. The same product, ethylbenzene, is formed by direct insertion of singlet CH_2. Some 45 years ago Skell predicted that triplet carbenes would add to olefins to give mixtures of diastereomers rather than undergoing the stereospecific addition associated with singlet carbenes [3].

Considerable recent effort has gone into making carbenes as unreactive as possible [4]. Bertrand [5] and Arduengo [6] have made and isolated a number of molecules that they designate as 'stable carbenes.' These are singlet states, and display some reactions expected of carbenes, [7] but the extent to which contributions of trivalent zwitterionic resonance structures compromise their status as carbenes is not entirely clear [8]. Tomioka [9] has increased the lifetime of triplet diarylcarbenes to the point that they can certainly be described as persistent ($t_{1/2}$ up to 19 min. at room temperature) [10]. For these species too questions arise regarding contributions from diradical resonance structures in which the carbenic carbon is converted to the central atom in an allene unit [11].

With this background, the quest for triplet silylenes can be described. Why might it be of interest? The trivial Mount Everest aspect of the problem aside—no one has previously demonstrated the formation of a triplet silylene—if they can be made, then one may be able to test the ideas about why they have been so elusive. This would hone the predictive capabilities of physical organic chemists. Given the distinctive differences between the chemistry of singlet and triplet carbenes, exploring the chemistry of triplet silylenes may uncover interesting new chemistry. Even if the chemical differences between triplet and singlet silylenes turn out to be small, one will have learned something important about differences between the covalent chemistry of the first and second row. Another aspect of this quest is related to synthesis—without the development of methods for the formation of highly congested silicon–silicon bonds, the quest could not succeed.

A schematic comparison between silylenes and carbenes, Fig. 2, offers an explanation for the scarcity of triplet silylenes. The larger size of the valence orbitals of silicon in comparison with those of carbon leads to a decrease in the electron–electron repulsion of the lone pair of the singlet silylene. This in turn attenuates the lowering of energy upon separating these electrons in the triplet state. But it is this decrease in electron–electron repulsion that must compensate for the energy increase upon promoting a nonbonding electron from a hybrid orbital to a pure 3p-orbital, if the ground state is to be a triplet. Thus, for a 'normal' silylene, the ground state is a singlet, because, the separation of the nonbonding electrons necessary to attain the triplet configuration requires an increase in energy larger than the accompanying decrease in electron–electron repulsion. Since there is nothing that one can do about the size of an orbital, the only factor that can be controlled is the promotion energy. The promotion energy can be reduced by making the two nonbonding orbitals as similar as possible.

In 1984 [12], we suggested that a fruitful approach to triplet ground states might be the generation of silylenes with such bulky substituents that the bond angle would be greatly enlarged from the 92° found for SiH_2 [13]. With an increase in the bond angle at the divalent silicon atom, there is an increase in the p-character of the in-plane nonbonding orbital occupied by the unshared electrons of the lowest singlet. This increases the similarity of the nonbonding orbitals and reduces the energy difference between the in-plane nonbonding orbital and the pure 3p out-of-plane orbital, thus decreasing the promotion energy required to reach the triplet configuration.

Our first efforts to prepare a silylene with a triplet ground state were influenced by calculations of Gordon [14]. In Fig. 3 the energies of the lowest singlet and triplet electronic states of the parent silylene SiH_2 are plotted against the H–Si–H bond angle. Given the discussion above, it is not surprising that the singlet state at its equilibrium bond angle of 93° is indeed lower in energy than the triplet state at its most stable bond angle of 120°. What we found interesting is that the singlet and triplet energy curves *cross* at a moderate angle. At angles greater than ca. 125° the triplet is lower in energy than the singlet! A hand-waving explanation points to the change in energy of the unshared electrons as the bond angle increases. The in-plane orbital starts as nearly pure 3s- and increases in 3p-character as the bond angle increases, and thus increases in energy. Since two electrons occupy this orbital in the singlet (cf. Fig. 2), the increase in energy of the singlet state with increasing bond angle will be greater than that of the triplet, which has only one electron in this orbital and another in a pure 3p-orbital whose energy will not vary with bond angle. Similar changes in bond strength with bond order for both states are thus assumed.

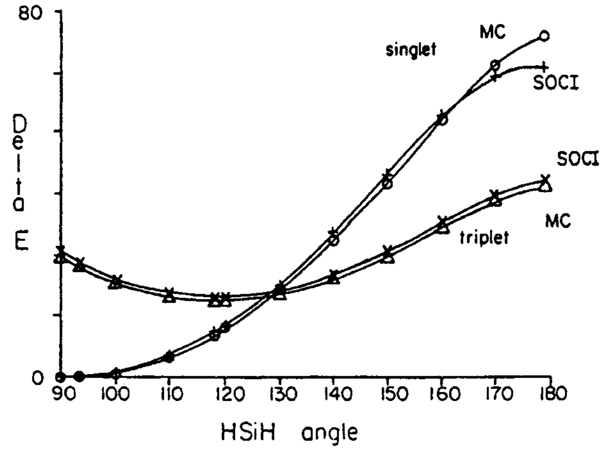


Fig. 3. Multiconfiguration SCF and second order CI potential energy curves for singlet and triplet SiH_2. Relative energies in kcal mol^{-1}, angles in degrees (Gordon, 1985).

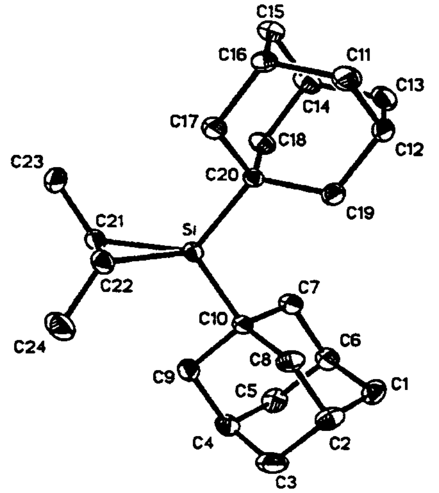


Fig. 4. ORTEP drawing of the X-ray crystal structure of *trans*-1,1-diadamantyl-2-3,dimethylsilirane. Selected bond distances (Å) and angles (°): Si–C(21) 1.866(4); Si–C(20) 1.911(3); C(21)–Si–C(22) 49.5(2); C(10)–Si–C(20) 116.8(1) (Pae, 1991).

