Organometallics **1993**, *12*, 197-209

Photolysis of 1,3-Dimesitylhexamethyltrisilane and 1,2-Dimesityltetramethyldisilane

Janet Braddock-Wilking, Michael Y. Chiang, and Peter P. Gaspar*

Department of Chemistry, Washington University, St. Louis, Missouri 63130

Received June 11, 1992

Irradiation at 254 nm of solutions containing 1,3-dimesitylhexamethyltrisilane, $(MesMe_2Si)_2SiMe_2$, leads to the formation of 1-mesityl-1-methylsilene, $MesMeSi{=}CH_2$, in addition to the anticipated dimethylsilylene, Me_2Si:. The coproduct of dimethylsilylene extrusion, 1,2-dimesityltetramethyldisilane, $(MesMe_2Si)_2$, is itself photolabile, producing high yields of mesityldimethylsilane, $MesMe_2SiH$, and 1-mesityl-1-methylsilene. Trapping experiments indicate that both molecular elimination and silicon–silicon bond homolysis followed by disproportionation lead to the silene, whose dimerization yields *cis*- and *trans*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutanes. Both the *cis*- and *trans*-1,3-disilacyclobutanes were structurally characterized by X-ray crystallography. The silene can be trapped by a variety of reagents in high yield.

Introduction

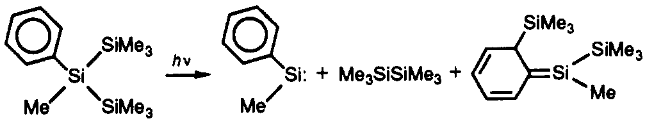
The ultraviolet irradiation of polysilanes is a well-established method for the generation of silylenes,[1] but a chain of at least four silicon atoms is needed for efficient photoextrusion of silylenes in the absence of a chromophore.[2] When the chromophore is an aromatic ring, migration of a silyl group to the ring, leading to the formation of a silene, can compete with silylene extrusion, as illustrated by the case of 2-phenylheptamethyltrisilane, shown in Scheme I.[3]

When the ortho positions of an aromatic ring are substituted, the formal 1,3-silyl shift seems to be suppressed.[4] Thus 2,2-dimesitylhexamethyltrisilane has been found by Conlin to undergo photolysis exclusively to dimesitylsilylene (Scheme II).[5]

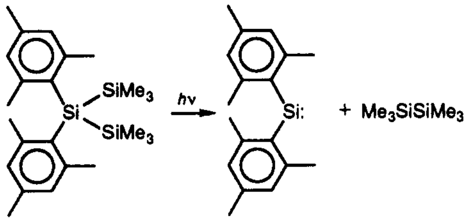
For extrusion of the central silicon in a three-atom chain in the form of a silylene, the chromophore need not be attached to the central atom. West and co-workers found that matrix photolysis of 1,3-diphenylhexamethyltrisilane led to the formation of dimethylsilylene, Me_2Si:.[6]

Thus the stage was set for the synthesis of a useful class of photochemical silylene generators, $(MesMe_2Si)_2SiYZ$. The presence of mesityl chromophore units should insure a convenient wavelength such as 254 nm for efficient photolysis, *without* 1,3-migration of a silyl group to the ortho-position competing with silylene extrusion. The placement of chromophores at the termini of the trisilane chain is expected to permit a variety of silylenes :SiYZ to be generated from such a family of precursors.

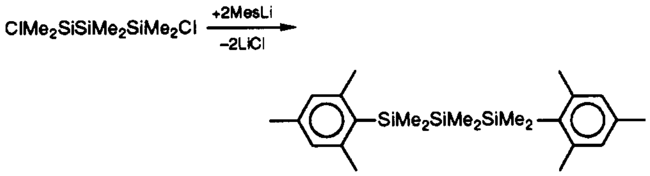
Scheme I



Scheme II



Scheme III



Results

Irradiation of 1,3-Dimesitylhexamethyltrisilane. 1,3-Dimesitylhexamethyltrisilane was synthesized in a straightforward manner by condensing mesityllithium with 1,3-dichlorohexamethyltrisilane (Scheme III).

Irradiation of a 10^{-1} M solution of 1,3-dimesitylhexamethyltrisilane in cyclohexane containing a 10-fold excess of a silylene trapping agent, triethylsilane, led to the formation of the expected product of insertion by dimethylsilylene, Me_2Si:, into the Si–H bond of $HSiEt_3$. However the 28% yield of $HSiMe_2SiEt_3$ was disappointingly modest, and the even lower yield, 13%, of the coproduct of silylene extrusion, 1,2-dimesityltetramethyldisilane, was striking. The other seven products, shown in Scheme IV, reveal that silylene extrusion is *not* the dominant primary process. Yields are reported as moles of product per mole of starting material consumed, ×100.

The *cis*- and *trans*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutanes were indicative of the formation of

---

* Author to whom correspondence should be addressed.

[1] Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Moss, R. A., Eds.; John Wiley & Sons: New York, 1978; Vol. 1, p 229; 1981; Vol. 2, p 335; 1985; Vol. 3, p 333.

[2] (a) Ishikawa, M.; Kumada, M. *J. Organomet. Chem.* **1972**, *42*, 325. (b) Davidson, I. M. T.; Michl, J.; Simpson, T. *Organometallics* **1991**, *10*, 842. (c) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

[3] Ishikawa, M.; Nakagawa, K. I.; Enokida, R.; Kumada, M. *J. Organomet. Chem.* **1980**, *201*, 151. Ishikawa, M.; Nakagawa, K. I.; Ishiguro, M.; Ohi, F.; Kumada, M. *J. Organomet. Chem.* **1978**, *152*, 155. See, also: Nakao, R.; Oka, K.; Irie, S.; Dohmaru, T.; Abe, Y.; Horii, T.; Kitao, T. *J. Chem. Soc., Perkin Trans. 2* **1991**, 755.

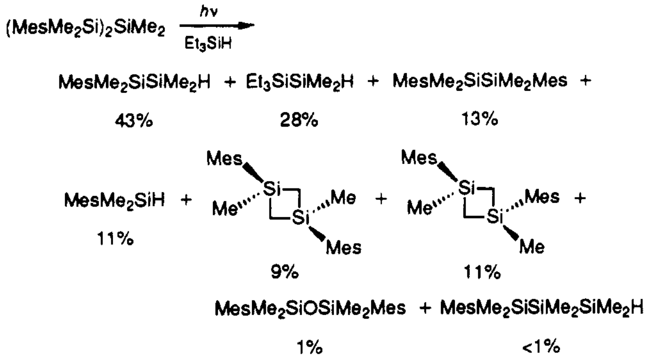
[4] Sakurai, H.; Sugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837.

[5] Conlin, R. T.; Netto-Ferreira, J. C.; Zhang, S.; Scaiano, J. C. *Organometallics* **1990**, *9*, 1332.

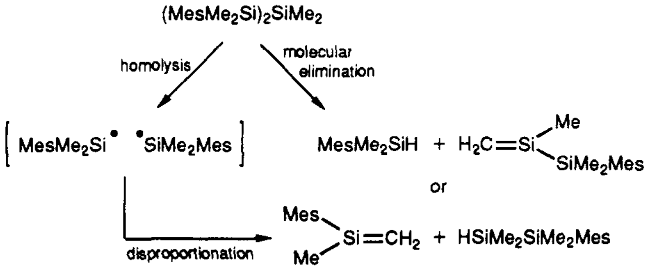
[6] Vančik, H.; Raabe, G.; Michalczyk, M. J.; West, R.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 4097.

0276-7333/93/2312-0197$04.00/0

Scheme IV



Scheme V



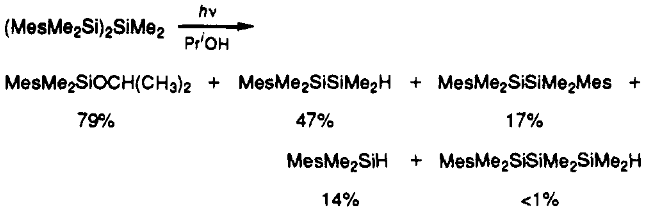
1-mesityl-1-methylsilene, $MesMeSi{=}CH_2$, as a reactive intermediate whose presence was confirmed by trapping experiments described below. All but the most sterically encumbered silenes have been found to undergo head-to-tail dimerization.[7]

Mesityldimethylsilane, $MesMe_2SiH$, and the mesityltetramethyldisilane, $MesMe_2SiSiMe_2H$, can be regarded as coproducts of the formation of the silene $MesMeSi{=}CH_2$ by either molecular elimination or a silicon–silicon bond homolysis, radical-disproportionation sequence, as shown in Scheme V.

No products were detected, indicating the formation of the other silene $H_2C{=}SiMe(SiMe_2Mes)$. This molecule would have been expected to form stable products either by self-dimerization to afford the corresponding 1,3-disilacyclobutanes or through a bimolecular reaction with the silene $MesMeSi{=}CH_2$, whose existence has been demonstrated below. Trapping experiments were also unsuccessful at intercepting $H_2C{=}SiMe(SiMe_2Mes)$. It is conceivable that this silene was generated, but its end products were not detected by gas chromatography or were unstable with respect to thermal decomposition under gas chromatographic conditions.

Additional evidence for the generation of $MesMeSi{=}CH_2$ is provided by the formation of the disiloxane $(MesMe_2Si)_2O$, which was obtained as a minor product in many of the photochemical experiments reported here. Independent trapping experiments indicated that the disiloxane was due to trace amounts of adventitious water in the photochemical reaction mixture. Water efficiently traps $MesMeSi{=}CH_2$ by addition, giving the silanol $MesMe_2SiOH$. Mesityldimethylsilanol was characterized by ^1H NMR and mass spectrometry, but was found to be unstable and readily converted to the disiloxane. Spectroscopic data for $(MesMe_2Si)_2O$ were identical to those obtained from a sample prepared by an independent route (see the Experimental Section).

Scheme VI



The formation of the minor product $MesMe_2SiSiMe_2SiMe_2H$ can be ascribed to cleavage of a mesityl carbon–silicon bond followed by hydrogen atom abstraction by the resulting silicon-centered radical. Mesitylene (2,4,6-trimethylphenyl) was detected in trace amounts by gas chromatography. Traces of acid could be responsible for mesitylene formation by protiodesilylation.

The generation of the siloxane $MesMe_2SiOSiEt_3$ may be due to reaction of $MesMe_2SiOH$ with the trapping agent Et_3SiH.

When the irradiation of dimesitylhexamethyltrisilane was carried out in the presence of a 10-fold excess of 2-propanol, expected to efficiently trap a silene by addition,[8] the formation of disilacyclobutane products was completely suppressed, and the expected 2-propanol adduct of $MesMeSi{=}CH_2$ was obtained in 79% yield (Scheme VI). None of the expected silylene O–H insertion product $Me_2HSiO(Pr^i)$ was detected.[8]

Characterization of the 1,3-Disilacyclobutanes. The X-ray crystal structures of both stereoisomers of the 1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane were determined. Only a few of the 1,3-disilacyclobutanes whose crystal structures have been reported previously are unsubstituted at the ring carbon atoms. In the present case, the cis and trans isomers were found to differ in the geometry of the disilacyclobutane ring. As the ORTEP drawings displayed in Figures 1 and 2 indicate, the four-membered ring of the trans isomer is planar and square, but in the cis isomer it is puckered, with a rather large fold angle of 24.4° and 25.5°, for the two independent molecules in the unit cell.[9]

Brook et al. have reported the crystal structures for several sterically encumbered 1,3-disilacyclobutanes bearing bulky substituents at both carbon and silicon of the four-membered ring. Ring fold angles were found to be small, 2–6°.[10] Fritz et al. observed a ring pucker angle of 17.8° for *cis*-2,4-dichloro-2,4-bis(trimethylsilyl)-1,1,3,3-tetramethyl-1,3-disilacyclobutane.[11] Gas-phase electron diffraction studies of 1,1,3,3-tetrahydro- and 1,1,3,3-tetrachloro-1,3-disilacyclobutane revealed ring pucker angles of 25° and 14°, respectively.[12]

Most recently, Seyferth and co-workers reported the X-ray crystal structure of 2-lithio-1,1,3,3-tetramethyl-1,3-disilacyclobutane-*N*,*N*,*N*′,*N*′-tetramethylethylenediamine. The four-membered ring was found to deviate from planarity by 19°.[13]

---

[7] Raabe, G.; Michl, J. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Vol. 2, p 1015.

[8] While most silenes undergo addition by alcohols to give high yields of alkoxysilanes, the reactions of silylenes with alcohols often give low yields of O–H insertion products.

[9] The ring fold angle is defined as the interplanar angle between the two Si–Si–C planes in the silacyclobutane ring.

[10] Baines, K. M.; Brook, A. G.; Lickiss, P. D.; Sawyer, J. F. *Organometallics* **1989**, *8*, 709.

[11] Fritz, G.; Thomas, J.; Peters, K.; Peters, E. M.; Von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1984**, *514*, 61.

[12] See ref 23 in D'Yachenko, O. A. *J. Struct. Chem.* **1983**, *24*, 775.

[13] Robison, J. L.; Davis, W. M.; Seyferth, D. *Organometallics* **1991**, *10*, 3385.

