9-Acetoxy-3-methoxy-10-phenylphenanthrene (6f) and 9-Acetoxy-10-(*p*-methoxyphenyl)phenanthrene (6g) were identified on the basis of their HPLC retention times in comparison with those of the products from the separately performed photocyclization of the vinyl acetates **3f** and **3g**.

3,6-Dimethoxy-9-(*p*-methoxyphenyl)phenanthrene (7a): UV λ_{max} 246 nm (ϵ 20600), 275 (11900), 300 (8500), 350 (4300), 368 (4000); ^{1}H NMR δ 3.90 (s, 3 H, OCH_3), 4.03 (s, 6 H, 2 OCH_3), 6.98–8.03 (m, 11 H, ArH); MS *m/z* (relative intensity) 344 (M^+, 100), 329 ($M^+ - CH_3$, 42), 301 ($M^+ - CH_3 - CO$, 13); high-resolution MS *m/z* 344.1421 ($C_{23}H_{20}O_3$ requires 344.1412).

3-Methoxy-9-phenylphenanthrene (7d): UV λ_{max} 253 nm (ϵ 36300), 277 (14200), 308 (10500), 342 (1700), 358 (1600); ^{1}H NMR δ 3.85 (s, 3 H, OCH_3), 6.65–7.81 (m, 11 H, ArH), 7.93 (s, 1 H, H-4), 8.54 (d, 1 H, H-5); MS *m/z* (relative intensity) 284 (M^+, 100), 269 ($M^+ - CH_3$, 21), 241 ($M^+ - CH_3 - CO$, 16), 240 (24), 239 (58), 226 (16); high-resolution MS *m/z* 284.1213 ($C_{21}H_{16}O$ requires 284.1201).

13-Bromo-3-methoxy-8-oxonaphtho[2,3,4-*de*]anthracene (10): UV λ_{max} 229 (ϵ 40200), 265 (39400), 291 (18700), 304 (17500), 376 (12400), 393 (13300), 413 (15000); ^{1}H NMR δ 4.08 (s, 3 H, OCH_3), 7.26–8.04 (m, 5 H, ArH), 8.41–9.08 (m, 5 H, ArH); MS *m/z* (relative intensity) 390, 388 (M^+, 100, 100), 375, 373 ($M^+ - CH_3$, 4, 4), 347, 345 ($M^+ - CH_3 - CO$, 11, 11); high-resolution MS *m/z* 388.0099 ($C_{22}H_{13}O_2Br$ requires 388.0089).

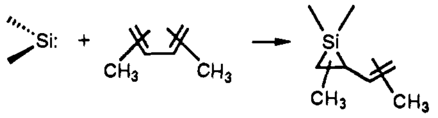
Acknowledgment. We thank Ir. Peter Bode of the Interfaculty Reactor Institute, University of Delft, The Netherlands, for the generous and continuing supply of [^{82}Br]Et_4NBr and Roel H. Fokkens of the Institute of Mass Spectrometry, University of Amsterdam, The Netherlands, for the measurement of the high-resolution mass spectra.

Stable 2-Vinylsiliranes

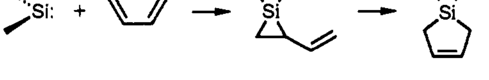
S. Zhang and R. T. Conlin*

Contribution from the Center for Organometallic Research and Education, Department of Chemistry, University of North Texas, Denton, Texas 76203. *Received June 4, 1990. Revised Manuscript Received February 1, 1991*

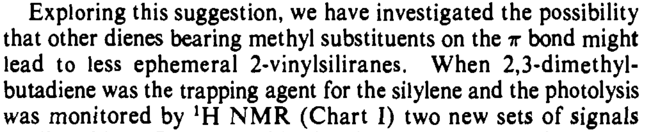
Abstract: Seven 2-vinyl-1,1-dimesitylsiliranes, stable at room temperature over months, have been synthesized from the addition of dimesitylsilylene to 2,3-dimethylbutadiene, 2-methylbutadiene, *trans,trans*-2,4-hexadiene, *cis,cis*-2,4-hexadiene, and *cis,-trans*-2,4-hexadiene. Addition of dimesitylsilylene to the π bond of the diene was stereospecific as indicated by ^{29}Si NMR. Secondary photodecomposition of 2-vinylsiliranes containing a vinylic hydrogen α to the silirane ring led to 2,3-dienylsilanes. Formation of *cis*-2,5-dimethyl-1,1-dimesitylsilacyclopent-3-ene from photolysis of solutions containing *trans,trans*-2,4-hexadiene, 2,2-dimesitylhexamethyltrisilane, and *trans*-2-methyl-3-(1-*trans*-propenyl)-1,1-dimesitylsilirane was stereospecific.



