

Silylenes, Silylenium Ions, and Multiply Bonded Silicon Compounds

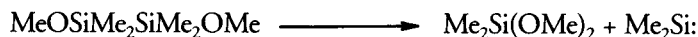
Mark J. Fink
 Department of Chemistry
 Tulane University
 New Orleans, LA 70118

The field of organosilicon reactive intermediates is an intensely studied area with wide ranging connections to electronics, commercial processes, and organic synthesis. Many organosilicon intermediates have formal analogs in organic chemistry: silylenes vs carbenes, silyl radicals vs carbon radicals, silylenium ions vs carbenium ions, and silyl anions vs carbanions. However, one large class of compounds which are considered reactive intermediates in silicon chemistry, but not generally in organic chemistry, are multiply bonded compounds containing silicon.¹ This article highlights some of the major themes and exciting new developments in the area of silylenes, silylenium ions, and multiply bonded silicon compounds.

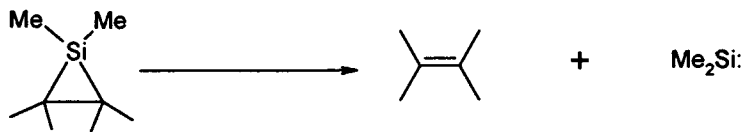
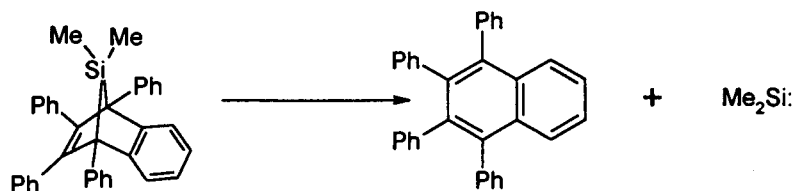
Organosilylenes

Organosilylenes, $R_2Si:$, are divalent organosilicon intermediates implicated in a wide variety of organosilicon thermal and photochemical reactions.² Compared to carbenes, silylenes are relatively more important as reactive intermediates, a consequence of the "inert" pair effect which is seen more prominently for heavier main group elements.

Organosilylenes can be generated thermally through α -elimination reactions of alkoxy- or halosilanes at moderate temperatures.



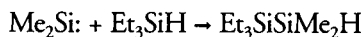
Silylenes can also be produced through thermal decomposition of 7-silanorbornadienes³ and silacyclopropanes.⁴



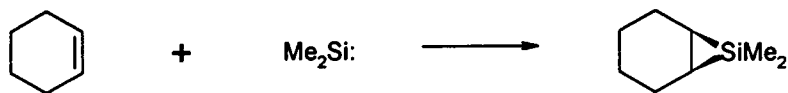
Photolysis of polysilanes often yield silylenes in excellent yields. Popular photochemical sources include 2-aryltrisilanes and cyclic polysilanes.⁵



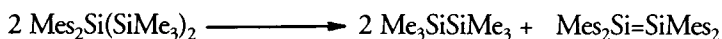
Organosilylenes undergo insertion and addition reactions similar to singlet carbenes. Silylenes are known to insert into Si-H, Si-O, O-H, and N-H bonds amongst others. Insertion of silylenes into C-H and C-C bonds are relatively rare. A diagnostic reaction for organosilylenes is insertion into the Si-H bond of triethylsilane.



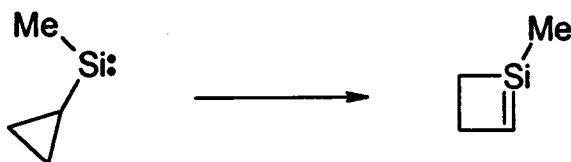
Addition of silylenes to organic π bonds occur stereospecifically to give *cis* products.⁶



In the absence of reactive substrates, silylenes typically dimerize to form disilenes as intermediates in route to oligomeric or polymeric polysilanes. If substituents are large enough on silicon, kinetically stable disilenes may be isolated.^{7,8}