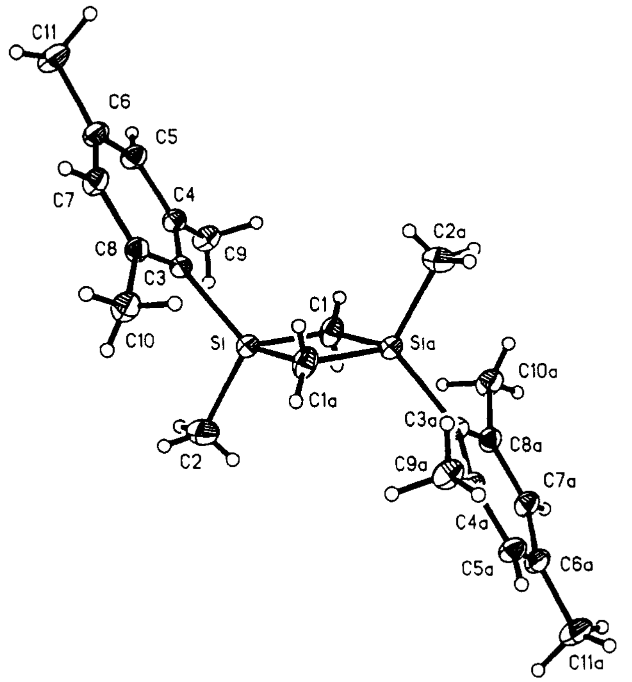


Figure 1. ORTEP drawing of the X-ray crystal structure of *trans*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane. Selected bond distances and angles: Si–C(1), 1.881 (3); Si–C(1A), 1.886 (4); Si–Si(A), 2.651 (2); Si–C(2), 1.858 (4); Si–C(3), 1.886 (2); C(1)–H(1B), 0.798 (30); C(1)–H(1A), 0.967 (31); C(1)–Si–C(1A), 90.5 (1); Si–C(1)–Si(A), 89.5 (1); C(1)–Si–C(3), 116.9 (1); C(1)–Si–C(2), 110.3 (2); C(3)–Si–C(2), 111.9 (2); C(2)–Si–C(1A), 110.2 (2); H(1A)–C(1)–H(1B), 97.0 (29); C(3)–Si–C(1A), 115.2 (1).

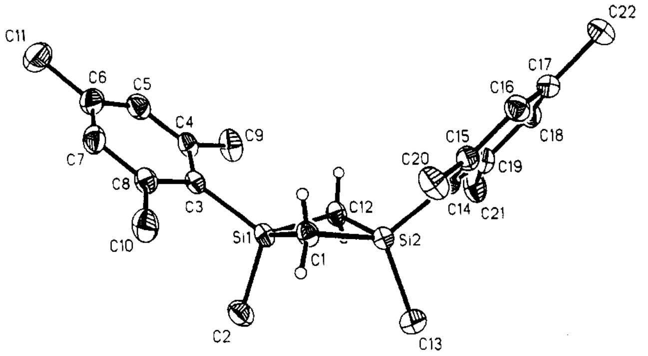
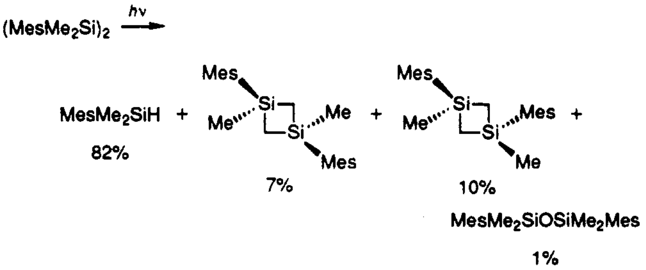
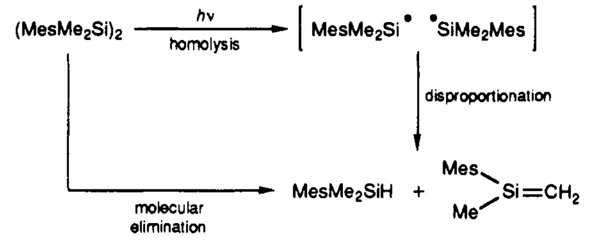


Figure 2. ORTEP drawing of the X-ray crystal structure of *cis*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane. Selected bond distances and angles: Si(1)–C(2), 1.871 (5); Si(1)–C(1), 1.895 (4); Si(1)–Si(2), 2.640 (2); Si(1)–C(3), 1.884 (4); Si(2)–C(12), 1.892 (4); Si(2)–C(1), 1.890 (4); Si(2)–C(13), 1.871 (5); Si(2)–C(14), 1.896 (5); C(1)–Si(1)–C(12), 88.9 (2); Si(1)–C(12)–Si(2), 88.6 (2); Si(1)–C(1)–Si(2), 88.5 (2); C(1)–Si(2)–C(12), 88.9 (2); C(2)–Si(1)–C(12), 109.8 (2); C(3)–Si(1)–C(12), 119.3 (2); C(2)–Si(1)–C(3), 108.9 (2); C(1)–Si(1)–C(3), 114.9 (2); C(1)–Si(1)–C(2), 114.0 (2); C(12)–Si(2)–C(14), 114.0 (2); C(12)–Si(2)–C(13), 113.3 (3); C(13)–Si(2)–C(14), 110.2 (2); C(1)–Si(2)–C(14), 118.3 (2); C(1)–Si(2)–C(13), 110.8 (2); mean deviation from planarity, 24.4° and 25.5°.

Scheme VII



Scheme VIII



Irradiation of 1,2-Dimesityltetramethyldisilane. The low yield of the coproduct of Me_2Si: extrusion from $(MesMe_2Si)_2SiMe_2$, $(MesMe_2Si)_2$, suggested that this molecule might be undergoing secondary photolysis that could contribute to the products observed upon irradiation of $(MesMe_2Si)_2SiMe_2$. Indeed, prolonged photolysis of $(MesMe_2Si)_2SiMe_2$ did result in a decreased yield of $(MesMe_2Si)_2$. It was therefore decided to concentrate effort on the photochemistry of $(MesMe_2Si)_2$. This molecule could be regarded as a frustrated, if not entirely foiled, disilane, discouraged from both silylene extrusion, which generally requires at least a three-silicon chain, and from rearrangement to a silene via a formal 1,3-silicon shift that is hindered by the *o*-methyl groups.

1,2-Dimesityltetramethyldisilane was synthesized by a reaction analogous to that described previously for the trisilane $(MesMe_2Si)_2SiMe_2$, condensation of 1,2-dichlorotetramethyldisilane with 2 equiv of mesityllithium.

$$ClMe_2SiSiMe_2Cl \xrightarrow{+\,2MesLi} (MesMe_2Si)_2$$

Irradiation of a 10^{-1} M cyclohexane solution of 1,2-dimesityltetramethyldisilane in the absence of a trapping reagent afforded four products as shown in Scheme VII, all of which were also found in the trisilane photolysis system already described.

The photolysis of $(MesMe_2Si)_2$ was monitored over several time intervals to ascertain the photolability of the isolated products. No significant change in the identity or yields of the products was observed. Si recovery was 59%.

Again, as in the case of the trisilane photolysis, the formation of the isomeric 1,3-disilacyclobutanes suggests the intermediacy of the silene $MesMeSi{=}CH_2$. The formation of $MesMe_2SiH$ and the *cis*- and *trans*-1,3-disilacyclobutanes as the major reaction products indicated that two photochemical pathways are plausible: silicon–silicon bond homolysis followed by silyl radical disproportionation, and direct molecular elimination (Scheme VIII).

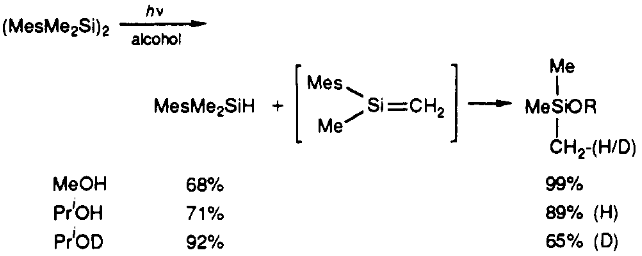
Disproportionation of silyl radicals derived from a disilane precursor has been reported to yield a molecule of a silane and a silene.[14] Potzinger reported the UV photolysis of hexamethyldisilane, $Me_3SiSiMe_3$, in the gas phase and found that the major decomposition pathway was Si–Si bond rupture, yielding $Me_3Si^•$ radicals to an extent of ~71%.[15] Direct molecular elimination to

---

[14] Cornett, B. J.; Choo, K. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1980**, *102*, 377.

[15] Brix, T. H.; Bastian, E.; Potzinger, P. *J. Photochem. Photobiol. A: Chem.* **1989**, *49*, 287.

Scheme IX



Me_3SiH and $Me_2Si{=}CH_2$ led to a contribution of ~27%. Conversion of two trimethylsilyl radicals to trimethylsilane and 2-methyl-2-silapropene has been estimated to be exothermic by 27 ± 6 kcal/mol.[16]

Sakurai et al. have reported the UV photolysis of several aryldisilanes and have suggested Si–Si bond homolysis as one of the possible decomposition channels. ESR experiments confirmed the generation of silyl radicals which were detected as adducts with $CH_2{=}C(Bu^t)_2$.[17]

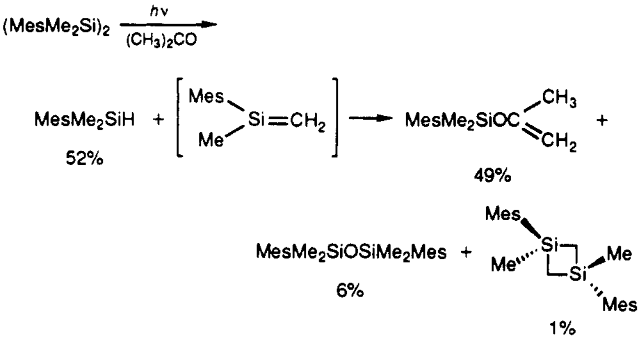
The photolysis of $(MesMe_2Si)_2$ was carried out in perdeuteriocyclohexane, C_6D_{12}, in the absence of a trapping reagent, to determine if hydrogen abstraction from solvent by $MesMe_2Si^\bullet$ radicals was the mode of formation of $MesMe_2SiH$. Irradiation of $(MesMe_2Si)_2$ in the absence of a trap in C_6D_{12} led to *no* deuterium incorporation in $MesMe_2SiH$, as determined by ^1H NMR and mass spectrometry. This indicated that the formation of $MesMe_2SiH$ was occurring by silyl radical disproportionation or molecular elimination, and *not* by hydrogen atom abstraction from solvent.[18]

When tetrahydrofuran was employed as the solvent, no change was observed in the identity or yields of the products, indicating an absence of involvement of a charge-separated intermediate complex, whose formation might be expected in a polar solvent medium.[4]

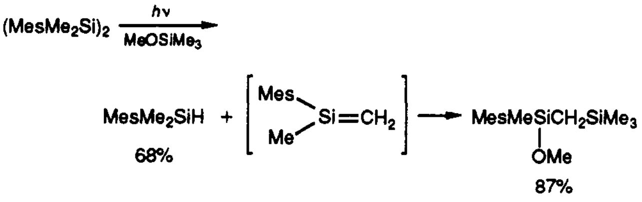
Silenes are known to readily undergo regiospecific addition by the O–H bond of an alcohol to the Si=C double bond to produce an alkoxysilane.[7] Photolysis of $(MesMe_2Si)_2$ in the presence of alcohols afforded high yields of the silene-trapped products, as shown in Scheme IX. Irradiation in the presence of Pr^iOD resulted in a high yield of the deuteriomethylalkoxysilane.

Photolysis of $(MesMe_2Si)_2$ in the presence of acetone affords an "ene reaction" product as shown in Scheme X. A minor amount of *trans*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane was obtained. The cis isomer was not detected.

Scheme X



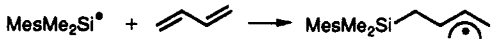
Photochemical decomposition of $(MesMe_2Si)_2$ in the presence of methoxytrimethylsilane produced a high yield of the corresponding alkoxysilane in addition to $MesMe_2SiH$. Methoxytrimethylsilane has been reported to be an excellent regio- and stereospecific trapping reagent for silenes.[19]



Formation of the *cis*- and *trans*-1,3-disilacyclobutanes was completely suppressed in these reactions with oxygenated substrates, except when acetone was the trapping reagent. These reactions are presumably driven by the formation of strong Si–O bonds in the observed products (Si–O bond strength ~120 kcal/mol).[20]

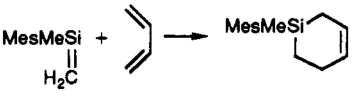
Another experiment was designed to obtain further evidence for the formation of a silene intermediate and information about the mechanism of its formation. The irradiation of $(MesMe_2Si)_2$ was carried out in the presence of an excess of 1,3-butadiene, which can serve as a dual substrate, trapping both the silene $MesMeSi{=}CH_2$ and silyl radicals such as $MesMe_2Si^\bullet$.

Silyl radicals are known to add to unsaturated substrates such as olefins and carbonyl compounds.[21] With butadiene, addition of a silyl radical to one of the terminal positions of the diene unit would result in the formation of a resonance stabilized allyl radical. The allyl radical is then capable of subsequent reactions as discussed below.



A

Silenes react with dienes in a [4 + 2] Diels–Alder-type addition reaction to yield silacyclohexene products, a reaction that is often generally accepted as evidence for the intermediacy of reactive silenes.[7]



The ability of 1,3-butadiene to trap both silyl radicals and silenes molecules was expected to lead to products

---

(16) Bastian, E.; Potzinger, P.; Ritter, A.; Schuchmann, H. P.; Von Sonntag, C.; Weddle, G. *Ber. Bunsen.-Ges. Phys. Chem.* **1980**, *84*, 56.

(17) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261. Sakurai, H.; Nakadaira, Y.; Kira, M.; Sugiyama, H.; Yoshida, K.; Takiguchi, T. *J. Organomet. Chem.* **1980**, *184*, C36.