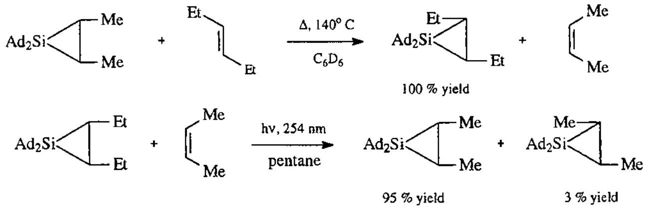


Fig. 5. Stereochemistry of thermally induced extrusion of diadamantylsilylene from a silirane and the stereochemistry of Ad_2Si addition to olefins (representative results Pae, 1991).

If the variation of energy with bond angle for a dialkylsilylene resembled that calculated by Gordon, then one should be able to produce a silylene with a triplet ground state by forcing open the bond angle to greater than 120°. We hoped that the bond angle in diadamantylsilylene Ad_2Si would be opened to the extent that the triplet would be lower in energy than the singlet. Some very primitive calculations had suggested that adamantyl groups might be sufficiently large—126° was the predicted bond angle—and, on that basis, precursors for diadamantyl-silylene were synthesized [15]. Fig. 4 shows a crystal structure of *trans*-1,1-diadamantyl-2,3-dimethylsilirane.

The thermally induced extrusion of silylenes from siliranes had been found by Seyferth in 1975, [16] and in 1988 Boudjouk made the important discovery that silylenes could also be generated from siliranes upon irradiation at 254 nm, even without a chromophore other than the silirane ring [17]. We therefore expected 1,1-diadamantylsiliranes to extrude diadamantylsilylene upon thermolysis and photolysis, and we were not disappointed.

What did disappoint us was the stereospecific addition to olefins by diadamantylsilylene, as seen in Fig. 5. We recall that triplet carbenes undergo nonstereospecific addition to *cis*-olefins, while singlet carbenes add stereospecifically [1]. The empirical generalization known as the 'Skell rule' [3] that predicted such results led to the expectation that triplet silylenes would also undergo nonstereospecific addition.

These results and our inability to detect a triplet ESR signal from attempts to generate diadamantylsilylene in a frozen glass convinced us that either we had overestimated the C–Si–C bond angle for diadamantylsilylene, or the assumption that the potential surfaces for the lowest singlet and triplet states of diadamantylsilylene would resemble those of parent SiH_2 was incorrect. Both of these turned out to be the case. For the singlet silylene Ad_2Si the bond angle predicted by an STO-3G geometry optimization is only 106.8°, [18] well below the 'crossover angle' predicted by Gordon for SiH_2.

But there is more. Grev and Schaefer carried out ab initio calculations (two configuration SCF with a 6-31G* basis set) on dimethylsilylene $(CH_3)_2Si$ and disilylsilylene $(SiH_3)_2Si$ (Fig. 6) [19]. The curves have the same shapes as Gordon's results for SiH_2, and the ground state is still a singlet, but for $(CH_3)_2Si$ the 'crossover angle' is at a much larger value, 140°, com-

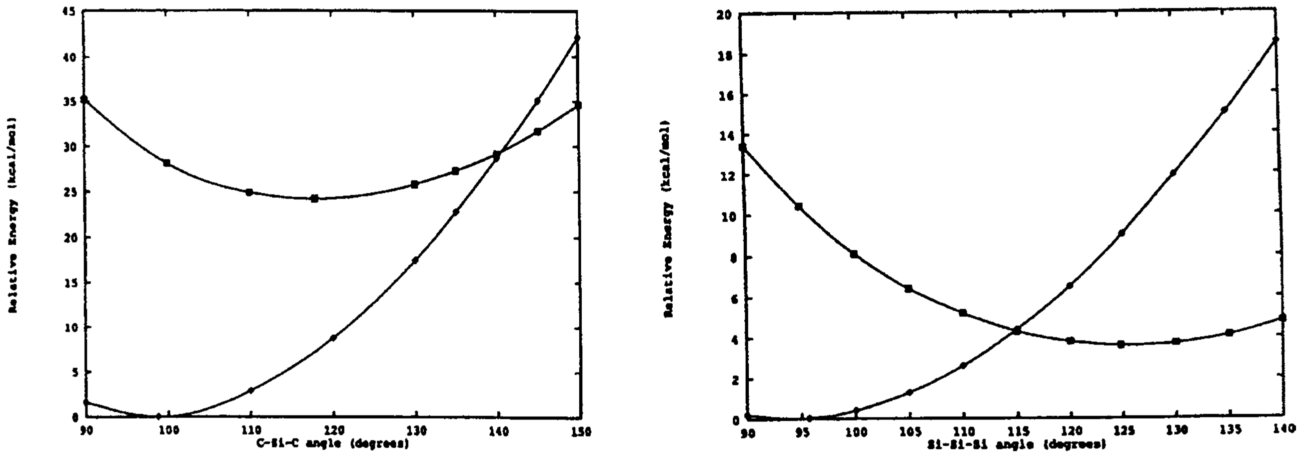


Fig. 6. Potential energy curves for $(CH_3)_2Si$ (left) and $(SiH_3)_2Si$ (right) $^3B_1$ (□), $^1A_1$ (◆) (Grev, 1991).

pared with 125° for SiH_2. The difference is due to the strong influence of the electronegativity of the substituents at the divalent silicon atom on the energy of the in-plane nonbonding orbital. Carbon is more electronegative than hydrogen, and the crossover angle is greater.

With substituents *less* electronegative than hydrogen, such as silyl groups, the crossover angle *decreases* to less than 120°. That provided a clue as to how to design a triplet ground state silylene. The strategy is explained schematically in Fig. 7. The promotion energy necessary to change the electronic configuration of a singlet silylene to that of a triplet decreases with increasing p-character of the in-plane nonbonding orbital, which in turn increases with increasing bond angle *and* with decreasing electronegativity of the substituents. At any bond angle, a decrease in the electronegativity of the substituents increases the s-character of the atomic orbital on the silicon employed to form the σ-bond.