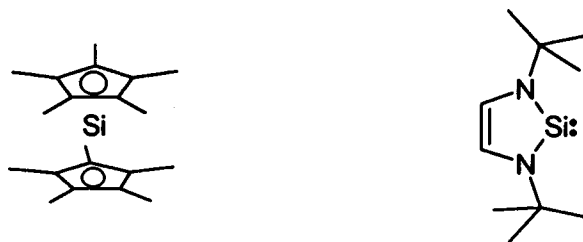


In some cases, silylenes undergo intramolecular rearrangements, often yielding unusual intermediates.⁹



Organosilylenes have been subjected to a number of physical studies in cold inert matrices and in the gas phase. They are singlets in the ground state and possess a characteristic $n \rightarrow p$ electronic transition in the visible region of the spectrum. However, the first example of a triplet ground state for a silylene has been reported for $(i\text{-Pr}_3\text{Si})_2\text{Si}:$.¹⁰ The triplet state is favored by a wide Si-Si-Si angle and by the electron donating properties of the silyl substituents.¹¹

Several types of "stable" silylenes have been reported. One example is siliconocene¹² and another is a cyclic diamidosilylene. Only the latter qualifies as a divalent dicoordinate silylene. Remarkably, it survives 4 months at 150°C without decomposition. It is believed that this cyclic silylene has considerable aromatic character.¹³



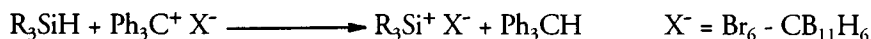
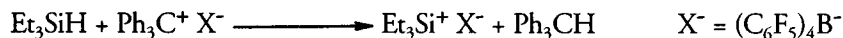
Silylenium Ions

Silylenium ions (R_3Si^+) are thermodynamically more stable than analogous carbenium ions (R_3C^+) in the gas phase.^{14,15}



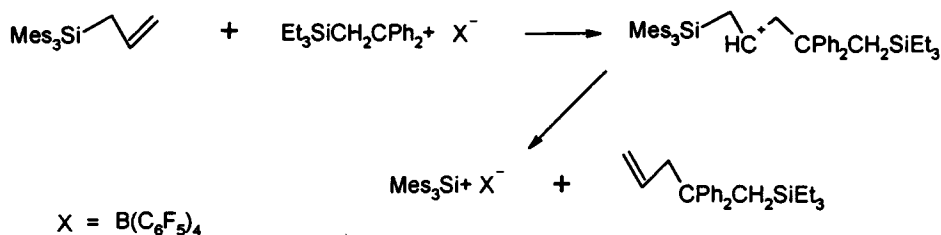
The highly electrophilic nature of the silylenium ions, however, makes their free existence in condensed phases extremely difficult. Superacid media employed for the generation for free carbenium ions fails for silylenium ions.¹⁶

The use of nonbasic solvents and a new generation of non-coordinating counterions promises to be a successful strategy for the production of free silylenium ions. Typically, the trityl cation is used as a hydride abstractor to generate the silylenium ion.



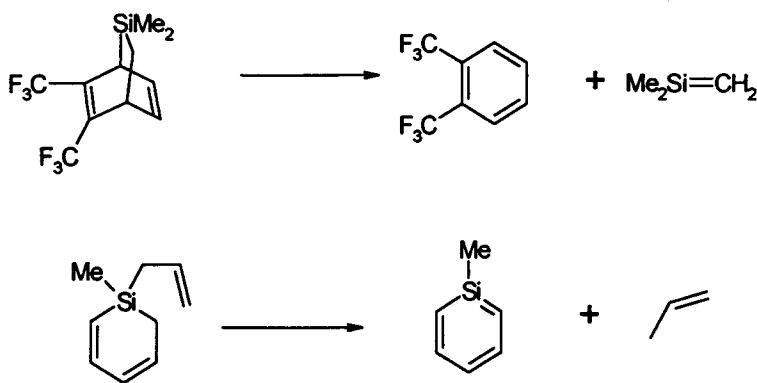
To date, crystal structures of these silylenium ions still show weak interactions between the highly electrophilic silylenium ion and either the counterion or the solvent itself. In the case of $\text{Et}_3\text{Si}^+ \text{B}(\text{C}_6\text{F}_5)_4^-$, the triethylsilylenium ion coordinates in a 1η fashion with a toluene molecule in the solid state.¹⁷ Solid state structures of silylenium ions with hexabromocborane counterions, likewise show weak interactions between the bromine of the counterion and the silicon center.^{18,19}

The closest example of a "free" silylenium ion is that of the sterically congested Mes_3Si^+ which is generated in the elegant sequence shown below.²⁰ Although no solid state structure is reported at this time, the non-associated nature of the silylenium ion is reflected by an extraordinary downfield chemical shift value of 225.5 ppm which is insensitive to the nature of the aromatic solvent.