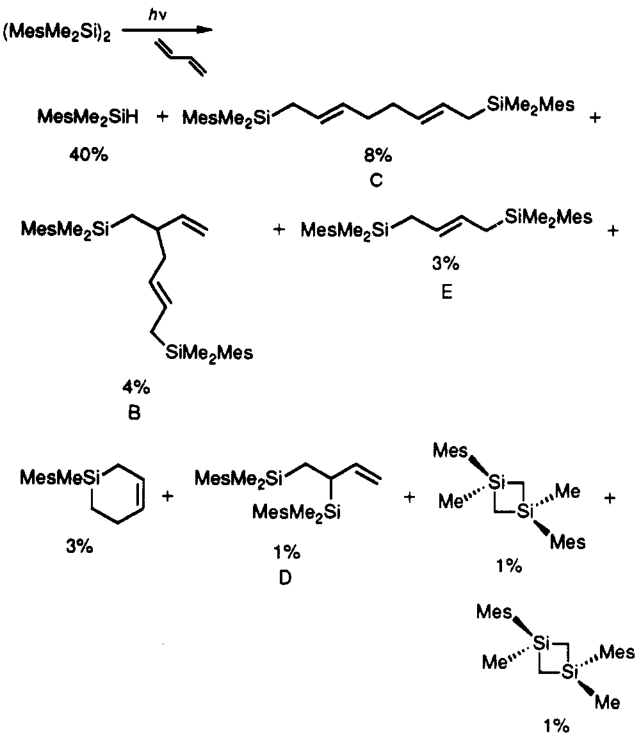
(18) The products included $MesMe_2SiH$ (75%), *trans*- and *cis*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane (8 and 6%, respectively), $(MesMe_2Si)_2O$ (1%), (Si mass recovery 52%), and $(C_6D_{11})_2$ (29% based on consumed $(MesMe_2Si)_2$). That the dicyclohexyl is *not* the result of silyl radical chemistry was demonstrated in a control photolysis of pure C_6D_{12} in which a comparable amount of $(C_6D_{11})_2$ was formed. The presence of adventitious mercury vapor from freeze–pump–thaw degassing on a vacuum line equipped with a mercury diffusion pump was responsible. An oil diffusion pump was employed in all subsequent experiments, and a series of control experiments was carried out on the photolysis of $(MesMe_2Si)_2$ to determine whether the presence of mercury vapor changed the yields of the silicon-containing products. No change was found, but all subsequent experiments were carried out in mercury-free reaction mixtures.

(19) Jones, P. R.; Lee, M. E. *J. Am. Chem. Soc.* **1983**, *105*, 6725. Jones, P. R.; Lee, M. E.; Lin, L. T. *Organometallics* **1983**, *2*, 1039.

(20) Corey, J. Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Vol. 1, p 1.

(21) Wilt, J. W. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum Press: New York, 1983; Vol. 3, p 113.

Scheme XI



that would provide insight into the relative contributions made by the two competing pathways, homolysis and molecular elimination. With the use of a very large excess of butadiene, the wall of the cage containing the geminate pair of silyl radicals contains a high percentage of butadiene molecules, so that many of the silyl radicals should be trapped. The contribution of the sum of the molecular elimination and in-cage disproportionation can be estimated by examining the yields of the products derived from a silene vs those derived from silyl radicals.

Irradiation of $(MesMe_2Si)_2$ in the presence of a 100-fold excess of 1,3-butadiene yielded several products as shown in Scheme XI. A significant amount of polymeric material was also observed, and the silicon mass recovery was only 41%.

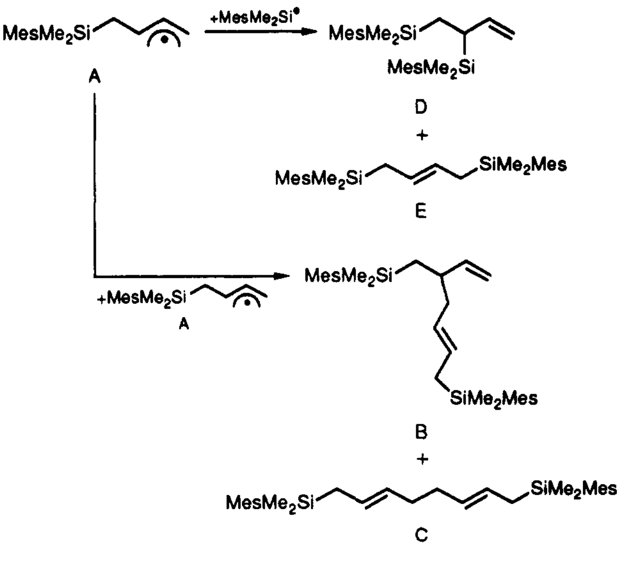
Several important conclusions can be deduced from these results. The formation of the silacyclohexene product, even in low yield, clearly indicates trapping of the silene $MesMeSi{=}CH_2$ by butadiene. The formation of the silyl-substituted alkenes and dienes denote trapping of the silyl radicals by 1,3-butadiene. This is also indicated by the *reduction* in the yield of $MesMe_2SiH$, presumed to be due to the trapping of silyl radicals that undergo disproportionation in the absence of butadiene. The formation of these products is rationalized by the mechanism shown in Scheme XII.

An upper limit for the sum of molecular elimination and in-cage disproportionation can be estimated from the yield obtained for $MesMe_2SiH$ in the presence of butadiene and is therefore on the order of ~40%. This implies that the major photodecomposition pathway for $(MesMe_2Si)_2$ is silicon–silicon bond homolysis to an extent of ~60%.

Irradiation of $(MesMe_2Si)_2$ was also performed with Bu_3SnH as the radical-trapping agent. Since organotin hydrides are known to undergo H-atom abstraction readily, it was thought that Bu_3SnH would intercept $MesMe_2Si^{\bullet}$ radicals produced from $(MesMe_2Si)_2$.

Irradiation of $(MesMe_2Si)_2$ in the presence of a 10-fold excess of Bu_3SnH led to three products as shown below.

Scheme XII



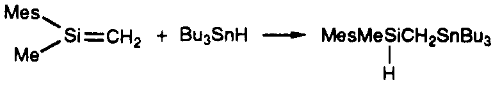
Silicon mass recovery was 74%.

$$(MesMe_2Si)_2 \xrightarrow[Bu_3SnH]{h\nu} \underset{119\%}{MesMe_2SiH} + \underset{34\%}{Bu_3SnSnBu_3} + \underset{28\%}{MesMe_2SiSnBu_3}$$

If Si–Si homolysis were the only pathway for photodissociation of $(MesMe_2Si)_2$, then the maximum yield of $MesMe_2SiH$ that could be obtained from trapping in the presence of Bu_3SnH would be 200% (1 mol of $(MesMe_2Si)_2$ would give 2 mol of $MesMe_2Si^{\bullet}$ radicals). The observed yield of $MesMe_2SiH$ places a lower limit of 20% and an upper limit of 60% on the extent of primary Si–Si homolysis, if quantitative scavenging of the $MesMe_2Si^{\bullet}$ radical is assumed.

The increased yield of $MesMe_2SiH$ obtained in this experiment supports the formation of silyl radicals from $(MesMe_2Si)_2$. The generation of $(Bu_3Sn)_2$ can be ascribed to coupling of two $Bu_3Sn^{\bullet}$ radicals. The stannylsilane $Bu_3SnSiMe_2Mes$ can be formed by coupling of the corresponding stannyl and silyl radicals, and if this process is responsible, then the upper limit of the extent of primary homolysis increases to 74%. The presence of tin in these products was confirmed by mass spectrometry.

The likelihood of direct addition of an Sn–H bond to the silene $MesMeSi{=}CH_2$ is small, since there is little evidence for the uncatalyzed addition of M–H (M = Si, Ge, Sn) bonds to Si=C double bonds.[22] If this reaction were to occur, the addition would be expected to take place in accordance with the polarity of the Si=C ($Si^{\delta+}{=}C^{\delta-}$) bond of the silene and the Sn–H ($Sn^{\delta+}H^{\delta-}$) bond of the tin hydride.

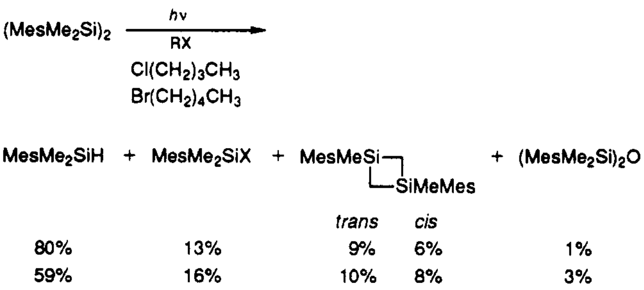


$$Mes(Me)Si{=}CH_2 + Bu_3SnH \longrightarrow MesMeSi(H)CH_2SnBu_3$$

---

[22] Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorsphol, K. *Organometallics* **1987**, *6*, 1246.

Scheme XIII



Photolysis of $(MesMe_2Si)_2$ in the presence of both Bu_3SnH and $MeOSiMe_3$ was performed in order to determine the extent of silene formation when $(MesMe_2Si)_2$ was irradiated in the presence of tributyltin hydride. An additional trapping agent was needed that would insure reaction of any silene formed with the added substrate rather than with $Bu_3Sn^•$ generated from Bu_3SnH. Methoxytrimethylsilane was chosen over alcohol trapping agents since the former should not react with $Bu_3Sn^•$ radicals.

The photolysis of $(MesMe_2Si)_2$ in the presence of a 1-fold excess of Bu_3SnH and a 10-fold excess of $MeOSiMe_3$ afforded four products as shown below.

Trapping of the silene $MesMeSi{=}CH_2$ was confirmed by the formation of the alkoxysilane. The yields of $MesMe_2SiH$ and $(Bu_3Sn)_2$ did not alter dramatically. However, the yield of $MesMe_2SiSnBu_3$ decreased considerably, probably due to the lower concentration of the Bu_3SnH trapping agent. Silicon mass recovery was 98%.

$$(MesMe_2Si)_2 \xrightarrow[\substack{Bu_3SnH \\ MeOSiMe_3}]{h\nu} \underset{122\%}{MesMe_2SiH} + \underset{64\%}{MesMeSi(OMe)CH_2SiMe_3} + \underset{19\%}{Bu_3SnSnBu_3} + \underset{6\%}{MesMe_2SiSnBu_3}$$

Since the concentration of Bu_3SnH in this experiment was only twice that of $(MesMe_2Si)_2$, there was opportunity for silyl radical disproportionation to compete with hydrogen abstraction from Bu_3SnH. If one believed that those $MesMe_2Si^•$ radicals that escaped the cage were effectively scavenged at this concentration of Bu_3SnH, the 64% yield of silene–methoxytrimethylsilane adduct would have to be ascribed entirely to molecular elimination plus in-cage disproportionation. This would leave a 58% yield of $MesMe_2SiH$ due to $MesMe_2Si^•$ that escaped the cage, giving a lower limit of 29% for primary photochemical Si–Si bond homolysis.

Alkyl halides were also employed as radical scavengers. Silyl radicals are known to readily abstract halogen atoms from alkyl halides.[23] However, for $MesMe_2Si^•$ radicals produced from $(MesMe_2Si)_2$, only modest yields of $MesMe_2SiX$ (X = Cl, Br) were obtained when chlorobutane and bromopentane were the trapping agents employed (Scheme XIII). The presence of chlorobutane did not lead to a decrease in the yield of $MesMe_2SiH$, but a decrease of ca. one-fifth (from ca. 80% to ca. 65%) occurred with bromopentane scavenger. Silicon recoveries in these experiments were 55% and 48%, respectively.

The low yield of the bromosilane was rather surprising, since the abstraction of halogen from alkyl halides has been reported to be the most facile with alkyl bromides.[23] High yields of chlorosilanes and germanes were reported in the photochemical decomposition of $PhMe_2M{-}M'Me_3$ (M, M′ = Si, Ge) derivatives in the presence of CCl_4.[24] Also noteworthy are the yields of the isomeric disilacyclobutanes obtained in these experiments, undiminished by the presence of alkyl halides. These results indicate that disproportionation of the silyl radicals within the solvent cage is more facile than escape from the cage and subsequent trapping by the alkyl halide. While a high proportion of molecular elimination would also account for the results of the alkyl halide scavenger experiments, this explanation is rendered unlikely by the results of the butadiene and tin hydride trapping experiments presented above.

The photolysis of $(MesMe_2Si)_2$ was also investigated in the presence of triplet photosensitizers such as benzene, naphthalene, and triphenylene to see if triplet energy transfer to $(MesMe_2Si)_2$ would occur to give a triplet silyl radical pair within a cage. If the triplet radical pair were formed, it is conceivable that escape from the solvent cage might be favored by spin conservation over in-cage disproportionation. Photolysis of $(MesMe_2Si)_2$ in benzene resulted in yields of $MesMe_2SiH$ (81%) and the *cis*- and *trans*-disilacyclobutanes (13% and 8%, respectively) nearly unchanged from the yields obtain upon direct irradiation. In addition, small amounts of $(MesMe_2Si)_2O$ (7%) and $MesMe_2SiPh$ (6%) were detected, the latter presumably arising from silyl radical attack on the aromatic ring of benzene.[25]

The excitation energy for the lowest triplet state of benzene is 84 kcal/mol.[26] The lowest excited state singlet and triplet energies for $(MesMe_2Si)_2$ are not known. The possibility therefore exists that the disilane quenches the lowest single excited state of benzene, and thus the sensitized reaction resembles the direct irradiation.

Koob and George have studied the photochemical behavior of 1,1-dimethyl-1-silacyclobutane and 1,1,3-trimethyl-1-silacyclobutane in the gas phase in the presence of benzene as a triplet photosensitizer (with xenon added to increase the rate of intersystem crossing in C_6H_6). Quenching of triplet benzene was suggested, with the formation of a low-lying triplet state of the silacyclobutane.[27]

Irradiation of $(MesMe_2Si)_2$ in the presence of naphthalene (triplet energy 61 kcal/mol)[26] gave nearly unchanged yields of the two isomeric 1,3-disilacyclobutanes (cis 11%, trans 13%) and a small amount of $(MesMe_2Si)_2O$ (8%), but a dramatic decrease in the yield of $MesMe_2SiH$, to 17%, was observed. An obvious suggestion is that the silyl radicals are attacking the aromatic ring system of naphthalene. This, however, is *not* consistent with the

---

(23) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123.