It was predicted, on the basis of semiempirical MO calculations, [20] that triisopropylsilyl iPr$_3$Si substituents would be the smallest that would open the bond angle to the 'crossover angle' for bis-silylsilylenes predicted by Grev. This prediction has been supported by density functional calculations by Apeloig on the $(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{Si}$, but the resulting singlet-triplet energy difference is uncomfortably small at 1.7 kcal mol^{-1} [21]. Bis(tri-*tert*-butylsilyl)silylene $(t\text{-}\mathrm{Bu}_3\mathrm{Si})_2\mathrm{Si}$ has a much larger energy difference between the lowest singlet state and the ground triplet state, 7.1 kcal mol^{-1}, [21] but presented a synthetic challenge with which we were not ready to cope a decade ago.

Having decided that $(i\mathrm{Pr}_3\mathrm{Si})_2\mathrm{Si}$ was a good candidate for a ground state triplet silylene, we were content to let other groups attempt the synthesis of an appropriate precursor for this sterically congested silylene. But after several years of being asked how we were doing on the generation of a triplet silylene, we did decide to take an active role. Our first attempt seemed to go awry, since instead of synthesizing a desired dichlorosilane $[(i\mathrm{Pr})_3\mathrm{Si}]_2\mathrm{SiCl}_2$ that could be converted into several silylene precursors, we accidently produced a beautiful, but not obviously relevant molecule, tris(triisopropylsilyl)silane (Fig. 8) [18]. The central silicon is seen to be nearly coplanar with the three attached silicon atoms!

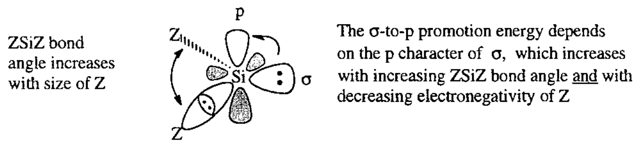


Fig. 7. Effects of bond angle and substituent electronegativity on the promotion energy required for the conversion of a singlet to a triplet silylene.

$$2(i\mathrm{Pr})_3\mathrm{SiK} + \mathrm{SiCl}_4 \xrightarrow[\text{heptane}]{77\text{ K to rt}} ? \xrightarrow[\text{pentane}]{-10\ ^\circ\mathrm{C}} (i\mathrm{Pr})_3\mathrm{SiSi}(i\mathrm{Pr})_3 + [(i\mathrm{Pr})_3\mathrm{Si}]_3\mathrm{SiH}$$

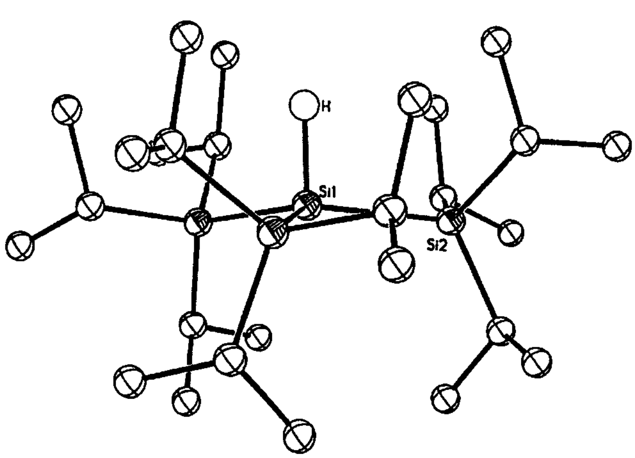


Fig. 8. Serendipitious synthesis of tris(triisopropylsilyl)silane $[(i\mathrm{Pr})_3\mathrm{Si}]\mathrm{d}_3\mathrm{SiH}$ and its neutron diffraction structure, r(Si–Si) = 2;398(2) Å, r(Si–H) = 1.506(2) Å, ∠Si–Si–Si = 118.41(5)°, ∠Si–Si–H = 97.30(9)° (Gaspar, 1999).

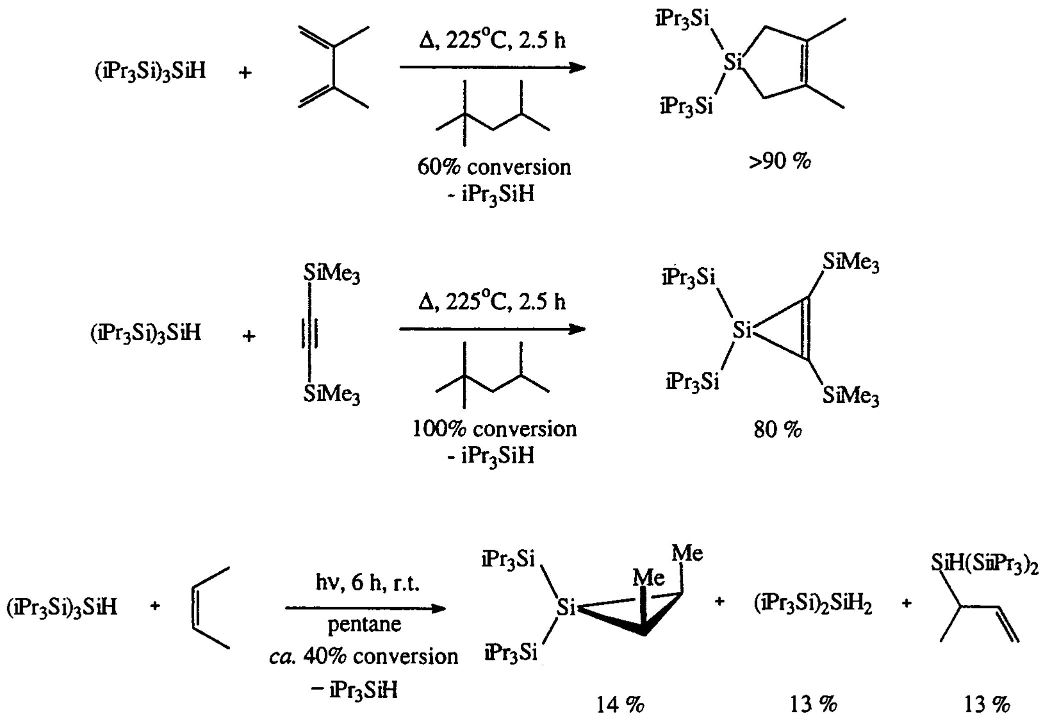


Fig. 9. Addition products from (iPr$_3$Si)$_2$Si formed by pyrolysis and photolysis of (iPr$_3$Si)$_3$H.

This is another example of the bending of silicon–silicon bonds to reduce congestion being more prominent than bond-stretching. The enlargement of the bond-angle caused by the triisopropylsilyl groups was encouraging with regard to the prospects of the (iPr$_3$Si)$_2$Si having a triplet ground state.