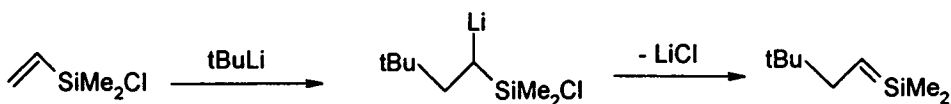


Silenes

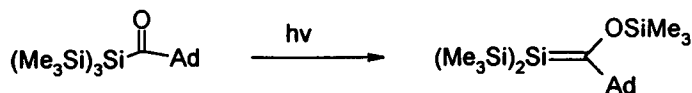
Silenes possess a polar Si=C bond with a significant π bond strength.²¹ The Si=C bond is generated by a variety of thermal and photochemical reactions. Retro-Diels Alder²² and retroene²³ reactions are two possible thermal routes.



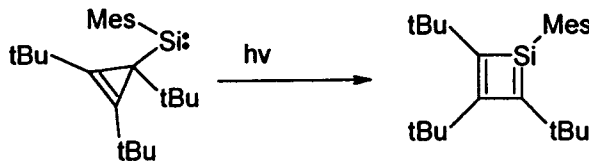
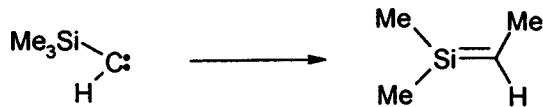
Elimination of metal halides across the silicon-carbon bond provides another route to these species.²⁴



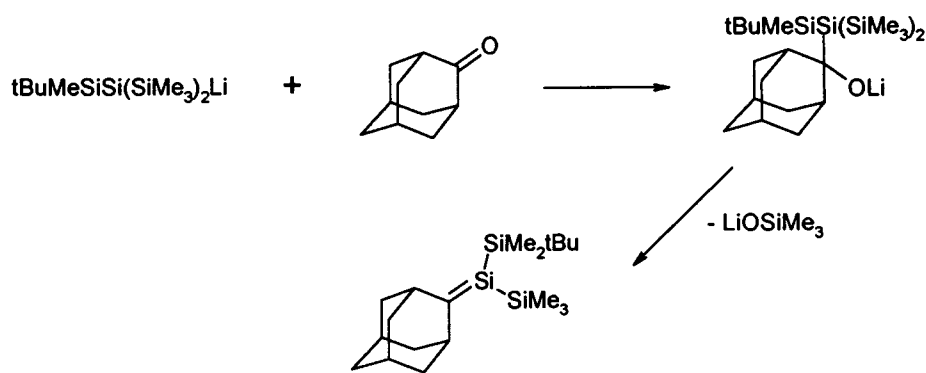
Photolysis of acylpolysilanes provided the first synthetic route to kinetically stable silenes.²⁵



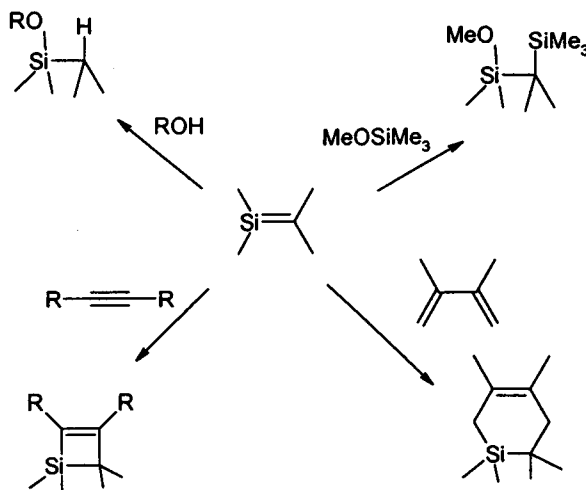
Silylene and carbene rearrangements may also give silenes as products.^{26,27}