Dienes have long been the reagents of choice for detecting the presence the silylenes from a wide variety of thermal, photochemical, and bimolecular sources in both solution- and gas-phase experiments.[1] In most earlier studies the products have been silacyclopentenes although it has been suggested that these five-membered silacycles likely originate from secondary isomerization of the initial 1,2-adduct, a transient 2-vinyl-1-silirane.[2,3] Herein, we report preparation of seven vinylsiliranes from the addition of dimesitylsilylene to various 1,3-dienes as well as the stereoselectivity and stereospecificity of these reaction paths.



Dimesitylsilylene (**1**), generated from Hg irradiation of hexamethyl-2,2-dimesityltrisilane[4] (**2**) (0.1 M in pentane) for 3 h in a solution saturated with butadiene, afforded dimesitylsilacyclopent-3-ene (**3**) and 2,3-butadienyldimesitylsilane (**4**) in ~1:1 ratio.



At shorter photolysis times the same two products, **3** and **4** were again formed in a similar distribution. The isolation of **4**, a product observed once previously[3a] in earlier studies of thermal and photochemical silylene/diene reactions,[5] suggested that the initial adduct, a 2-vinylsilirane, might be sufficiently long-lived to undergo secondary photolysis to the allenylsilane.

Exploring this suggestion, we have investigated the possibility that other dienes bearing methyl substituents on the π bond might lead to less ephemeral 2-vinylsiliranes. When 2,3-dimethylbutadiene was the trapping agent for the silylene and the photolysis was monitored by ^{1}H NMR (Chart I) two new sets of signals attributable to **5a** appeared in the olefinic region as a doublet at δ 4.47 and a multiplet centered at δ 4.55 after 2-h photolysis.

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(1) For recent studies that offer compelling evidence for 2-vinylsiliranes as undetected but mechanistically required intermediates, see: (a) Lei, D.; Hwang, R.-J.; Gaspar, P. P. *J. Organomet. Chem.* **1984**, *271*, 1. (b) Lei, D.; Gaspar, P. P. *Organometallics* **1985**, *4*, 1471. (c) Gaspar, P. P.; Lei, D. *Organometallics* **1986**, *5*, 1276. (d) Clarke, M. P.; Davidson, I. M. T. *J. Chem. Soc., Chem. Commun.* **1988**, 241.

(2) Gaspar, P. P.; Hwang, R.-J. *J. Am. Chem. Soc.* **1974**, *96*, 6198.

(3) Evidence for the existence of stable vinylsiliranes has been presented earlier, but spectroscopic evidence was not put forth. (a) Ishikawa, M.; Nakagawa, K.-I.; Enokida, R.; Kumada, M. *J. Organomet. Chem.* **1980**, *201*, 151. (b) Nakadaira, Y.; Kanouchui, S.; Sakurai, H. *J. Am. Chem. Soc.* **1974**, *96*, 5621, 5623.

(4) (a) West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343. In the course of our work with dimesitylsilylene from photolysis of **2**, we have found that Hg photolyses also produced very small amounts, <5%, of mesityltrimethylsilane. (b) Sipe, H. J., Jr.; West, R. *J. Organomet. Chem.* **1974**, *70*, 367.

(5) For a review of earlier trisilane photolyses with dienes, see: Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51. More recently: Tortorelli, V.; Jones, M., Jr.; Wu, S. *Organometallics* **1982**, *2*, 759.