(24) Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261. Sakurai, H.; Nakadaira, Y.; Kira, M.; Sugiyama, H.; Yoshida, K.; Takiguchi, T. *J. Organomet. Chem.* **1980**, *184*, C36.

(25) Bennett, S. W.; Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Organomet. Chem.* **1971**, *28*, 59. Kira, M.; Sugiyama, H.; Sakurai, H. *J. Am. Chem. Soc.* **1983**, *105*, 6436.

(26) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co. Inc.: Menlo, CA, 1978.

(27) George, C.; Koob, R. D. *Organometallics* **1983**, *2*, 39. George, C. A.; Koob, R. D. *Chem. Phys. Lett.* **1984**, *112*, 588. George, C. A.; Koob, R. D. *J. Phys. Chem.* **1985**, *89*, 5086.

yields obtained for the disilacyclobutanes. Both mechanistic pathways suggested for the photolysis of $(MesMe_2Si)_2$, Si–Si bond homolysis followed by disproportionation, and molecular elimination, should result in the formation of 1 mol of $MesMe_2SiH$ for each mole of $MesMeSi{=}CH_2$. This gives a minimum value of 2 for the molar ratio of $MesMe_2SiH$ and disilacyclobutane products, but the observed ratio in this experiment was 1.06. A reasonable, but unproven, explanation for the decreased yield of $MesMe_2SiH$ in this experiment is that this product is being consumed by a photoreaction of naphthalene and $MesMe_2SiH$ whose products were not detected.

No loss of $(MesMe_2Si)_2$ was observed when it was irradiated in the presence of triphenylene (triplet energy 67 kcal/mol).[26]

Conclusion

$(MesMe_2Si)_2SiMe_2$ appears to decompose by two competing pathways. Approximately 30% of the photoreactions lead to the generation of dimethylsilylene Me_2Si: with the concomitant formation of $(MesMe_2Si)_2$. Bond cleavage by molecular elimination of a silane, forming a silene, or silicon–silicon bond homolysis followed by disproportionation of two silyl radicals to a silane molecule and a silene, dominate the photolysis of $(MesMe_2Si)_2SiMe_2$. The generation of Me_2Si and $MesMeSi{=}CH_2$ was supported by the results of trapping experiments, including silene dimerization to stereoisomeric 1,3-disilacyclobutanes whose structures were determined by X-ray crystallography.

The coproduct, $(MesMe_2Si)_2$, of silylene extrusion from $(MesMe_2Si)_2SiMe_2$ was also found to be photolabile. Irradiation of $(MesMe_2Si)_2$ in the absence of a trapping agent afforded $MesMe_2SiH$, and both the *cis*- and *trans*-1,3-disilacyclobutanes. The contributions of two decomposition pathways suggested for $(MesMe_2Si)_2$, silicon–silicon bond homolysis and direct molecular elimination, were probed in a series of trapping and scavenging experiments.

From butadiene trapping experiments, the sum of the contributions to the photodecomposition of $(MesMe_2Si)_2$ of the molecular elimination pathway and Si–Si bond homolysis followed by in-cage radical disproportionation was estimated to be approximately 40%. The contribution of Si–Si bond homolysis to the overall decomposition pathway was thus estimated to be greater than 60%. Trapping experiments with Bu_3SnH placed an upper limit of 74% on the extent of primary Si–Si bond homolysis and a lower limit of 29% on the extent of primary bond homolysis.

Thus the quest for a new class of silylene precursors, $(MesMe_2Si)_2SiYZ$, revealed that the photochemistry of the molecule with Y = Z = Me was rather complex and that other pathways were competing favorably. The presence of the mesityl chromophore does seem to suppress silence generation by a 1,3-silyl shift to the ortho position of the aryl ring in both $(MesMe_2Si)_2SiMe_2$ and $(MesMe_2Si)_2$, but at the expense of silicon–silicon bond rupture.

While these studies have helped to clarify the photochemistry of $(MesMe_2Si)_2SiMe_2$ and $(MesMe_2Si)_2$, the search for an impeccable class of silylene precursors must continue. Recent reports of fluorescence from two discrete excited singlet states of arylpolysilanes,[28] and hints that arylpolysilane photochemistry may be state specific, and controllable through solvent and substituent effects,[29] provide directions for this search.

Experimental Section

General Data. All preparative reactions were performed under an inert atmosphere of argon using oven-dried glassware. Photolyses were carried out in a Rayonet RS photochemical reactor equipped with low-pressure mercury lamps emitting 254-nm radiation at 20 °C using a quartz cell. Solvents were dried and distilled under nitrogen atmosphere prior to use. Cyclohexane and benzene were distilled over Na. Tetrahydrofuran was distilled from benzophenone sodium ketyl. Solutions prepared for photolysis were assembled in an inert atmosphere drybox (Vacuum Atmosphere Drybox He-493 equipped with dry-train purifier).

^1H, ^2D, and ^{13}C NMR were recorded on a Varian XL-300 or Gemini-300 FT spectrometer. ^{29}Si NMR were recorded on a Varian XL-300 or Varian XL-500 MHz spectrometer using the INEPT sequence.[30] Infrared spectra were recorded on a Mattson Polaris FT-IR spectrophotometer. Spectra were run in solution, neat, or as a KBr pellet. Ultraviolet spectra were recorded on a Cary-219 ultraviolet spectrophotometer using Beckman 1-cm quartz cells. Mass spectra were obtained on a Finnigan 9500 GC-MS spectrometer at either 35- or 70-eV ionization voltage. Low-resolution CI-MS spectra were obtained on a Finnigan 3300 GC-MS spectrometer with methane as the reagent gas. High-resolution mass spectra were obtained on a VG ZAB-SE mass spectrometer. Perfluorokerosene was used for the mass calibration. Analytical gas chromatography was carried out on a Hewlett-Packard Model 5890 Series II instrument employing a flame-ionization detector and equipped with a 30-m × 0.32-mm capillary column with a methylpolysiloxane bonded phase. The yields of products were calculated as moles of product formed per mole of starting material consumed (expressed as a percentage), as determined from relative peak areas in gas chromatograms, with use of an internal standard (dodecane or hexadecane). Response factors were calculated for each product.

Materials. Alcohols were distilled over Mg turnings. Acetone and chlorosilanes were distilled over K_2CO_3.

$AlCl_3$ (anhydrous, Aldrich >99%), 2-bromomesitylene (Aldrich 99%), *n*-butyllithium (1.6 or 2.5 M in hexanes, Aldrich), hydrogen chloride (Matheson Gas Co., technical grade), triethylsilane (Petrarch, distilled over CaH_2), methoxytrimethylsilane (Aldrich 99%, distilled over CaH_2), C_6D_{12} (MSD Isotopes, 99.5 atom % D), chlorotrimethylsilane (Petrarch 98%), chlorodimethylphenylsilane (Petrarch), naphthalene (Fisher), triphenylene (Aldrich 99%), tributyltin hydride (Aldrich 97%), bromopentane (Eastman Organic Chemical Co.), chlorobutane (Fisher), hexadecane (Aldrich 99%), dodecane (Aldrich 99%), 1,3-dichloro-1,1,3,3-tetramethyldisiloxane (Petrarch), 2-propanol-*d* (Aldrich 98+ % D), dichlorodimethylsilane (Petrarch), 1,3-butadiene (Matheson Gas Co., distilled over CaH_2), lithium metal (rods, Aldrich 99%), magnesium metal (turnings, Aldrich 98%). Mesityllithium was prepared by the method described by West and co-workers.[31]

1,2-Dichlorotetramethyldisilane.[32] In a three-neck round-bottom flask equipped with a reflux condenser, a gas inlet tube (pasteur disposable pipet), and a magnetic stirring bar, were

---

[28] Sakurai, H.; Shugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837.

[29] Bobbitt, K. L. Photochemical Generation of Germylenes and Silylenes: Mechanism of Germylene and Silylene Addition to 1,3-Dienes. Doctoral Dissertation, Washington University, St. Louis, MO, Dec. 1990.

[30] Blinka, T. A.; Helmer, B. J.; West, R. *Adv. Organomet. Chem.* **1984**, *23*, 193.

[31] Zigler, S. S.; Johnson, L. M.; West, R. *J. Organomet. Chem.* **1988**, *341*, 187.

[32] Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478.

placed 39.46 g (0.146 moles) of $(PhMe_2Si)_2$,[33] 300 mL of C_6H_6, and a small amount of anhydrous $AlCl_3$ (2–4 spatula scoops). Anhydrous HCl gas was bubbled through the solution, and the reaction was monitored by gas chromatography. After approximately 2.5 h most of $(PhMe_2Si)_2$ had been consumed. The solvent was then removed by distillation under argon. The remaining residue was fractionally distilled under reduced pressure to give 14.65 g (0.078 mol) of $(ClMe_2Si)_2$ as a colorless liquid: bp 75–79 °C (20 mm), lit. bp 146 °C (760 mm);[34] yield 53%; ^1H NMR ($CDCl_3$) δ 0.46 (s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.9; MS (EI, 70 eV) *m/e* (relative intensity) 188 (M^+, 6), 186 (M^+, 9), 153 (6), 151 (16), 95 (55), 94 (13), 93 (99), 74 (12), 73 (99), 65 (28), 63 (12), 59 (15), 58 (100).

1,2-Dimesityltetramethyldisilane. In a three-neck round-bottom flask equipped with a 125-mL pressure-equilibrated addition funnel were placed 30.29 g (0.15 mol) of 2-bromomesitylene and 100 mL of diethyl ether. The flask was cooled with a dry ice/CCl_4 bath (−23 °C). Butyllithium (120 mL, 2.5 M in hexanes) was transferred to the addition funnel with a cannula and added dropwise to the solution over 1 h. The reaction mixture was warmed to room temperature and stirred for 12 h. The liquid portion of the reaction mixture was removed to a cold trap, and the remaining off-white solid (MesLi) was washed twice with 50 mL of diethyl ether. The mesityllithium (19 g, 0.15 mol) was then dissolved in 125 mL of THF and transferred with a cannula to a separate three-neck round-bottom flask equipped with a reflux condenser and a 125-mL pressure-equilibrated addition funnel. The reaction flask was cooled with an ice bath. In the addition funnel was charged 14.65 g (0.078 mol) of $(ClMe_2Si)_2$ in 50 mL of THF. The chlorosilane was added dropwise to the mesityllithium solution over 1 h. The solution was stirred for 4 h and then allowed to warm to room temperature. Hexane (50 mL) and 10% aqueous $NaHSO_4$ (50 mL) were added and the resulting solution stirred for 15 min. The organic layer was extracted and dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue recrystallized from hexane (0 °C). The resulting white crystalline solid was washed with cold hexane to give 11.9 g (0.034 mol) of $(MesMe_2Si)_2$: mp 77–79 °C; yield 43%; ^1H NMR (C_6D_6) δ 0.50 (s, 12 H, SiMe), 2.08 (s, 6 H, *p*-CH_3), 2.26 (s, 12 H, *o*-CH_3), 6.68 (s, 4 H, ArH); ^{31}C NMR (C_6D_6, 75 MHz) δ 3.2, 21.1, 25.4, 129.4, 132.7, 138.0, 144.2; ^{29}Si NMR (C_6D_6, 99 MHz) δ −20.9; MS (EI, 70 eV) *m/e* (relative intensity) 354 (M^+, 1), 339 (1), 179 (11), 178 (42), 177 (100), 161 (29), 159 (15), 149 (27), 147 (13), 145 (10), 133 (10), 121 (11), 120 (11), 119 (20), 105 (27), 91 (13), 59 (29); exact mass determination for $C_{22}H_{34}Si_2$ calcd 354.2199, obs 354.2217; UV-vis (C_6H_{12}) λ_{max} = 249 nm (ϵ = 22 000). Anal. Calcd for $C_{22}H_{34}Si_2$: C, 74.53; H, 9.67. Found: C, 73.00; H, 9.75.

1,3-Diphenylhexamethyltrisilane.[6] In a three-neck round-bottom flask equipped with a reflux condenser and a 125-mL pressure-equilibrated addition funnel were placed 3.4 g (0.47 mol) of Li metal (cut into small pieces) and 60 mL of THF. In the addition funnel were placed 18.5 g (0.11 mol) of $PhMe_2SiCl$ in 30 mL of THF. The chlorosilane was added dropwise over 30 minutes. After stirring for 1.5 h, the solution became deep red and was stirred for an additional 6 h. In a separate three-neck round-bottom flask equipped with a reflux condenser and a pressure-equilibrated addition funnel was placed 7.16 g (0.055 moles) of Me_2SiCl_2 in 40 mL of THF. The flask was cooled with an ice bath. The solution containing $PhMe_2SiLi$ was transferred with a cannula to the addition funnel and added dropwise to the solution over 1.5 h. The reaction mixture was warmed to room temperature and stirred for 15 h. H_2O (30 mL) was added dropwise over 15 min followed by addition of 100 mL of hexane. The organic layer was extracted and dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue fractionally distilled under reduced pressure to give 7.41 g (0.022 mol) of $(PhMe_2Si)_2SiMe_2$ as a viscous colorless liquid: bp 137–142 °C (0.5 mm), lit. bp 156–160 °C (1.2 mm); yield 42%; ^1H NMR ($CDCl_3$) δ 0.11 (s, 6 H, $SiSiMe_2Si$), 0.31 (s, 12 H, $Ph\mathit{Me}_2Si$), 7.32–7.41 (m, 10 H, $\mathit{Ph}Me_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −6.5, −3.3, 127.7, 128.3, 133.7, 139.6; ^{29}Si NMR (C_6D_6, 59 MHz) δ −48.1, −18.4; MS (EI, 35 eV) *m/e* (relative intensity) 328 (M^+, 8), 313 (2), 193 (37), 178 (15), 177 (12), 163 (18), 136 (14), 135 (100), 117 (12), 116 (74), 73 (13).