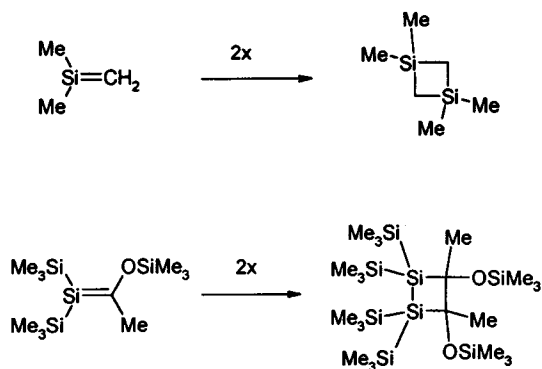
Recently, a stable silene has been produced by the silicon analog of a Peterson reaction.²⁸



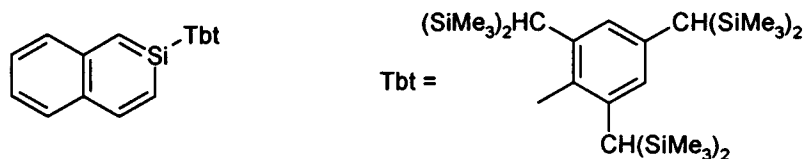
The Si=C bond typically undergoes regiospecific addition reactions with polar substrates, the regiochemistry governed by the normal polarity of the Si-C bond. Cycloaddition reactions, including Diels-Alder, occur with many organic π systems.



A head to tail dimerization of silenes to give 1,3 disilacyclobutanes typically occurs in the absence of bimolecular reactions. However, severely electronically perturbed silenes may undergo head to head dimerizations to give 1,2 disilacyclobutanes.

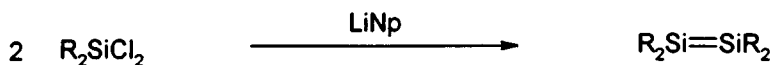
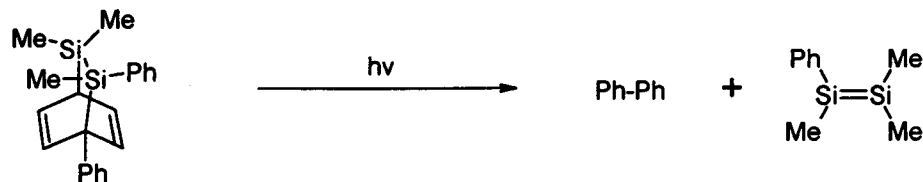
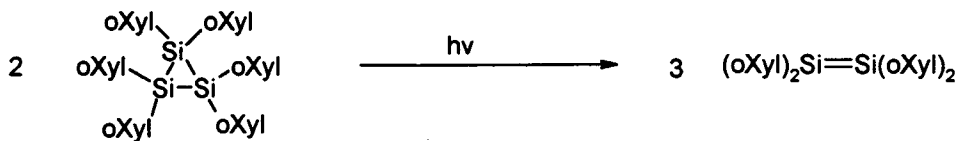


Kinetically stable silenes are often produced when the Si=C bond is sterically shielded. A remarkable example is the 2-silanaphthalene molecule. NMR and X-ray structural data support a high degree of aromatic character in the silicon containing ring.²⁹

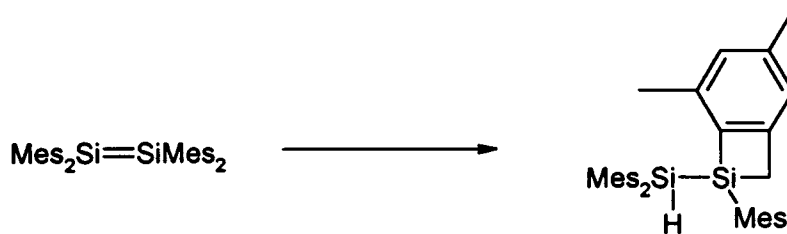


Disilenes

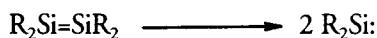
Disilenes are molecules which possess a Si=Si double bond.³⁰ As mentioned previously, they may arise from the dimerization of silylenes. They may also be generated by the photolysis of cyclotrisilanes,³¹ retro-Diels Alder reactions,^{32,33} and reduction of dihalosilanes.³⁴