This compound did help us make the silylene, as the results in Fig. 9 demonstrate [18]. It was no surprise that pyrolysis of the tris(silyl)silane liberated the desired silylene, since thermally-induced α-eliminations have long served as clean sources of silylenes [22]. Needed for experiments that might reveal the electronic ground state was a precursor for photochemical generation of the silylene, but photochemical generation of silylenes form oligosilanes is expected to favor the elimination of a disilane. It was thus a pleasant surprise when room-temperature irradiation of (iPr$_3$Si)$_3$SiH at 254 nm led to the trapping of the desired silylene. No hexaisopropyldisilane is formed in this photolysis, presumably, because, the silicon atoms of the iPr$_3$Si groups are held too far apart, even in the photoexcited state of (iPr$_3$Si)$_3$SiH, for the concerted elimination to occur via Si–Si bond formation.

The products shown in Fig. 9 convinced us that (iPr$_3$Si)$_2$Si had been generated, but there remained the need to establish its electronic state. The ultimate test for a triplet state is its ESR spectrum, but to record the ESR spectrum one must be able to generate the silylene in a frozen matrix. Our experiences with several precursors for the photochemical generation of the silylene were frustrating, as shown in Fig. 10. Precursors that work splendidly in solution at room temperature, as gauged by the trapping of the silylene by insertion into an H–Si bond, or by addition to π-bonds, *failed* when the irradiation was carried out on an organic glass at 77 K. Either no reaction at all occurred, as was the case with the tris(silyl)silane, or rearrangement took place. Liberation of the silylene at 77 K, as judged by the formation of trapping products when the glass was doped with trapping agent so that thawing it should allow the silylene to react, *failed.*

We, therefore, turned to chemical probes for the triplet state, based on the precedents of carbene chemistry, [1] perhaps not a particularly safe precedent for a group that was searching for possible differences between the chemistry of silylenes and carbenes.

Our expectation that triplet silylenes would show biradical character led us to focus attention on (iPr$_3$Si)$_2$SiH$_2$, a molecule that is formally related to the silylene by the abstraction of two hydrogen atoms and is a minor product from many of the reactions of (iPr$_3$Si)$_2$Si. Since normal singlet silylenes, like singlet carbenes, are not known to abstract hydrogen atoms, but triplet carbenes are known to do so [1], we thought that an increased yield of (iPr$_3$Si)$_2$SiH$_2$, as a byproduct of insertion into a hydrogen–silicon bond might be due to hydrogen abstraction by the silylene, a process plausibly associated with a triplet silylene.

We were again disappointed, since the results shown in Fig. 11 indicate that while the insertion product dutifully incorporates a deuterium atom, the product which we hoped to associate with hydrogen abstraction by the silylene does *not*. We did not think that special pleading—that the hydrogen abstraction has so low a barrier that it is unselective—would convince anyone.

Another possibility for establishing a triplet ground state for $(i\mathrm{Pr_3Si})_2\mathrm{Si}$ involved the stereochemistry of addition of the silylene to *cis*- and *trans*-butene. For triplet carbenes the 'Skell rule' successfully predicted nonstereospecific addition, in contrast to the stereospecific *cis*-addition observed for singlet carbenes [1]. It was found, however, that the addition of $(i\mathrm{Pr_3Si})_2\mathrm{Si}$ is, within experimental error, totally stereospecific, [18] as seen for *cis*-2-butene in Fig. 9. Does this result indicate that the ground state of bis(triisopropylsilyl)silylene is a singlet? No, it does not. One explanation is that the first excited singlet state is more reactive than the triplet, and lies so close in energy to the ground triplet that the triplet is siphoned off by reactions of the singlet. Fig. 12 shows such a reaction scheme.

If the energy difference between the singlet and triplet is the 1.7 kcal mol^{-1} predicted by Apeloig's high level density functional calculations, [21] the equilibrium constant is about 1/50 at room temperature. That means that, if the reactions of the singlet are 500 times as rapid as those of the triplet, more than 90% of the reaction products would come from the singlet, despite a triplet ground state. But for $(t\text{-}\mathrm{Bu_3Si})_2\mathrm{Si}$, with a predicted energy difference between excited singlet and ground-state triplet of 7.1 kcal mol^{-1}, [21] the

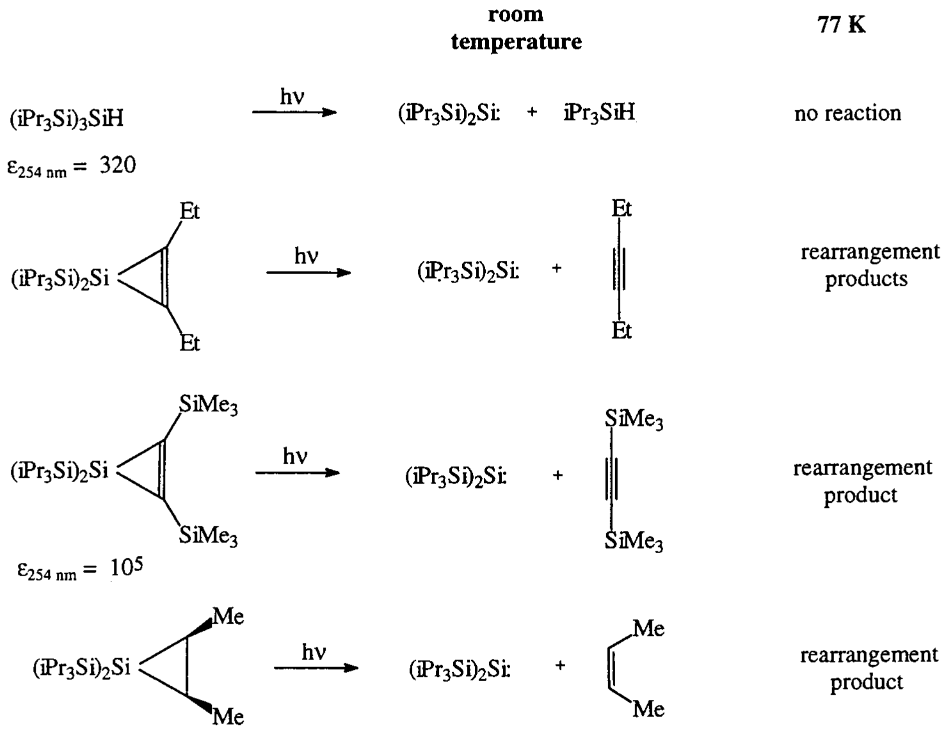


Fig. 10. Photochemistry of bis(triisopropylsilyl)silylene precursors at 77 K vs. room temperature.