1,3-Dichlorohexamethyltrisilane.[31] In a three-neck round-bottom flask equipped with a reflux condenser and a gas inlet bubbler were placed 13.90 g (0.042 mol) of $(PhMe_2Si)_2SiMe_2$ in 125 mL of C_6H_6 and a small amount of anhydrous $AlCl_3$. Gaseous HCl was bubbled through the solution for 5 h, and the reaction was monitored by gas chromatography. After about 5 h nearly all of $(PhMe_2Si)_2SiMe_2$ had been consumed. The solvent was removed by distillation and the residue fractionally distilled under reduced pressure to give 6.48 g (0.026 mol) of $(ClMe_2Si)_2SiMe_2$ as a colorless liquid: bp 135–139 °C (33 mm), lit. bp 82–83 °C (11 mm);[34] yield 63%; ^1H NMR (C_6D_6) δ 0.15 (s, 6 H, $SiSiMe_2Si$), 0.39 ($ClMe_2Si$); ^{13}C NMR (C_6D_6, 75 MHz) δ −7.7, 2.9; MS (EI, 70 eV) *m/e* (relative intensity) 246 (M^+, 0.1), 244 (M^+, 0.1), 153 (19), 151 (48), 131 (14), 116 (42), 93 (15), 73 (100).

1,3-Dimesitylhexamethyltrisilane. Mesityllithium was prepared from 10.97 g (0.055 mol) 2-bromomesitylene and 105 mL of Bu^nLi (1.6 M in hexane) in 75 mL Et_2O as described above in the synthesis of $(MesMe_2Si)_2$. In a three-neck round-bottom flask equipped with a reflux condenser and a 125-mL pressure-equilibrated addition funnel was placed 6.48 g (0.026 mol) of $(ClMe_2Si)_2SiMe_2$ in 75 mL of THF. The reaction flask was cooled with an ice bath. The mesityllithium, in 75 mL THF, was transferred by cannula to the addition funnel and added dropwise to the solution over 1 h. The reaction mixture was warmed to room temperature and stirred for an additional 4 h. Hexane (150 mL) and 10% aqueous $NaHSO_4$ (15 mL) were added followed by 20 mL of H_2O. The organic layer was extracted and dried over $MgSO_4$. The solvent was removed on a rotary evaporator to give a viscous yellow liquid. The crude product was separated by flash silica gel column chromatography to give 10.92 g (0.026 mol) of $(MesMe_2Si)_2SiMe_2$ as a viscous colorless liquid, yield 20%: ^1H NMR ($CDCl_3$) δ 0.16 (s, 6 H, $SiSiMe_2Si$), 0.47 (s, 12 H, $Mes\mathit{Me}_2Si$), 2.26 (s, 6 H, *p*-CH_3), 2.31 (s, 12 H, *o*-CH_3), 6.77 (s, 4 H, Ar–H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −3.4, 3.1, 20.9, 25.2, 128.9, 132.6, 138.0, 144.1; ^{29}Si NMR ($CDCl_3$, 59 MHz) δ −43.8, −19.3; MS (EI, 35 eV) *m/e* (relative intensity) 412 (M^+, 6), 236 (10), 235 (39), 220 (12), 178 (22), 177 (100, 161 (40), 159 (10), 149 (18), 116 (24), 73 (33); exact mass determination for $C_{24}H_{40}Si_3$ calcd 412.2474, obs 412.2446; UV-vis (C_6H_{12}) λ_{max} = 250 nm (ϵ = 22 000).

1,3-Dimesityltetramethyldisiloxane. Mesityllithium was prepared from 10.12 g (0.051 mol) of 2-bromomesitylene and 100 mL of Bu^nCl (1.6 M in hexane) in 50 mL of Et_2O as described above in the synthesis of $(MesMe_2Si)_2$. In a three-neck round-bottom flask equipped with a reflux condenser and a 50-mL pressure-equilibrated addition funnel was placed 6.08 g (0.030 mol) of $(ClMe_2Si)_2O$ in 60 mL of THF. The mesityllithium, in 35 mL of THF, was transferred with a cannula to the addition funnel and added dropwise to the solution over 45 min. The flask was warmed to room temperature an stirred for 6 h. Hexane (100 mL) and H_2O (50 mL) were added, and the organic layer was extracted and dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the crude product separated by flash silica gel column chromatography to give 1.69 g (4.5 mmol) of $(MesMe_2Si)_2O$ as a viscous colorless liquid, yield 15%: ^1H NMR (C_6D_6) δ 0.45 (s, 12 H, SiMe), 2.09 (s, 6 H, *p*-CH_3), 2.41 (s, 12 H, *o*-CH_3), 6.72 (s, 4 H, ArH); ^{13}C NMR (C_6D_6, 75 MHz), δ 5.0, 20.5, 24.2, 129.6, 133.0, 138.8, 143.9; ^{29}Si NMR (C_6D_6, 99 MHz) δ −0.9; MS (+CI, CH_4) *m/e* (relative intensity) 370 (M^+, 1), 355 (14), 253 (14), 252 (33), 251 (100), 250 (14), 149 (19), 135 (11), 133 (48), 122 (12), 121 (89), 120 (20), 119 (42); exact mass determination for $C_{22}H_{34}Si_2O$ calcd 370.2148, $C_{21}H_{31}Si_2O$ (M − 15) calcd 355.1913, obs 355.1900; IR (neat) ν = 1070, 1032 cm^{-1} (br, Si–O–Si).

Procedure for the Photolysis of 1,3-Dimesitylhexamethyltrisilane and 1,2-Dimesityltetramethyldisilane. Cyclohexane (or in special cases C_6D_{12}, THF, or C_6H_6) solutions of

---

(33) Gilman, H.; Ingham, R. K.; Smith, A. G. *J. Org. Chem.* **1953**, *18*, 1743.

(34) Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1963**, *1*, 153.

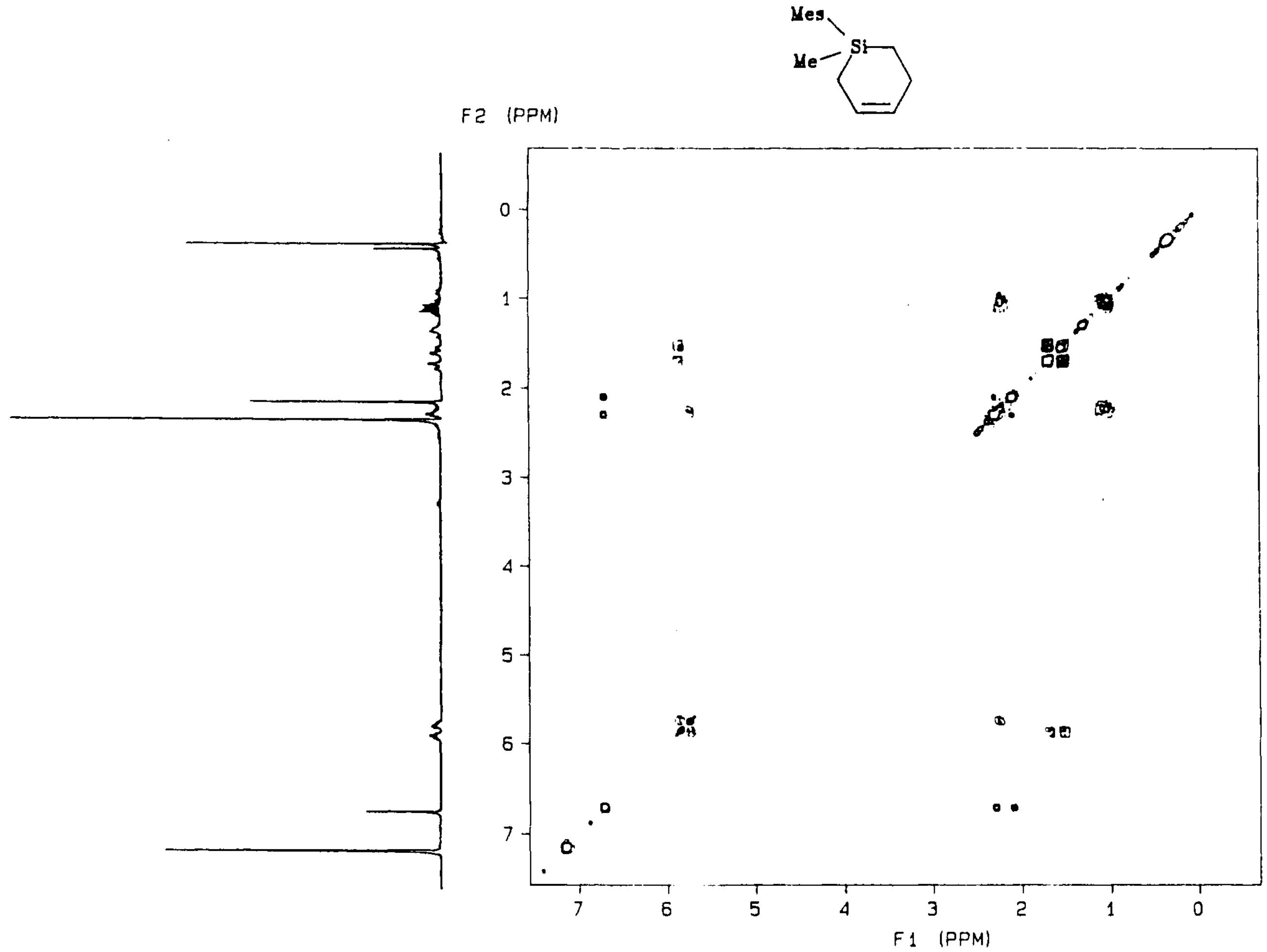


Figure 3. Two-dimensional COSY experiment for 1-mesityl-1-methyl-1-silacyclohex-3-ene in C_6D_6 at 300 MHz.

the reactants were loaded into a quartz photolysis tube equipped with a Teflon stopcock with Viton O-rings in the drybox under nitrogen. Typically, 0.11–0.44 mmol of silane precursor and internal standard (dodecane or hexadecane) at concentrations of 10^{-1} molar were used with an excess of trapping reagent (7–11 molar equiv). The reaction mixtures were degassed to 0.02 Torr by freeze–pump–thaw cycles on a vaccum line and then irradiated with an array of low-pressure mercury lamps in a Rayonet photochemical reactor at 254 nm. Conversions of 54% to 84% were obtained with irradiation times of 4–12 h. Product yields were determined by gas chromatography. The products were separated and purified by preparative gas chromatography and then characterized spectroscopically, as listed below.

$Et_3SiSiMe_2H$:[35] ^{1}H NMR ($CDCl_3$) δ 0.14 (d, 6 H, Si*Me*$_2$H, *J* = 4 Hz), 0.62 (quartet, 6 H, CH_3C*H*$_2$Si, *J* = 8 Hz), 0.95 (t, 9 H, C*H*$_3$CH$_2$Si, *J* = 8 Hz), 3.68 (septet, 1 H, SiH, *J* = 4 Hz); MS (EI, 35 eV) *m*/*e* (relative intensity) 174 (M^+, 13), 117 (54), 116 (23), 115 (98), 114 (10), 103 (13), 90 (11), 89 (92), 88 (39), 87 (99), 86 (23), 85 (13), 73 (26), 71 (15), 59 (100), 58 (19), 57 (11).

$MesMe_2SiH$: ^{1}H NMR (C_6D_6) δ 0.30 (d, 6 H, SiMe, *J* = 4 Hz), 2.11 (s, 3 H, *p*-CH$_3$), 2.37 (s, 6 H, *o*-CH$_3$), 4.93 (septet, 1 H, SiH, *J* = 4 Hz), 6.73 (s, 2 H, ArH); ^{13}C NMR (C_6D_6, 75 MHz) δ −2.7, 20.7, 23.6, 129.0, 131.0, 139.0, 144.2; ^{29}Si NMR (C_6D_6, 99 MHz) δ −26.1; MS (EI, 70 eV) *m*/*e* (relative intensity) 178 (M^+, 43), 177 (11), 164 (17), 163 (100), 162 (20), 161 (52), 160 (10), 159 (23), 147 (16), 145 (14), 135 (20), 133 (15), 119 (36), 118 (11), 117 (13), 115 (15), 105 (23), 103 (12), 91 (32), 79 (12), 78 (10), 77 (22), 73 (21), 72 (25), 67 (15), 65 (10), 59 (70), 58 (39), 53 (18), 51 (10); exact mass determination for $C_{11}H_{18}Si$ calcd 178.1178, obs 178.1175; IR (neat) ν = 2146 cm^{-1} (s, Si–H).

$MesMe_2SiSiMe_2H$: ^{1}H NMR (C_6D_6) δ 0.13 (d, 6 H, Si*Me*$_2$H, *J* = 4 Hz), 0.46 (s, 6 H, Mes*Me*$_2$Si), 2.10 (s, 3 H, *p*-CH$_3$), 2.37 (s, 6 H, *o*-CH$_3$), 4.10 (septet, 1 H, SiH, *J* = 4 Hz), 6.72 (s, 2 H, ArH); ^{13}C NMR (C_6D_6, 75 MHz) δ −6.3, 1.2, 20.5, 24.7, 129.4, 131.7, 138.4 144.3; ^{29}Si NMR (C_6D_6, 59 MHz) δ −34.8, −23.0; MS (EI, 70 eV) *m*/*e* (relative intensity) 236 (M^+, 1), 178 (18), 177 (100), 161 (39), 159 (15), 149 (28), 147 (14), 145 (11), 133 (10), 121 (10), 119 (20), 116 (22), 105 (18), 91 (15), 73 (37), 69 (11), 67 (14), 59 (83), 58 (13), 55 (10), 53 (17); exact mass determination for $C_{13}H_{24}Si_2$ calcd 236.1416, obs 236.1437; IR (neat) ν = 2094 cm^{-1} (s, Si–H).