Disilenes are unstable to oligomerization and polymerization reactions. Large substituents on silicon can lend kinetic stability towards bimolecular processes. For example, $\text{Mes}_2\text{Si}=\text{SiMes}_2$ is stable to 176°C before it decomposes via an intramolecular process.³⁵

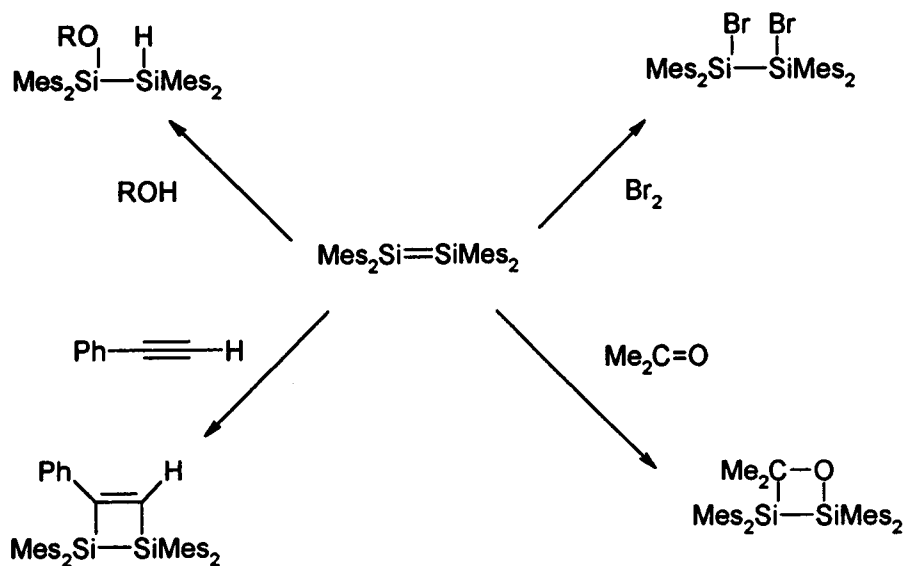


In extreme cases, bulky substitution may weaken the Si=Si bond, promoting the formation of silylenes under mild conditions.³⁶

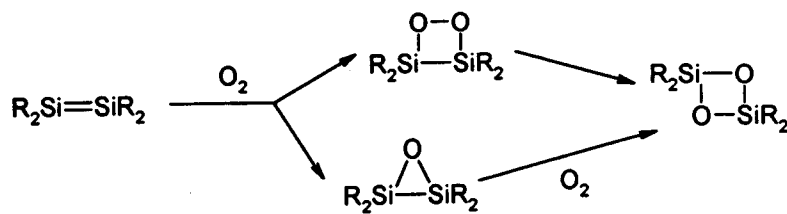


Stable disilenes show a prominent $\pi \rightarrow \pi^*$ transition in the range of 400-475 nm, giving these compounds a light yellow to orange appearance. Many disilenes are thermochromic. The Si-Si π bond strength has been experimentally estimated to be 28.8 kcal/mol based on the *cis-trans* isomerization of a stable disilene.³⁷

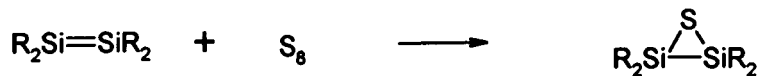
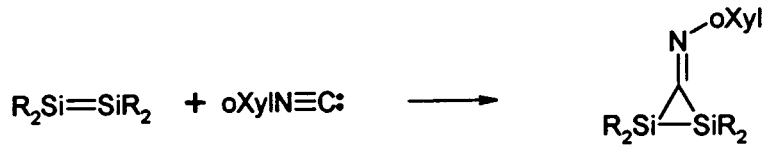
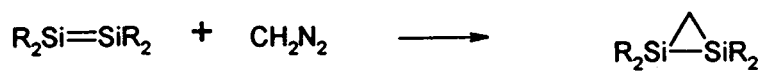
The Si=Si bond in disilenes undergoes a variety of addition reactions with inorganic and organic substrates.³⁸