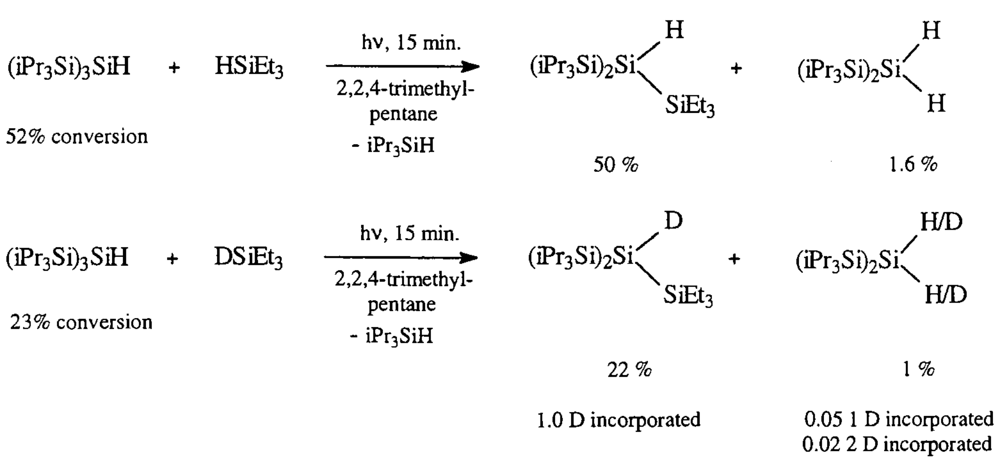
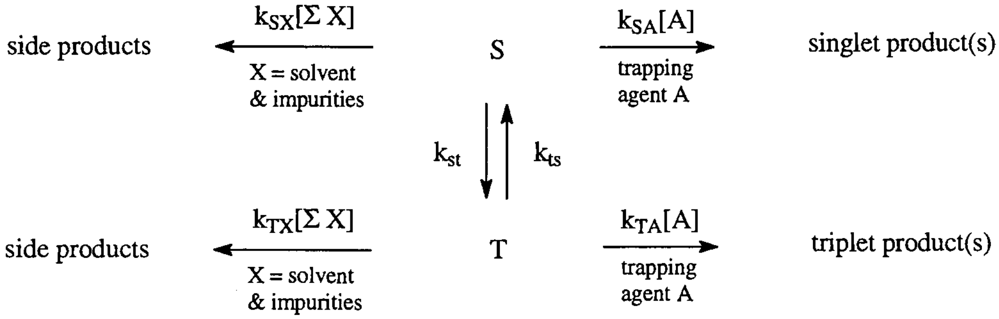


Fig. 11. Products from the photochemical generation of $(i\mathrm{Pr_3Si})_2\mathrm{Si}$ in the presence of triethylsilane.



$$K = k_{ts}/k_{st} = (1/3)\, e^{-\Delta E/RT} = 0.019 \quad \text{at } 25\ {}^{\circ}\text{C for } \Delta E = 1.7 \text{ kcal/mol } (\text{iPr}_3\text{Si})_2\text{Si}$$

$$= 0.0000020 \text{ at } 25\ {}^{\circ}\text{C for } \Delta E = 7.1 \text{ kcal/mol } (\text{tBu}_3\text{Si})_2\text{Si}$$

To observe triplet product(s), k_{TA} must be larger than Kk_{SA}, $Kk_{SX}[\Sigma X]$, $k_{TX}[\Sigma X]$

Fig. 12. Competition between the reactions of an excited singlet state S and a ground triplet state T.

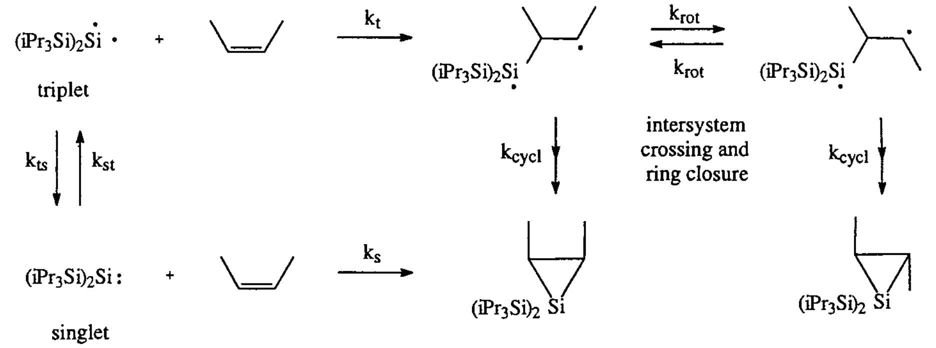


Fig. 13. Stereospecific addition by triplet $(i\text{Pr}_3\text{Si})_2\text{Si}$ if $k_{cyct} \gg k_{rot}$ or if $k_{ts}k_s \gg k_t$.

equilibrium constant is four orders of magnitude smaller, so even a 1000-fold more reactive singlet would account for less than one percent of the product.

There is another, more interesting, explanation for stereospecific addition by a triplet silylene—the possible failure of the Skell rule for elements below the first-row of the periodic table. Fig. 13 reminds us that, for nonstereospecific addition to result from a diradical intermediate in the addition of triplet $(i\text{Pr}_3\text{Si})_2\text{Si}$ to *cis*-butene, rotation around the single bond that was the double bond of the olefin must be rapid relative to intersystem crossing and ring closure. This requirement holds, but just barely, in the case of carbenes [1]. But experiments with β-substituted carbon-centered radicals have indicated that rotation about such a carbon–carbon bond could be significantly slowed by hyperconjugation if the bond to the β-carbon atom is quite polarizable, as is certainly the case for a carbon–silicon bond [23]. Of course, as shown in Fig. 13, siphoning off the triplet silylene via addition of the singlet would also produce stereospecific addition.