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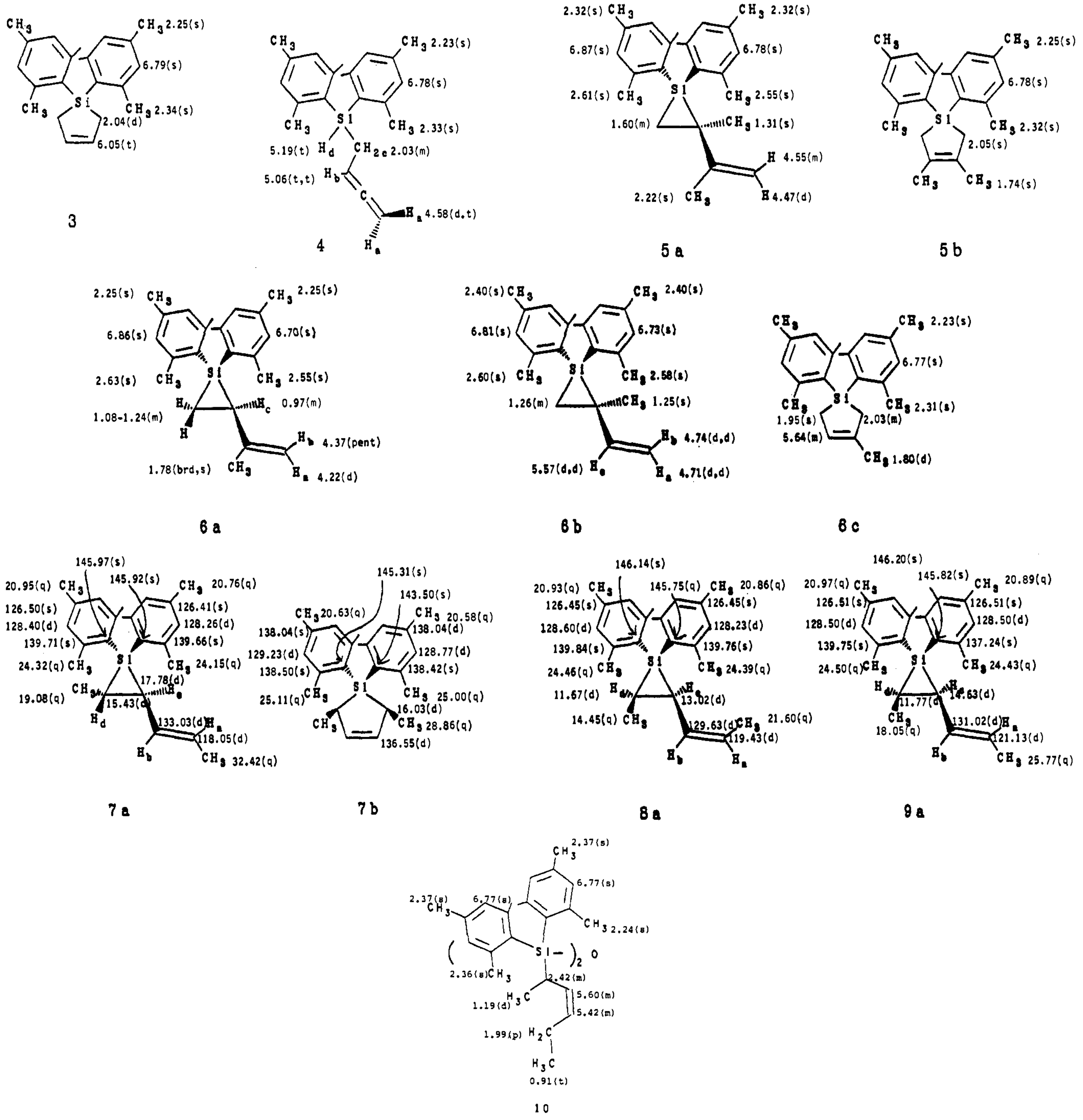
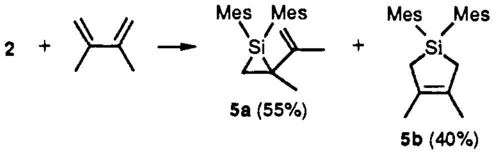
Chart I. ^1H NMR Spectral Data ($CDCl_3$)



Additional signals whose chemical shift and peak multiplicity indicated 1,1-dimesityl-3,4-dimethylsilacyclopent-3-ene (**5b**) and unreacted **2** (70%) were also present in the reaction mixture.[6]



Notable in the ^{13}C spectrum (Chart II) were the prominent off-resonance triplet at δ 105.53 and singlet at δ 150.21 and the upfield ^{29}Si signal at δ −74.12. The remarkably far upfield chemical shift for the silicon atom previously has been associated with the 1,1-dimesitylsilirane ring system,[7] while the position and multiplicity of the proton and carbon chemical shifts indicated atoms of the isopropenyl substituent of **5a**.[8] At longer photolysis times (>6 h), NMR peaks associated with **5a** disappeared and **5b** became the sole product, >90% yield, isolated by vpc.