$MesMe_2SiSiMe_2SiMe_2H$: ^{1}H NMR (C_6D_6) δ 0.10 (d, 6 H, Si*Me*$_2$H, *J* = 4 Hz), 0.18 (s, 6 H, SiSi*Me*$_2$Si), 0.52 (s, 6 H, Mes*Me*$_2$Si), 2.10 (s, 3 H, *p*-CH$_3$), 2.36 (s, 6 H, *o*-CH$_3$), 4.04 (septet, 1 H, SiH, *J* = 4 Hz), 6.72 (s, 2 H, ArH); ^{13}C NMR (C_6D_6, 75 MHz) δ −6.6, −5.5, 2.6, 20.5, 25.1, 129.4, 132.3, 138.3, 144.1; ^{29}Si NMR (C_6D_6, 59 MHz) δ −45.5, −35.5, −20.3; MS (EI, 70 eV) *m*/*e* (relative intensity) 294 (M^+, 0.6), 178 (25), 177 (98), 175 (24), 161 (39), 159 (20), 149 (25), 147 (12), 145 (11), 119 (14), 118 (10), 117 (24), 116 (100), 73 (68), 59 (42); exact mass determination for $C_{15}H_{30}Si_3$ calcd 294.1655, obs 294.1640; IR (neat) ν = 2092 cm^{-1} (s, Si–H).

$MesMe_2SiOSiEt_3$: ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6 H, SiMe$_2$), 0.55 (quart, 6 H, CH$_3$C*H*$_2$Si, *J* = 8 Hz), 0.91 (t, 9 H, C*H*$_3$CH$_2$Si, *J* = 8 Hz), 2.24 (s, 3 H, *p*-CH$_3$), 2.42 (s, 6 H, *o*-CH$_3$), 6.79 (s, 2 H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz), δ 4.9, 6.1, 6.5, 20.7, 24.0, 129.2, 133.4, 138.9, 144.1; ^{29}Si NMR ($CDCl_3$, 59 MHz) δ −11.0, −1.9; MS (EI, 70 eV) *m*/*e* (relative intensity) 308 (M^+, 0.1), 279 (11), 251 (14), 223 (14), 221 (10), 193 (10), 188 (31), 161 (23), 159 (54), 149 (10), 147 (15), 145 (14), 135 (21), 133 (27), 131 (26), 125 (20), 121 (20), 120 (100), 119 (49), 118 (21), 117 (19), 112 (12), 111 (82), 110 (33), 107 (10), 105 (73), 104 (60), 103 (82), 97 (10), 96 (22), 91 (34), 89 (31), 87 (22), 77 (10), 73 (43), 59 (92); IR ($CDCl_3$) ν = 1071, 1050, 1009 cm^{-1} (br, Si–O–Si).

---

[35] Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288.

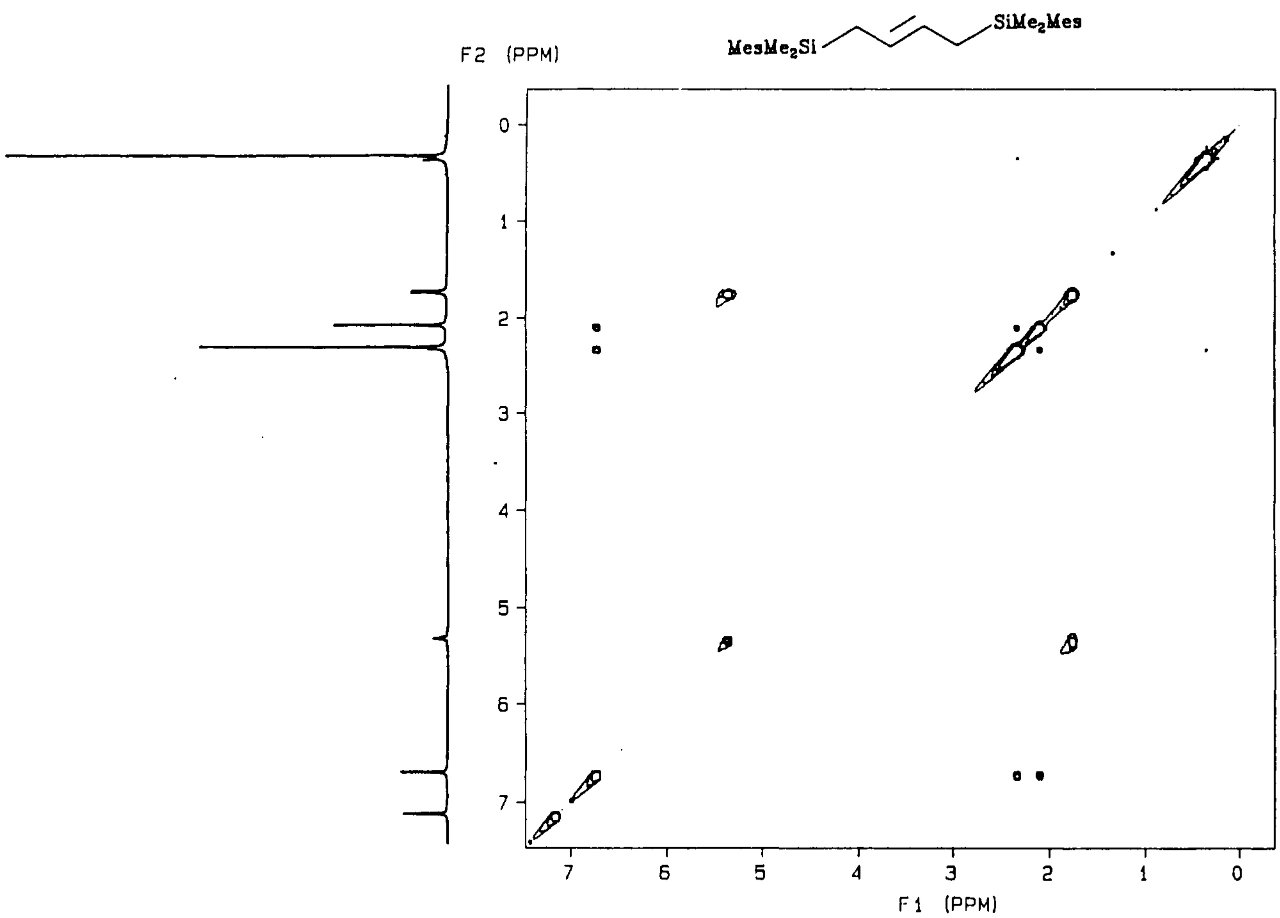


Figure 4. Two-dimensional COSY experiment for *trans*-1,2-bis(mesityldimethylsilyl)but-2-ene in C_6D_6 at 300 MHz.

***trans*-1,3-Dimesityl-1,3-dimethyl-1,3-disilacyclobutane**: ^1H NMR (C_6D_6) δ 0.35 (s, 6 H, SiMe), 0.89 (s, 4 H, ring-CH_2), 2.14 (s, 6 H, *p*-CH_3), 2.45 (s, 12 H, *o*-CH_3), 6.77 (s, 4 H, ArH); ^{13}C NMR (C_6D_6, 75 MHz), δ 2.1, 12.5, 20.7, 23.8, 129.0, 133.2, 138.8, 143.9; ^{29}Si NMR (C_6D_6, 59 MHz) δ −3.9; MS (EI, 35 eV) *m/e* (relative intensity) 352 (M^+, 0.6), 337 (15), 234 (28), 233 (100), 232 (42), 219 (10), 217 (21), 205 (36), 191 (17), 175 (14), 174 (18), 173 (99), 163 (14), 161 (30), 159 (35), 149 (13), 147 (14), 145 (16), 133 (22), 119 (16), 103 (25), 73 (21), 59 (20); exact mass determination for $C_{22}H_{32}Si_2$ calcd 352.2043, $C_{21}H_{29}Si_2$ (M − 15) 337.1808, obs 337.1808; mp 122–124 °C. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.96; H, 9.16. Found: C, 75.10; H, 8.79.

***cis*-1,3-Dimesityl-1,3-dimethyl-1,3-disilacyclobutane**: ^1H NMR (C_6D_6) δ 0.48 (s, 6 H, SiMe), 0.64–0.85 (dd, 4 H, ring-CH_2, J_{gem} = 13 Hz, J_{vic} = 3 Hz), 2.15 (s, 6 H, *p*-CH_3), 2.38 (s, 12 H, *o*-CH_3), 6.76 (s, 4 H, ArH); ^{13}C NMR (C_6D_6, 75 MHz) δ 0.5, 12.5, 20.7, 23.3, 128.8, 134.0, 138.7, 143.7; ^{29}Si NMR (C_6D_6, 99 MHz) δ −3.8; MS (EI, 35 eV) *m/e* (relative intensity) 352 (M^+, 1), 337 (14), 235 (10), 234 (28), 233 (100), 232 (43), 219 (10), 217 (21), 205 (36), 191 (16), 175 (14), 174 (18), 173 (95), 163 (13), 161 (30), 159 (35), 149 (14), 147 (14), 145 (16), 133 (23), 119 (16), 103 (24), 73 (23), 59 (23); exact mass determination for $C_{22}H_{32}Si_2$ calcd 352.2043, $C_{21}H_{29}Si_2$ (M − 15) calcd 337.1808, obs 337.1779; mp 115–116 °C. Anal. Calcd for $C_{22}H_{32}Si_2$: C, 74.96; H, 9.16. Found: C, 75.69; H, 9.70.

MesMe$_2$SiOCH(CH$_3$)$_2$: ^1H NMR (C_6D_6) δ 0.43 (s, 6 H, SiMe), 1.08 (d, 6 H, OCH(C*H*$_3$)$_2$, *J* = 6 Hz), 2.11 (s, 3 H, *p*-CH_3), 2.49 (s, 6 H, *o*-CH_3), 3.88 (septet, 1 H, OC*H*(CH$_3$)$_2$, *J* = 6 Hz), 6.76 (s, 2 H, ArH); ^{13}C NMR (C_6D_6, 75 MHz) δ 3.2, 20.6, 24.2, 25.5, 65.0, 129.5, 132.0, 138.9, 144.4; ^{29}Si NMR (C_6D_6, 59 MHz) δ 5.0; MS (EI, 70 eV) *m/e* (relative intensity) 236 (M^+, 8), 221 (29), 180 (16), 179 (100), 177 (18), 163 (36), 161 (35), 159 (12), 119 (32), 117 (30), 116 (60), 105 (18), 101 (57), 91 (22), 77 (15), 75 (86), 61 (12), 59 (13); exact mass determination for $C_{14}H_{24}SiO$ calcd 236.1596, obs 236.1594; IR (neat) ν = 1071, 1037 cm^{-1} (br, Si–O–C).

MesMe$_2$SiOMe: ^1H NMR (C_6D_6) δ 0.40 (s, 6 H, Mes*Me*$_2$Si), 2.11 (s, 3 H, *p*-CH_3), 2.44 (s, 6 H, *o*-CH_3), 3.25 (s, 3 H, SiOMe), 6.75 (s, 2 H, ArH); ^{13}C NMR (C_6D_6, 75 MHz) δ 2.0, 21.0, 24.1, 49.6, 129.5, 131.4, 138.9, 144.4; ^{29}Si NMR (C_6D_6, 59 MHz) δ 9.9; MS (EI, 35 eV) *m/e* (relative intensity) 208 (M^+, 19), 194 (17), 193 (100), 163 (23), 161 (28), 133 (16), 89 (16), 59 (13); exact mass determination for $C_{12}H_{20}SiO$ calcd 208.1283, obs 208.1298; IR (neat) ν = 1085, 1028 cm^{-1} (br, Si–O–C).

MesMeSi[OCH(CH$_3$)$_2$]CH$_2$D: ^1H NMR (C_6D_6) δ 0.41 (t, 2 H, SiCH$_2$D, *J* = 2 Hz), 0.43 (s, 3 H, Mes*Me*Si), 1.09 (d, 6 H, OCH(C*H*$_3$)$_2$, *J* = 6 Hz), 2.11 (s, 3 H, *p*-CH_3), 2.49 (s, 6 H, *o*-CH_3), 3.88 (septet, 1 H, OC*H*(CH$_3$)$_2$, *J* = 6 Hz), 6.76 (s, 2 H, ArH); ^2D NMR (C_6D_6, 46 MHz) δ 0.41 (t, 1 D, SiCH$_2$D, *J* = 2 Hz); ^{13}C NMR (C_6D_6, 75 MHz) δ 2.6, 2.9 (CH$_2$D, should be a 1:1:1 triplet but third peak probably overlapping with another resonance at 3.1 ppm), 3.1, 20.5, 24.2, 25.4, 64.9, 129.5, 132.0, 138.9, 144.4; ^{29}Si NMR (C_6D_6, 59 MHz) δ 5.0; MS (EI, 70 eV) *m/e* (relative intensity) 237 (M^+, 6), 222 (14), 221 (11), 180 (53), 179 (52), 178 (17), 164 (19), 163 (29), 162 (23), 161 (24), 120 (13), 119 (38), 118 (28), 117 (68), 105 (19), 103 (12), 102 (40), 101 (35), 91 (28), 78 (10), 77 (23), 76 (100), 75 (13), 73 (10), 61 (12), 60 (17), 59 (12), 53 (10); exact mass determination for $C_{14}H_{23}SiOD$ calcd 237.1659, obs 237.1684; IR (neat) ν = 1069, 1022 cm^{-1} (br, Si–O–C).