The notion that addition of a triplet diradical to an olefin can be stereospecific is not hypothetical. Mesitylphosphinidene Mes-P, is a member of the nitrene family whose triplet ground state has been verified by ESR spectroscopy [24]. For an aryl phosphinidene, the lowest singlet state lies at least 20 kcal mol^{-1} higher than the ground triplet, [25] so there is no chance that the ground triplet is being siphoned off via the lowest singlet state. Yet mesitylphosphinidene adds stereospecifically to *cis*- and *trans*-butene even when it is generated in a frozen glass doped with the olefin and ample time is allowed for relaxation to the ground state before reaction is initiated by thawing the glass [26]!

The chemical evidence for the ground state of bis(triisopropylsilyl)silylene is inconclusive. Of all the precursors to $(i\text{Pr}_3\text{Si})_2\text{Si}$ found to date, only one, $(i\text{Pr}_3\text{Si})_3\text{SiBr}$, has been found to liberate the silylene in a matrix at 77 K (Fig. 14). When the frozen glass was further cooled to the temperature of liquid helium, an ESR signal was recorded with a peak at 9750 Gauss at X-band that could be the long sought proof for a silylene with a triplet ground state [27]. But victory cannot yet be declared. Many artefacts appear in such spectra, and we have been fooled before. Before the triplet silylene is accepted as the source of this signal, the same signal must be found in a series of experiments carried out in different solvents. Even better would be a second or third precursor that gives the same ESR signal.

We decided 2 years ago to focus our resources on a different silylene, one with a larger central bond angle and hence a larger energy difference between lowest singlet state and ground triplet state [28]. A logical choice would seem to have been (t-Bu$_3$Si)$_2$Si, for which calculations by Apeloig had already predicted a healthy 7 kcal mol^{-1} singlet-triplet splitting, some four times as large as that predicted for (iPr$_3$Si)$_2$Si [21]. Attempts have already been made in the Munich laboratory of Nils Wiberg to generate this silylene (Fig. 15).

Treatment of (t-Bu$_3$Si)$_2$SiBr$_2$ with t-Bu$_3$SiNa led to products that were attributed to triplet (t-Bu$_3$Si)$_2$Si [29]. The four-membered ring could arise by insertion of the divalent silicon of the silylene into a C–H bond of a methyl group. That would be particularly interesting for a reaction carried out at room temperature or below, because, singlet silylenes only insert into C–H bonds with substantial activation energies of about 20 kcal mol^{-1} [30,31]. So this could be chemical evidence for a tripet state of (t-Bu$_3$Si)$_2$Si, and that is what Wiberg suggested. Recently Wiberg prepared the monohalo(mono-lithio)silanes (t-Bu$_3$Si)$_2$SiLiX (X = F, Br) and obtained the same products from their thermal decomposition as shown in Fig. 15 [32]. Unfortunately neither the Wiberg nor Gaspar groups have as yet been able to synthesize a precursor that liberates (t-Bu$_3$Si)$_2$Si in a photochemical process, and organometallic reactions like that depicted above are known to proceed through intermediates like (t-Bu$_3$Si)$_2$SiMX that behave as *silylenoids*. That is, they can mimic silylenes without ever becoming free silylenes. Also, all attempts to trap a silylene from this reaction as an intermolecular addition or insertion process have failed. So that even if free (t-Bu$_3$Si)$_2$Si was formed, attempts to learn about its chemistry may be frustrated by the same steric congestion that opened up its bond angle and imposed on it a triplet ground state.

We sought a silylene with a triplet ground state whose intermolecular reactions could be studied. Our new target was tri-*tert*-butylsilyl(triisopropylsilyl)silylene (t-Bu)$_3$Si–Si–Si(iPr)$_3$ [33]. The preparation of the key synthetic precursor is shown in Fig. 16.

A useful synthetic generalization was learned in the course of this synthesis. If one uses such a salt-elimination reaction to form a sterically hindered silicon–silicon bond, the more hindered reaction partner should be the nucleophile [34].

The data of Fig. 17 encouraged the hope that (t-Bu)$_3$Si–Si–Si(iPr)$_3$ would have a central bond angle and a singlet-triplet splitting intermediate between the values for (iPr$_3$Si)$_2$Si and (t-Bu$_3$Si)$_2$Si. It is seen that the Si–Si–Si bond angle in the model compound t-Bu$_3$Si(iPr$_3$Si)SiBr$_2$ is intermediate between that of (iPr$_3$Si)$_2$SiBr$_2$ and (t-Bu$_3$Si)$_2$SiBr$_2$. It was our prediction that (t-Bu)$_3$Si–Si–Si(iPr)$_3$ would be capable of intermolecular chemistry while possessing a sufficiently large singlet-triplet splitting to undergo reactions from its triplet ground state.

As shown in Fig. 18, reactions of t-Bu$_3$Si(iPr$_3$Si)SiBr$_2$ employing activated magnesium and reagents derived

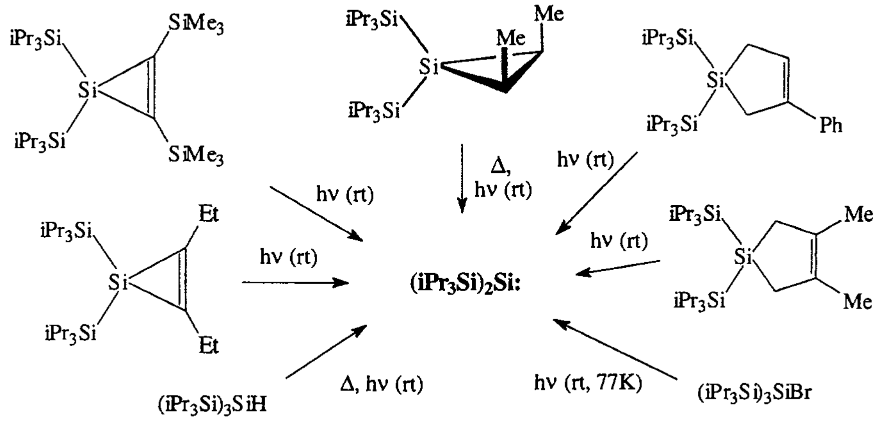


Fig. 14. All precursors of bis(triisopropylsilyl) silylene known to July, 2001.