In some cases, reaction chemistry gives very unusual and exotic products. For instance, the reaction of disilenes with dioxygen ultimately gives cyclodisiloxanes through the intermediacy of either 1,2 disiladioxetanes or disilaoxiranes.^{39,40}



Strained three member rings are obtained with a number of substrates.^{41,42,43}

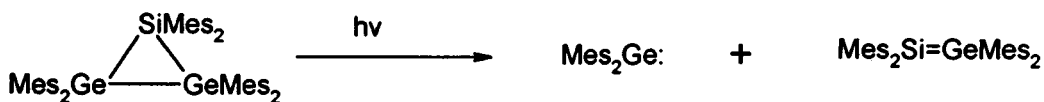
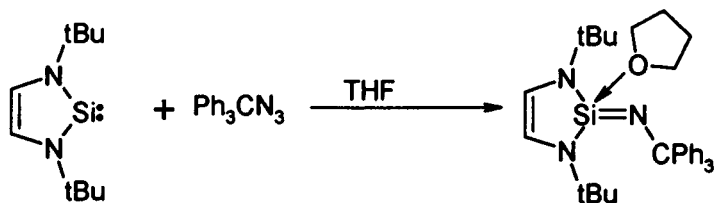
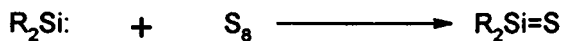
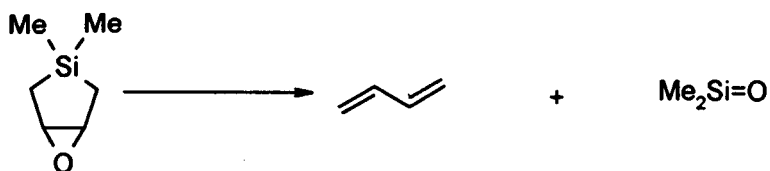


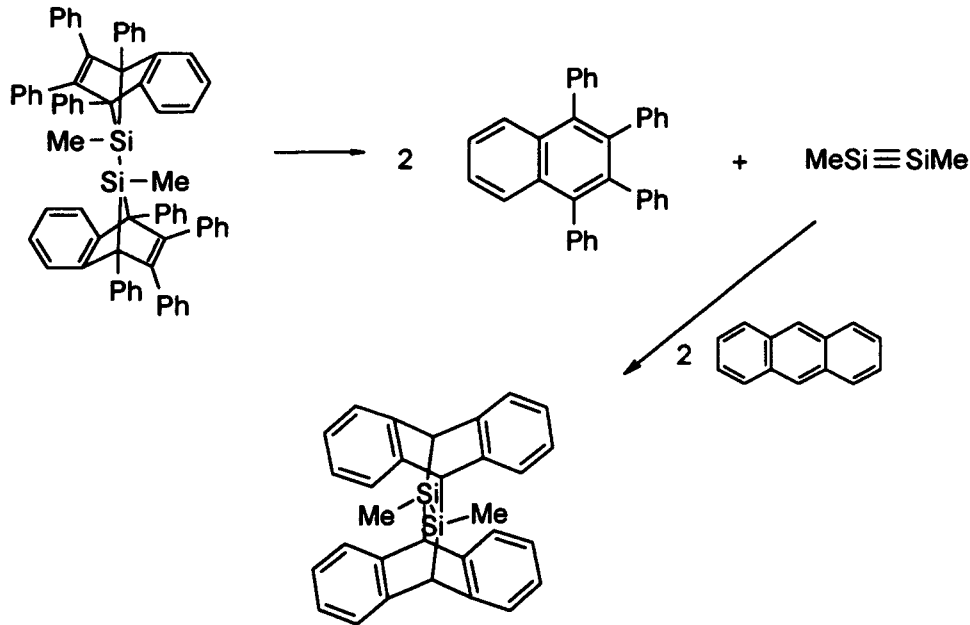
Disilenes can undergo reactions without analogy with olefin chemistry. For example, a tetraaryldisilene was found to undergo rearrangement via interchange of aryl groups across the Si=Si bond, presumably through a dyotropic mechanism.⁴⁴



Other Multiply Bonded Silicon Compounds

Although not as well studied as silenes and disilenes, there exists a variety of other novel multiply bonded silicon species including silanones ($\text{R}_2\text{Si}=\text{O}$),⁴⁵ silathiones ($\text{R}_2\text{Si}=\text{S}$),⁴⁶ silaimines ($\text{R}_2\text{Si}=\text{NR}$),⁴⁷ and silagermenes ($\text{R}_2\text{Si}=\text{GeR}_2$).⁴⁸ Examples of their generation are shown below.