MesMe$_2$SiOC(CH$_3$)═CH$_2$: ^1H NMR (C_6D_6) δ 0.50 (s, 6 H, Mes*Me*$_2$Si), 1.74 (s, 3 H, C(C*H*$_3$)═CH$_2$), 2.09 (s, 3 H, *p*-CH_3), 2.44 (s, 6 H, *o*-CH_3), 4.01 (s, 1 H, C═CH$_2$), 4.07 (s, 1 H, C═CH$_2$), 6.73 (s, 2 H, ArH); ^{13}C NMR (C_6D_6, 75 MHz) δ 2.3, 20.6, 22.6, 23.6, 90.6, 129.6, 131.4, 139.2, 144.1, 155.9; ^{29}Si NMR (C_6D_6, 59 MHz) δ 6.9; MS (EI, 70 eV) *m/e* (relative intensity) 234 (M^+, 6), 220 (10), 219 (51), 201 (11), 177 (14), 173 (15), 162 (14), 161 (90), 160 (13), 159 (33), 149 (14), 145 (20), 133 (15), 131 (11), 119 (32), 117 (12), 115 (23), 105 (20), 99 (23), 91 (40), 79 (13), 77 (27), 76 (10), 75 (100), 73 (14), 67 (12), 65 (10), 61 (19), 53 (13), 59 (31); exact mass determination for $C_{14}H_{22}SiO$ calcd 234.1440, obs 234.1442; IR (neat) ν = 1071, 1044 cm^{-1} (br, Si–O–C).

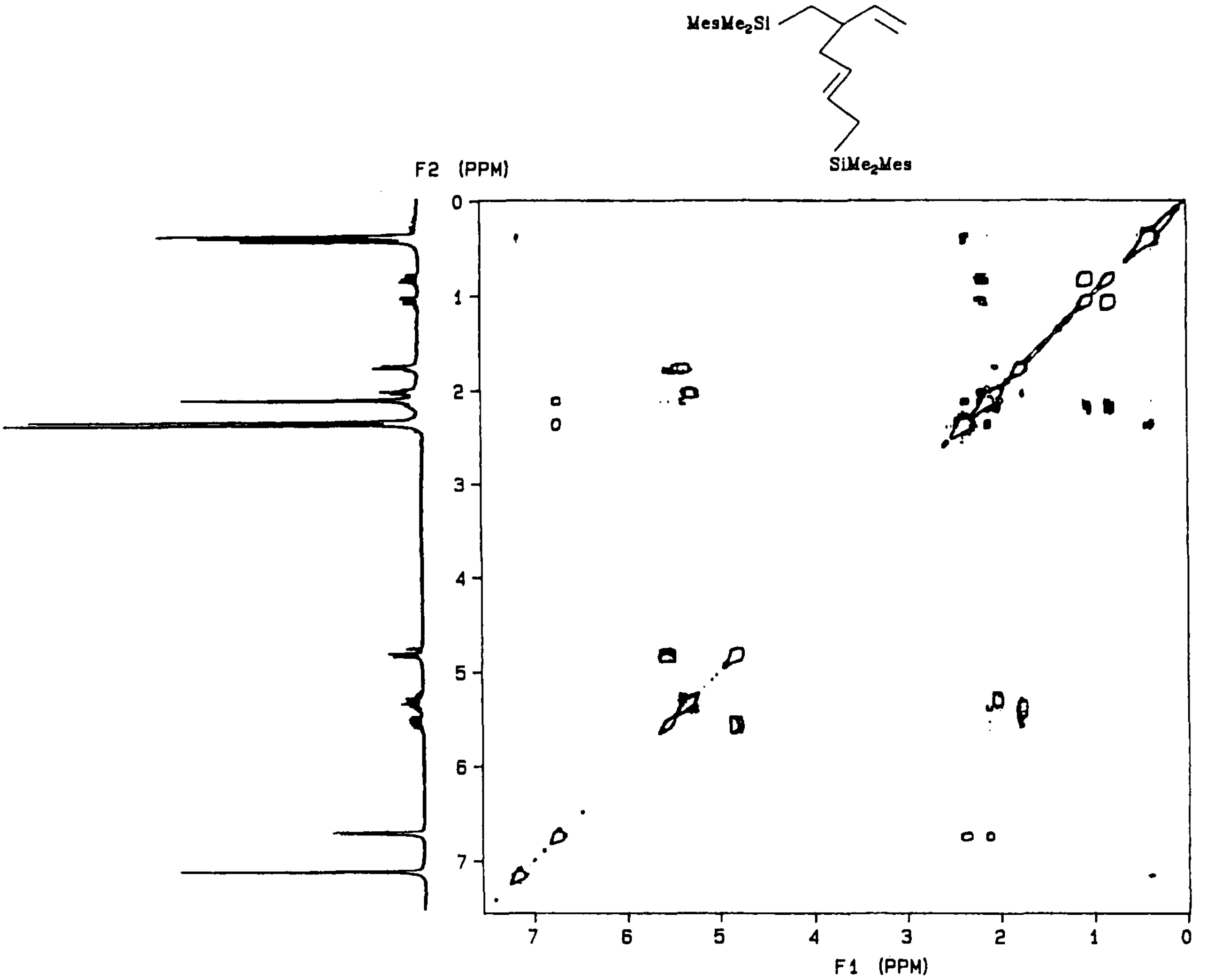


Figure 5. Two-dimensional COSY experiment for *trans*-7-(mesityldimethylsilyl)-3-(mesityldimethylsilylmethyl)-1,5-heptadiene in C_6D_6 at 300 MHz.

MesMeSi(OMe)CH$_2$SiMe$_3$: ^{1}H NMR (C_6D_6) δ 0.07 (s, 9 H, CH$_2$Si*Me*$_3$), 0.10 (s, 1 H, SiC*H*$_2$SiMe$_3$), 0.14 (s, 1 H, SiC*H*$_2$SiMe$_3$), 0.46 (s, 3 H, Mes*Me*$_2$Si), 2.11 (s, 3 H, *p*-CH$_3$), 2.47 (s, 6 H, *o*-CH$_3$), 3.23 (s, 3 H, SiOMe), 6.76 (s, 2 H, ArH); ^{13}C NMR (C_6D_6, 75 MHz) δ 1.2, 3.3, 6.0, 21.0, 24.1, 49.6, 129.6, 132.4, 138.8, 144.0; ^{29}Si NMR (C_6D_6, 59 MHz) δ 9.5, 0.2; MS (EI, 70 eV) *m/e* (relative intensity) 280 (M$^+$, 1), 267 (11), 266 (29), 265 (100), 235 (16), 233 (31), 194 (16), 193 (90), 177 (16), 173 (21), 163 (24), 162 (19), 161 (88), 160 (88), 159 (23), 147 (14), 145 (28), 133 (59), 132 (12), 131 (41), 120 (18), 119 (24), 117 (12), 115 (13), 105 (11), 91 (13), 89 (19), 73 (38), 59 (62); exact mass determination for $C_{15}H_{28}Si_2O$ calcd 280.1679, $C_{14}H_{25}Si_2O$ (M − 15) calcd 265.1444, obs 265.1457; IR (neat) ν = 1087, 1069, 1048 cm^{-1} (br, Si–O–C).

(Bu$_3$Sn)$_2$: MS (EI, 70 eV) *m/e* (relative intensity) 571 (0.3), 569 (0.4), 551 (0.3), 523 (M − 57, 1), 521 (0.8), 467 (0.8), 411 (2), 355 (2), 291 (2), 235 (3), 179 (50), 178 (18), 177 (60), 176 (22), 175 (42), 173 (13), 125 (17), 123 (47), 122 (14), 121 (100), 120 (46), 119 (76), 118 (32), 117 (39), 57 (7).

MesMe$_2$SiSnBu$_3$: MS (EI, 70 eV) *m/e* (relative intensity) 456 (0.4), 411 (M − 56, 3), 353 (1), 297 (3), 239 (4), 179 (22), 178 (20), 177 (100), 176 (10), 175 (17), 163 (20), 161 (30), 159 (17), 149 (35), 147 (14), 145 (12), 135 (19), 133 (19), 131 (11), 123 (19), 121 (59), 120 (35), 119 (92), 118 (24), 117 (28), 116 (10), 115 (10), 105 (12), 91 (13), 73 (10), 59 (55).

MesMe$_2$SiCl: MS (EI, 70 eV) *m/e* (relative intensity) 214 (M$^+$, 1), 212 (M$^+$, 3), 194 (14), 179 (18), 161 (23), 119 (16), 99 (15), 85 (51), 71 (79), 70 (13), 69 (11), 57 (100), 56 (15), 55 (21).

MesMe$_2$SiPh: MS (EI, 70 eV) *m/e* (relative intensity) 254 (M$^+$, 1), 239 (26), 237 (10), 193 (13), 178 (13), 177 (21), 176 (100), 161 (55), 159 (11), 145 (11), 135 (52), 133 (18), 131 (11), 121 (10), 119 (20), 107 (19), 105 (35), 93 (11), 91 (22), 67 (11), 59 (25), 53 (16).

Control Experiment on the Photolysis of 1,2-Dimesityltetramethyldisilane. A solution of 0.105 g (0.297 mmol) of (MesMe$_2$Si)$_2$ and 0.074 g (0.327 mmol) of hexadecane was dissolved in 3.13 mL of cyclohexane and then irradiated for 8 h and 40 min. The following products were detected by FID-GC and GC-MS (60% conversion of (MesMe$_2$Si)$_2$): MesMe$_2$SiH (82%), *trans*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane (10%), *cis*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane (7%), and (MesMe$_2$Si)$_2$O (1%). The yields of the individual products were also calculated by ^{1}H NMR spectroscopy. The solvent was removed from the photolysate mixture and the residue dissolved in C_6D_6. The observed integral for the *p*-CH$_3$ group on the mesityl ring for each component was measured and compared with that for the CH$_2$ resonance of hexadecane. The yields obtained were as follows: MesMe$_2$SiH (87%), *trans*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane (12%), *cis*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane (9%), and (MesMe$_2$Si)$_2$O (not detected). The nearly identical yields obtained from both the FID-GC and ^{1}H NMR analyses indicate that the products are thermally stable under the gas chromatographic conditions.

Photolysis of 1,2-Dimesityltetramethyldisilane in the Presence of Water. A mixture of 0.065 g (0.184 mmol) of (MesMe$_2$Si)$_2$, 0.036 g (0.209 mmol) of dodecane, and 100 μL (5.56 mmol) of H_2O dissolved in 1.90 mL of cyclohexane was irradiated for 10 h after which 82% of (MesMe$_2$Si)$_2$ had been consumed. The solubility of H_2O in C_6H_{12} is 0.01% by volume at 20 °C

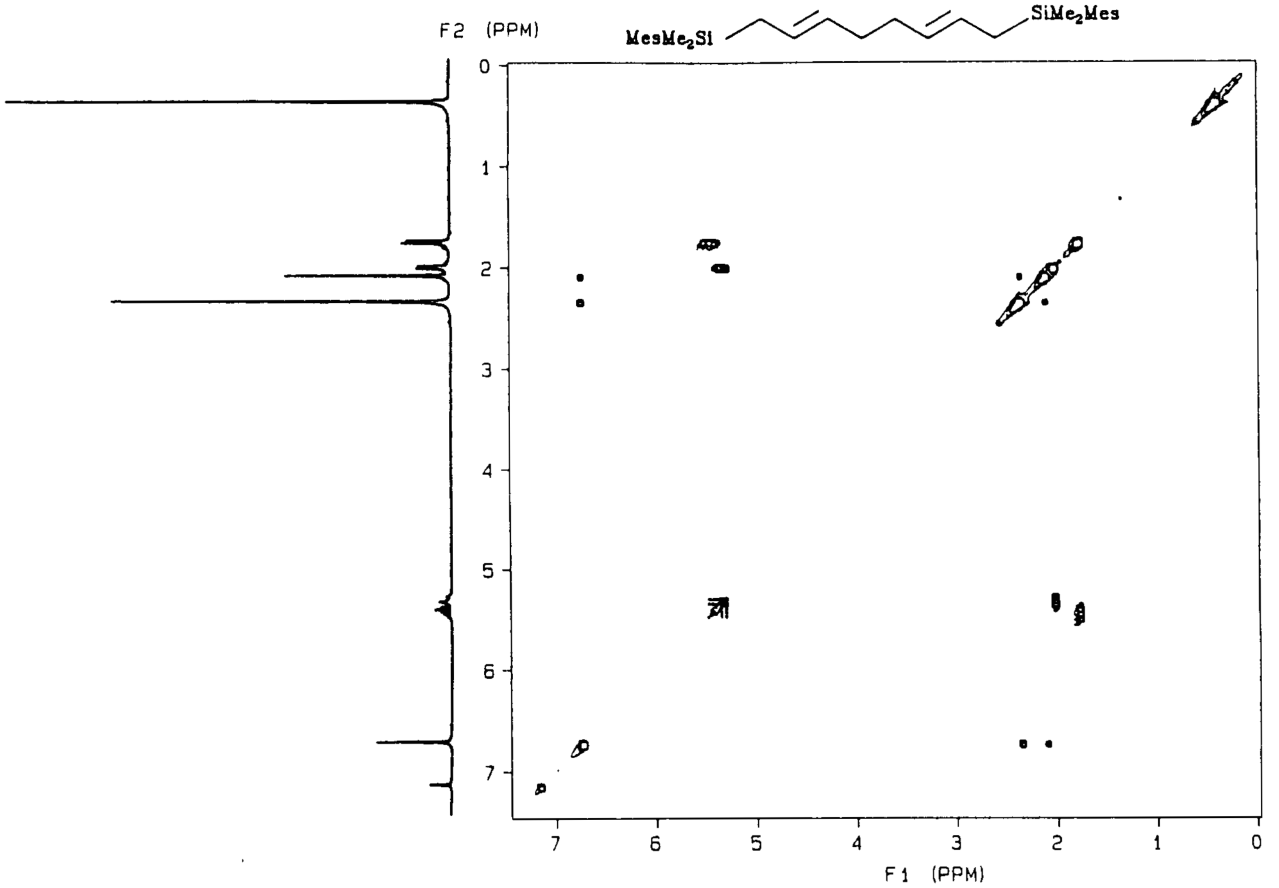


Figure 6. Two-dimensional COSY experiment for *trans,trans*-1,8-bis(mesityldimethylsilyl)-2,6-octadiene in C_6D_6 at 300 MHz.