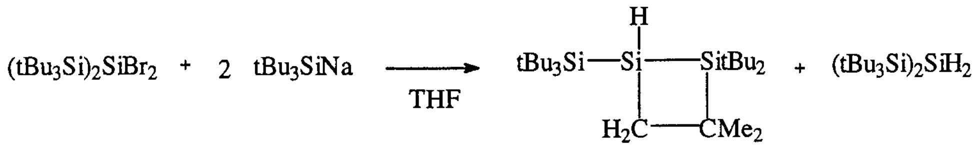


Fig. 15. Reductive dehalogenation of 2,2-dibromo-1,1,1,3,3,3-hexa-*tert*-butyltrisilane(Wiberg, 1997).

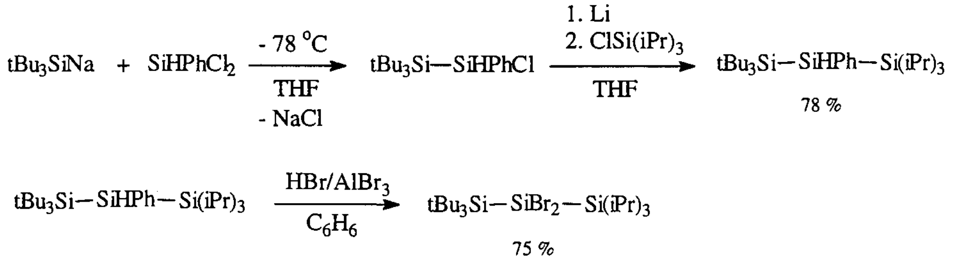


Fig. 16. Preparation of the key synthetic precursor for the generation of (t-Bu)$_3$ Si–Si–Si(iPr)$_3$.

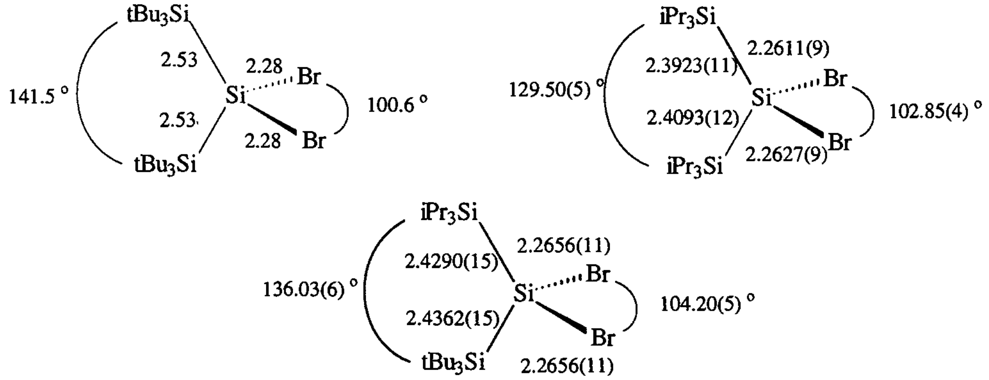


Fig. 17. Selected data from X-ray crystal structures of (t-Bu$_3$Si)$_2$SiBr$_2$[Wiberg, 1997], (iPr$_3$Si)$_2$SiBr$_2$ [Winchester, Rath, Gaspar, unpublished] and (t-Bu)$_3$Si–SiBr$_2$–Si(iPr)$_3$[Jiang, Rath Gaspar, unpublished].

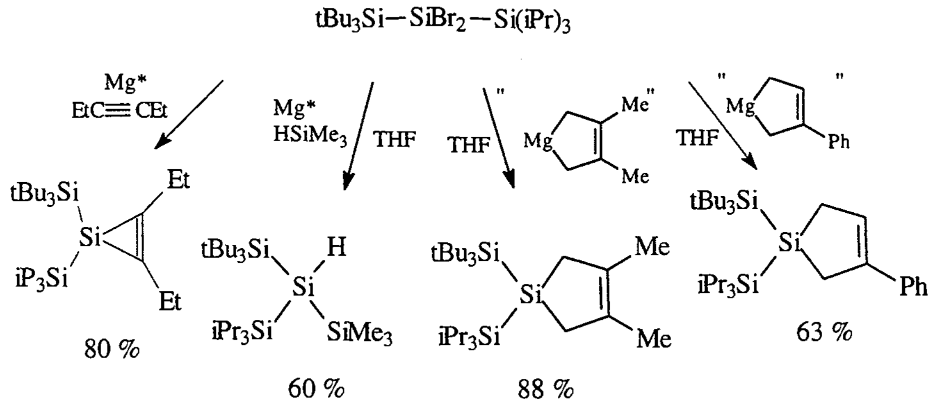


Fig. 18. Synthesis of expected products from, and precursors of, (t-Bu)$_3$Si–Si–Si(iPr)$_3$.

by reduction of 1,3-dienes with magnesium gave rise to products that look like silylene products but almost certainly are not [33]. Selectivity inversions between metal-free and organometallic reaction systems for the generation of silylenes and their equivalents, [15,17] suggest that silylenoid reactions are initiated by treatment of t-Bu$_3$Si(iPr$_3$Si)SiBr$_2$ with Mg*. Note that even insertion of a silylene into an H–Si bond is mimicked by an organometallic reaction.

Both the silirene and the silacyclopent-3-enes function well as precursors for the photochemical generation of (t-Bu)$_3$Si–Si–Si(iPr)$_3$, as shown by the reactions depicted in Fig. 19 [33]. While it has been known for 25 years that photochemical decomposition of silirenes can generate silylenes, this process has seen little use [35–37]. Extrusion of silylenes from silacyclopent-3-enes as a *thermal* reaction is well known [38,39]. But photochemical silylene extrusion from silacyclopentenes has only seldom been carried out [40]. The results shown here, although the yields are not uniformly high, are clearly those insertion and addition reactions expected for (t-Bu)$_3$Si–Si–Si(iPr)$_3$.

These precursors do not yield the silylene at 77 K, so an ESR experiment has not yet been possible. But there is a definitive product study that points to reaction of (t-Bu)$_3$Si–Si–Si(iPr)$_3$ from a triplet state [33]. As shown in Fig. 20, if no efficient silylene trapping agent is present, then a disilacyclobutane is formed similar to the one found by Wiberg in organometallic reactions which may have generated bis(tri-*tert*-butylsilyl)silylene (cf. Fig. 15). But in this case, there is no possibility of a silylenoid intermediate. Here, it is the free silylene (t-Bu)$_3$Si–Si–Si(iPr)$_3$ that has given the product of formal C–H insertion, a process with a significant barrier for a singlet silylene.