Triply bonded silicon compounds have remained to a great extent elusive. The parent disilyne, H_2Si_2 , does not have the classic structure of acetylene but instead adopts a structure in which the hydrogens bridge between the silicon atoms.⁴⁹ Diorganodisilynes, however, are predicted to have a $\text{Si} \equiv \text{Si}$ with a non-linear trans bent geometry.⁵⁰ One of the few directed attempts at a disilyne species is shown below.⁵¹ However, the trapping experiments with anthracene are not unambiguous. The existence of a free diorganodisilyne is yet to be shown with certainty and remains a much sought after synthetic target.

REFERENCES

1. Raabe, G.; Michl, J. in "Chemistry of Organic Silicon Compounds", S. Patai and Z. Rappoport, eds., Chap. 17, 1989, John Wiley, New York
2. a) Gaspar, P.P. *Reactive Intermediates*, 1978, 1, 229. b) *ibid.*, 1981, 335. c) *ibid.*, 1985, 3, 333
3. Gilman, H.; Cottis, S.G.; Atwell, W.H. *J. Am. Chem. Soc.*, 1964, 86, 1596
4. Seyferth, D. J. *Organomet. Chem.*, 1975, 100, 237
5. Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.*, 1981, 19, 51
6. Tortorelli, V.J.; Jones, M., Jr. *J. Am. Chem. Soc.*, 1980, 102, 1426
7. Michalczyk, M. J.; Fink, M. J.; DeYoung, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, J. *Silicon, Germanium, Tin, and Lead Compounds*, 1986, 9, 75-80.
8. West, R.; Fink, M. J.; Michl, J., *Science*, 1981, 214, 1343-1344.
9. Barton, T.J.; Burns, G.T.; Goure, W.F.; Wulff, W.D. *J. Amer. Chem. Soc.* 1982, 104, 1149
10. Gaspar, P.P.; Beatty, A.M.; Chen, T.; Haile, T.; Klooster, W.T.; Koetzle, T.F.; Lei, D.; Lin, T.S.; Winchester, W.R. "The Quest for a Triplet Silylene", 30th Organosilicon Symposium, Lonton, Ontario, May, 1997
11. Grev, R.; Schaefer, H.E.; Gaspar, P.P. *J. Am. Chem. Soc.*, 1991, 113, 5638
12. Jutzi, P.; Kanne, D.; Kruger, G. *Angew. Chem. Int. Ed. Engl.*, 1986, 25, 164
13. Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A.V.; Verne, H.P.; Haaland, A.; Wagner, M.; Metzler, N. *J. Am. Chem. Soc.*, 1994, 116, 2691
14. Schleyer, P.v.R.; Buzek, P.; Muller, T.; Apeloig, Y.; Siehl, H.U. *Angew. Chem. Int. Ed. Engl.* 1993, 32, 1471
15. Olsen, L.; Ottoson, C.H.; Cremer, D. *J. Amer. Chem. Soc.* 1995, 117, 7460
16. Olah, G.A.; O'Brien, D.H.; Lui, C.Y. *J. Amer. Chem. Soc.*, 1969, 91, 701
17. Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science*, 1993, 260, 1917
18. Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. *Organometallics*, 1995, 14, 3933
19. Xie, Z.; Manning, J.; Reed, R.W.; Mathur, R.; Boyd, P.D.W.; Benesi, A.; Reed, C.A. *J. Am. Chem. Soc.*, 1996, 118, 2922
20. Lambert, J.B.; Zhao, Y. *Angew. Chem. Int. Ed. Engl.* 1997, 36, 400