(would give approximately 5 × 10^{-3} mol or 0.06 mol equiv of H_2O to $(MesMe_2Si)_2$). Three products were formed: $MesMe_2SiH$ (82%), $MesMe_2SiOH$ (10%), and $(MesMe_2Si)_2O$ (34%). $MesMe_2SiOH$ was isolated by column chromatography using silica gel (40–60 mesh) with THF as the eluent.

MesMe$_2$SiOH: ^{1}H NMR (C_6D_6) δ 0.37 (s, 6 H, SiMe), 2.12 (s, 3 H, *p*-CH_3), 2.40 (s, 6 H, *o*-CH_3), 6.76 (s, 2 H, ArH) (the OH resonance was not observed); MS (EI, 70 eV) *m/e* (relative intensity) 194 (M^+, 18), 180 (16), 179 (100), 163 (11), 162 (10), 161 (75), 159 (14), 133 (14), 119 (65), 117 (15), 115 (17), 105 (14), 103 (12), 91 (46), 79 (12), 78 (11), 77 (28), 75 (79), 65 (15), 61 (23), 60 (15), 53 (12), 51 (13).

Photolysis of 1,2-Dimesityltetramethyldisilane in the Presence of 1,3-Butadiene. A mixture of 0.108 g (0.305 mmol) of $(MesMe_2Si)_2$ and 0.065 g (0.288 mmol) of hexadecane dissolved in 3.26 mL of cyclohexane was placed in the quartz cell and then degassed. 1,3-Butadiene (degassed, 2.60 mL, 31.3 mmol) was vacuum transferred to the solution then irradiated for 8 h and 30 min after which 84% of $(MesMe_2Si)_2$ had been consumed. FID-GC and GC-MS analyses showed the formation of several products: $MesMe_2SiH$ (40%), *trans*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane (1%), *cis*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane (1%), $(MesMe_2Si)_2O$ (1%), 1-mesityl-1-methyl-1-silacyclohex-3-ene (3%), 1,2-bis(mesityldimethylsilyl)but-3-ene (1%), *trans*-1,4-bis(mesityldimethylsilyl)but-2-ene (3%), *trans*-7-(mesityldimethylsilyl)-3-(mesityldimethylsilylmethyl)-1,5-heptadiene (4%), and *trans,trans*-1,8-bis(mesityldimethylsilyl)-2,6-octadiene (8%, + isomer 1%).

1-Mesityl-1-methyl-1-silacyclohex-3-ene: ^{1}H NMR (C_6D_6) δ 0.33 (s, 3 H, SiMe), 0.95–1.15 (m, 2 H, $\mathrm{SiC}\mathit{H}_2\mathrm{CH}_2$), 1.48–1.75 (m, 2 H, $\mathrm{SiC}\mathit{H}_2\mathrm{CH}$), 2.11 (s, 3 H, *p*-$CH_3$), 2.24 (m, 2 H, $\mathrm{SiCH_2C}\mathit{H}_2$), 2.30 (s, 6 H, *o*-$CH_3$), 5.70–5.78 (m, 1 H, $\mathrm{SiCH_2CH_2C}\mathit{H}$), 5.84–5.91 (m, 1 H, $\mathrm{SiCH_2C}\mathit{H}$), 6.72 (s, 2 H, ArH) [2-D ^{1}H NMR, Figure 3]; ^{13}C NMR (C_6D_6, 75 MHz) δ −1.4, 13.7, 17.0, 20.9, 23.6, 24.7, 126.7, 129.4, 130.1, 132.2, 138.5, 144.3; ^{29}Si NMR (C_6D_6, 59 MHz) δ −9.8; MS (EI, 70 eV) *m/e* (relative intensity) 230 (M^+, 0.8), 215 (0.7), 163 (41), 162 (10), 161 (57), 159 (12), 147 (10), 145 (11), 133 (14), 119 (17), 111 (20), 110 (100), 105 (14), 95 (14), 91 (11), 67 (16), 53 (11); exact mass determination for $C_{15}H_{22}Si$ calcd 230.1491, obs 230.1495.

1,2-Bis(mesityldimethylsilyl)but-3-ene: ^{1}H NMR (C_6D_6) δ (as mixture with *cis*-1,3-disilacyclobutane) 0.34, 0.36, 0.37, 0.38, 0.43 (s, 3 H each, SiMe region, the maximum number of SiMe resonances that should be observed is 4), 2.11 (s, 6 H, *p*-CH_3), 2.26 (s, 6 H, *o*-CH_3), 2.29 (s, 6 H, *o*-CH_3), 4.74–4.83 (m, 2 H, $\mathrm{CH{=}C}\mathit{H}_2$), 5.63–5.75 (m, 1 H, $\mathrm{C}\mathit{H}\mathrm{{=}CH_2}$), 6.70 (s, 2 H, ArH); MS (+CI, CH_4) *m/e* (relative intensity) 409 (M + 1, 1), 408 (M^+, 1), 393 (2), 289 (4), 217 (11), 179 (11), 178 (36), 177 (100), 149 (8), 121 (50), 119 (16), 113 (8), 97 (8), 73 (7).

***trans*-1,4-Bis(mesityldimethylsilyl)but-2-ene**: ^{1}H NMR (C_6D_6) δ 0.36 (s, 12 H, SiMe), 1.77 (dd, 4 H, $\mathrm{SiC}\mathit{H}_2\mathrm{CH{=}CH}$, *J* = 6, 2 Hz), 2.11 (s, 6 H, *p*-CH_3), 2.34 (s, 12 H, *o*-CH_3), 5.33–5.37 (m, 2 H, CH=CH), 6.73 (s, 4 H, Ar-H) [2-D ^{1}H NMR, Figure 4]; ^{13}C NMR (C_6D_6, 75 MHz) δ 1.8, 20.5, 24.1, 24.6, 125.5, 129.5, 132.0, 138.5, 144.4; ^{29}Si NMR (C_6D_6, 59 MHz) δ −5.2; MS (+CI, CH_4) *m/e* (relative intensity) 409 (M + 1, 1), 408 (M^+, 2), 393 (0.4), 201 (11), 178 (17), 177 (100), 121 (11), 73 (6); exact mass determination for $C_{26}H_{40}Si_2$ calcd 408.2668, obs 408.2669.

***trans*-7-(Mesityldimethylsilyl)-3-[(mesityldimethylsilyl)methyl]-1,5-heptadiene.** ^{1}H NMR (C_6D_6) δ 0.37 (s, 6 H, $\mathrm{Mes}\mathit{Me}_2\mathrm{SiCH_2CH{=}CH}$), 0.40 (s, 3 H, $\mathrm{Mes}\mathit{Me}_2\mathrm{SiCH_2CHCH_2{=}CH_2}$), 0.43 (s, 3 H, $\mathrm{Mes}\mathit{Me}_2\mathrm{SiCH_2CHCH{=}CH_2}$), 0.83 (dd, 1 H, $\mathrm{SiC}\mathit{H}_2\mathrm{CHCH{=}CH_2}$, *J* = 15, 9 Hz), 1.06 (dd, 1 H, $\mathrm{SiC}\mathit{H}_2\mathrm{CHCH{=}CH_2}$, *J* = 15, 5 Hz), 1.76 (d, 2 H, $\mathrm{SiC}\mathit{H}_2\mathrm{CH{=}CH}$, *J* = 7 Hz), 2.03 (m, 2 H, $\mathrm{CH_2CHC}\mathit{H}_2\mathrm{CH{=}CH}$, *J* = 6 Hz), 2.17 (m, not resolved, 1 H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH{=}CH_2}$, partially overlapping with *p*-CH_3's), 2.11 (s, 6 H, *p*-CH_3), 2.12 (s, 6 H, *p*-CH_3), 2.34 (s, 12 H, *o*-CH_3), 2.38 (s, 12 H, *o*-CH_3), 4.77–4.86 (m, 2 H, $\mathrm{HC{=}C}\mathit{H}_2$), 5.23–5.43 (m, 2 H, CH=CH), 5.49–5.61 (m, 1 H, $\mathit{H}\mathrm{C{=}CH_2}$), 6.73 (s, 4 H, ArH), 6.74 (s, 4 H, ArH) [2-D ^{1}H NMR, Figure 5]; ^{13}C NMR (C_6D_6, 75 MHz) δ 2.38, 2.42, 3.8, 4.4, 20.9, 23.98, 24.44, 24.93, 24.99, 41.5, 42.4, 113.1, 126.74, 127.07, 129.55, 129.58, 131.9, 132.5, 138.35, 138.48, 144.26, 144.36, 145.0; ^{29}Si NMR (C_6D_6, 59 MHz) δ −5.2, −3.9; MS (+CI, CH_4) *m/e* (relative intensity) 463 (M + 1, 0.5), 462 (M^+, 0.2), 447 (2), 343 (2), 178 (17), 177 (100), 151 (7), 121 (22), 119 (7), 57 (4); exact mass determination for $C_{30}H_{46}Si_2$ calcd 462.3138, $C_{21}H_{34}Si_2$ (M − 119) calcd 342.2199, obs 342.2177.

***trans,trans*-1,8-Bis(mesityldimethylsilyl)-2,6-octadiene:** ^{1}H NMR (C_6D_6) δ 0.39 (s, 12 H, SiMe), 1.78 (d, 4 H, SiCH_2CH=CH, J = 7 Hz), 2.02 (m, 4 H, CH_2CH_2), 2.11 (s, 6 H, pCH_3), 2.36 (s, 12 H, o-CH_3), 5.29–5.49 (m, 4 H, CH=CH), 6.73 (s, 4 H, ArH) [2D ^{1}H NMR, Figure 6]; ^{13}C NMR (C_6D_6, 75 MHz) δ 1.8, 20.5, 23.8, 24.6, 33.4, 126.6, 129.5, 131.9, 138.5, 144.4; ^{29}Si NMR (C_6D_6, 59 MHz) δ −5.2; MS (+CI, CH_4) *m/e* (relative intensity) 463 (M + 1, 0.3), 462 (M^+, 0.2), 343 (1), 178 (17), 177 (100), 151 (11), 121 (17), 75 (2), 73 (2); exact mass determination for $C_{30}H_{46}Si_2$ calcd 462.3138, $C_{29}H_{43}Si_2$ (M − 15) calcd 447.2903, obs 447.2940. Anal. Calcd for $C_{30}H_{46}Si_2$: C, 77.84; H, 10.01. Found: C, 74.77; H, 9.46.

X-ray Analysis. X-ray-quality crystals of *cis*- and *trans*-1,3-dimesityl-1,3-dimethyl-1,3disilacyclobutane were obtained from saturated solutions in C_6D_6 by slow evaporation of solvent. The crystals were isolated as colorless plates. *trans*-$C_{22}H_{32}Si_2$ (fw 352.7): triclinic, $P\bar{1}$, a = 8.279 (5) Å, b = 8.289 (5) Å, c = 8.466 (4) Å, α = 71.49 (4)°, β = 84.49 (4)°, γ = 75.38 (5)°, v = 533.0 (5) Å^3, z = 1. *cis*-$C_{22}H_{32}Si_2$ (fw 352.7): triclinic, $P\bar{1}$, a = 12.696 (5) Å, b = 13.230 (9) Å, c = 14.928 (7) Å, α = 93.91 (5)°, β = 114.25 (4)°, γ = 103.21 (5)°, v = 2188 (2) Å^3, z = 4; Mo Kα radiation (λ = 0.710 69 Å), 295 K, Siemens R3m/V diffractometer with graphite monochromator. *trans*: 3047 reflections were collected ($3.5 \le 2\theta \le 55.0°$) by use of $2\theta - \theta$ scans. Of these, 2859 reflections were unique (R_{int} = 2.53%) and 2231 were observed ($F > 6.0\sigma(F)$). *cis*: 17 605 reflections were collected ($3.5 \le 2\theta \le 55.0°$) by use of $2\theta - \theta$ scans. Of these, 10 111 reflections were unique (R_{int} = 1.61%) and 4483 were observed ($F > 6.0\sigma(F)$). Both structures were solved by Siemens SHELXTL Plus and refined by fullmatrix least square to R = 4.25%, R_w = 4.37% (*trans*) and R = 5.03%, R_w = 4.94% (*cis*).

Acknowledgment. We are grateful to the United States National Science Foundation for encouragement and support of the research under grant no. CHE-88-02677. We are grateful to Dr. Andrew Tyler and Mr. Dallas New for recording mass spectra, which were obtained at the Washington University Mass Spectrometry Resource, which is supported by National Institutes of Health (grant no. RR0954). We are also grateful to Dr. Andre D'Avignon for help in obtaining NMR data, which were obtained at the Washington University High Resolution NMR Service Facility which was funded in part by the National Institutes of Health Biomedical Research Support Instrument (grant no. 1 S10 RR02004) and by a gift from the Monsanto Company. The Washington University X-ray crystallography Facility has received support from the NSF Chemical Instrumentation program (grant no. CHE-88-11456).

Supplementary Material Available: Structure determination summary with tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates, for *cis*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane and *trans*-1,3-dimesityl-1,3-dimethyl-1,3-disilacyclobutane (37 pages). Ordering information is given on any current masthead page.

OM920339X