Furthermore, it has been demonstrated that there is competition between the formation of the four-membered ring and reactions with Si–H bonds. When triisopropylsilane is present in the reaction mixture, the yield of the four-membered ring decreases, but the yield of a product formally derived from the silylene by hydrogen-atom abstraction increases. In the presence of DSi(iPr)$_3$ t-Bu$_3$Si(iPr$_3$Si)SiHD is the major isotopomer of the dihydride product. It appears that HSi(iPr)$_3$ is too bulky to form a stable product of H–Si insertion (many attempts to synthesize that molecule have failed). We believe that, as shown in Fig. 21, donation of a hydrogen atom to the triplet silylene competes with intramolecular transfer of a hydrogen atom to the divalent silicon atom from a C–H bond. The intermediate diradical formed by intramolecular hydrogen-abstraction can close to the four-membered ring, while a sterically hindered monoradical resulting from intermolecular H-abstraction may wind up, in part, as (t-Bu)$_3$Si–SiH$_2$–Si(iPr)$_3$.

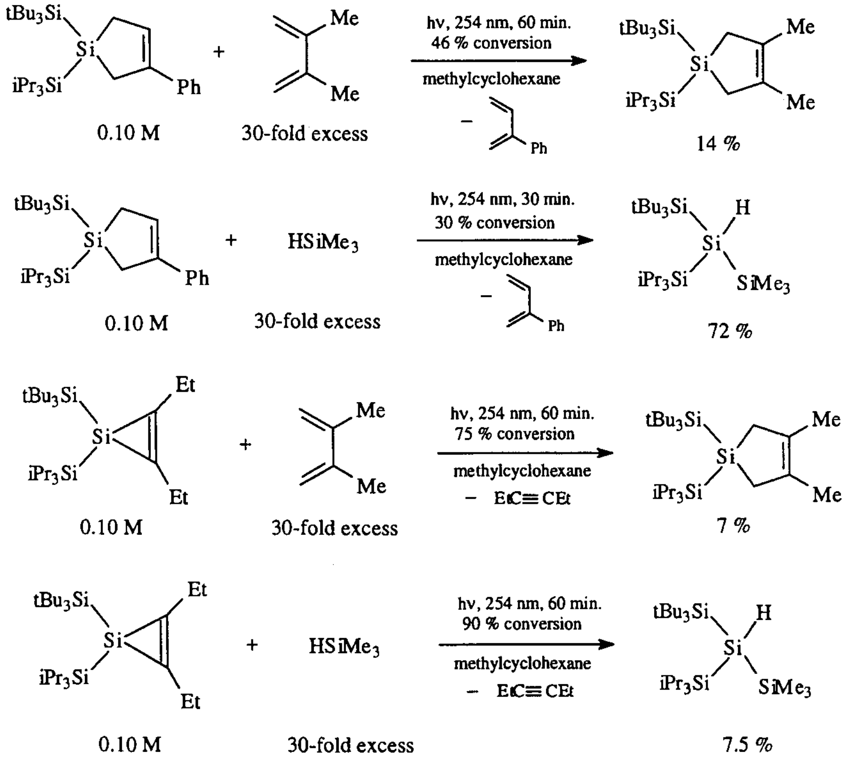


Fig. 19. Photochemical reactions leading to the trapping of (t-Bu)$_3$Si–Si–Si(iPr)$_3$.

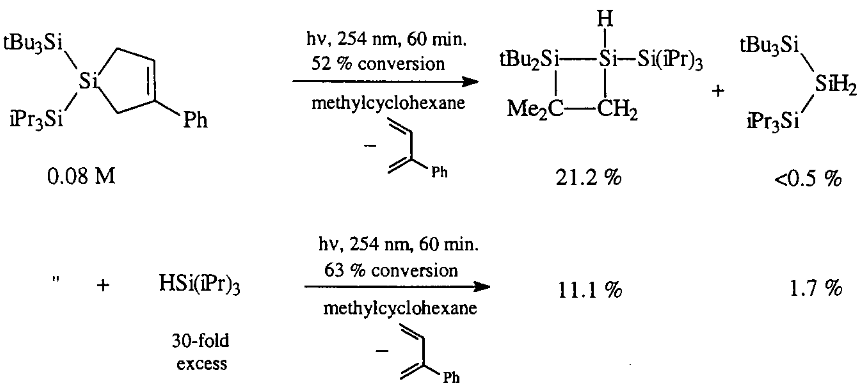


Fig. 20. Photochemical generation of (t-Bu)$_3$Si–Si–Si(iPr)$_3$ in the absence of trapping agents and in the presence of triisopropylsilane.

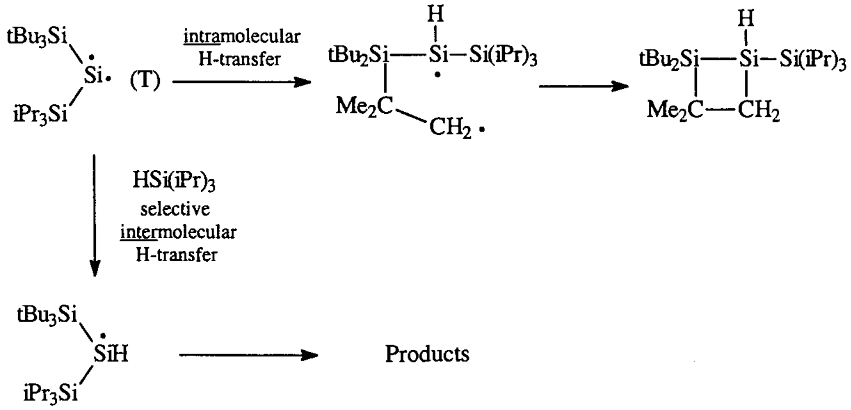


Fig. 21. Proposed mechanism for reactions of triplet (t-Bu)$_3$Si–Si–Si(iPr)$_3$.

The quest for a ground state triplet silylene is not quite complete. Confirmation of a triplet ground-state silylene must be accomplished via an indubitable triplet ESR signal, by a chemically induced dynamic nuclear polarization NMR experiment, or by detection of the silylene by kinetic ultraviolet spectroscopy. Theoretical predictions of the electronic absorption spectrum are not yet complete but are not terribly promising, since the longest wavelength absorption bands look like they will be in a sea of absorptions due to the sigma framework [41].

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