21. Brook, A.G.; Brook, M.A. *Adv. Organomet. Chem.* 1996, 39, 71
22. Maier, G.; Mihm, G.; Reisenauer, H.P. *Angew. Chem. Int. Ed. Engl.* 1981, 20, 597
23. Barton, T.J.; Burns, G.T. *J. Am. Chem. Soc.*, 1978, 100, 5246
24. Jones, P.R.; Lim, T.F.O. *J. Amer. Chem. Soc.*, 1977, 99, 2013
25. Brook, A.G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R.K. *J. Chem. Soc., Chem Commun.*, 1981, 191
26. Chapman, O.L.; C.C. Chang; Kolc, J.; Jung, M.E.; Lowe, J.A.; Barton, T.J.; Tuma, M.L. *J. Am. Chem. Soc.*, 1976, 98, 7844
27. Fink, M. J.; Puranik, D. B.; Johnson, M. P., *J. Am. Chem. Soc.*, 1988, 110, 1315-1316.
28. Apeloig, Y.; Bendikov, M.; Yuzefovich, M.; Nakash, M.; Bravo-Zhivotovskii; Blaser, D.; Boese, R. *J. Am. Chem. Soc.*, 1996, 114, 12227
29. Tokitoh, N.; Wakita, K.; Okazaki, R.; Nagase, S.; Schleyer, P.v.R.; Jiao, H. *J. Am. Chem. Soc.* 1997, 119, 6951
30. Okazaki, R.; West, R. *Adv. Organomet. Chem.*, 1996, 231
31. Masamune, S.; Hanazawa, Y.; Murakami; Bally, T.; Blount, J.F. *J. Am. Chem. Soc.*, 1982, 104, 1150
32. Roark, D.N.; Peddle, G.J.D. *J. Am. Chem. Soc.*, 1972, 94, 5837
33. Sekiguchi, A.; Maruki, I.; Sakurai, H. *J. Am. Chem. Soc.*, 1993, 115, 11460
34. Suzuki, H.; Tokitoh, N.; Okazaki, R.; Harada, J.; Ogawa, K.; Tomoda, S.; Goto, M. *Organometallics* 1995, 14, 1016
35. Fink, M. J.; DeYoung, D. J.; West, R.; Michl, J., *J. Amer. Chem. Soc.*, 1983, 105, 1070-1071.
36. Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.*, 1993, 115, 10428
37. Shepard, B. D.; Powell, D.R.; West, R. *Organometallics*, 1989, 8, 2664
38. West, R. *Angew. Chem. Int. Ed. Engl.*, 1987, 26, 1201
39. Millevolte, A. J.; Powell, D.R.; Johnson, S.G.; West, R. *Organometallics*, 1992, 11, 1091
40. McKillop, K.L.; Gillette, G.R.; Powell, D.R.; West, R. *J. Am. Chem. Soc.*, 1992, 114, 5203
41. Masamune, S.; Murakami, H.; Tobita, H. *J. Am. Chem. Soc.*, 1983, 105, 7776
42. Yokelson, H.B.; Millevolte, A.J.; Haller, K.J.; West, R. *J. Chem. Soc., Chem. Commun.* 1987, 1605
43. West, R.; De Young, D.J.; Haller, K.J. *J. Am. Chem. Soc.*, 1985, 107, 4942
44. Yokelson, H.B.; Siegel, D.A.; Millevolte; Maxka, J.; West, R. *Organometallics*, 1990, 9, 1005
45. Davidson, I.M.T.; Fenton, A.; Manuel, G.; Bertrand, G. *Organometallics*, 1985, 4, 1324
46. Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.*, 1994, 116, 11578
47. Denk, M.; Hayashi, R.K.; West, R. *J. Am. Chem. Soc.*, 1994, 116, 10813
48. Baines, K.M.; Cooke, J.A. *Organometallics*, 1992, 11, 3487
49. Colegrove, B.T.; Schaefer, H.F. *J. Phys. Chem.*, 1990, 94, 5593
50. Colegrove, B.T.; Scaeffler, H.F. III. *J. Am. Chem. Soc.*, 1991, 113, 1557
51. Sekiguchi, A.; Zigler, S.S.; West, R. *J. Am. Chem. Soc.*, 1986, 108, 4241