Although it is tempting to suggest that **5b** originated directly and *exclusively* from photoisomerization of **5a**, this conclusion is not justified at present. Among other mechanistic *possibilities*

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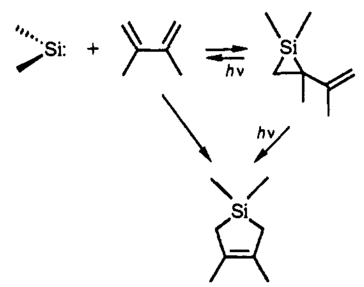
[6] Product ratios reported throughout this paper were determined from integration of the cleanly defined methyl protons of the mesityl groups of the siliranes relative to those of unreacted **2**. We realize that peak areas in NMR spectra may not provide an accurate measure of amounts of products due to possibly large variations in relaxation times and NOE effects. Accordingly, we have compared areas of signals for protons in similar environments.

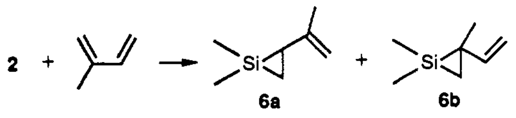
[7] Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310. Although we refer to the characteristic ^{29}Si spectrum δ ~80 as "diagnostic", it should be pointed out that tris(trimethylsilyl)silanes bearing an unsaturated substituent on the central silicon atom also display a ^{29}Si resonance in the same region.

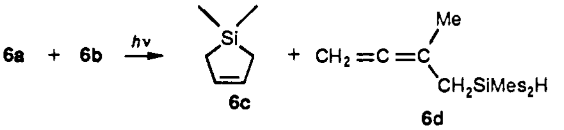
[8] For a recent review of ^{29}Si NMR, see: Williams, E. A. NMR spectroscopy of organosilicon compounds. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1989; p 511.

leading to photostable **5b** is a photoequilibrium between the vinylsilirane and silylene from which follows a minor, but nonreversible, 1,4-addition[9] across the termini of the diene. Thus, a more complex mechanistic picture may arise if **5b** is formed from both a unimolecular and a bimolecular path.[10,11]



The products of the sterically crowded silylene to 2-methylbutadiene revealed additional information but were more difficult to assign spectroscopically. After photolysis, ~2 h, two new signals characteristic of different vinylsiliranes **6a** and **6b** (3:2 ratio) appeared in the ^{29}Si NMR spectra at δ −84.91 and −73.95 and in the ^{13}C spectra as off-resonance triplets at δ 102.40 and 105.43, respectively. Two other products, the five-membered ring **6c** (56%) and (2-methylbuta-2,3-dienyl)silane (**6d**) (~3%), were identified from longer photolysis times, >5 h, and isolated by preparative gas chromatography.

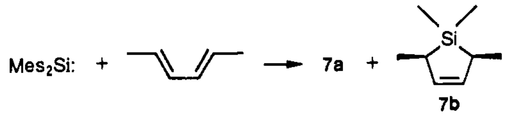




Assignment of the NMR spectra, ^{1}H, ^{13}C, and ^{29}Si, of **6a–6d** was simplified by the change in composition of the reaction mixture with photolysis time and the generally well-separated resonances in each structure. Our approach was to record the ^{29}Si spectrum of the reaction mixture at the shortest time required, typically 1–2 h, for the optimum silicon spectrum of the initially formed 2-vinylsiliranes **6a** and **6b**. Both ^{13}C and ^{1}H NMR spectra were also obtained on this sample. Maximum yields and cleanest spectra, carbon and proton NMR, of the vinylsiliranes were achieved by monitoring the ^{1}H NMR signals of the six ortho methyl protons of the two mesityl groups at δ 2.55 and 2.58 over 30-min photolysis intervals until the previously assigned signals of 3-methyl-1,1-dimesitylsilacyclopent-3-ene (**6c**) grew faster than those for **6a** and **6b**.

Determination of the more reactive π bond of the unsymmetrical diene is problematical since both **6a** and **6b** are photolabile. Nevertheless, at all photolysis times examined by NMR, 0.5–4 h, **6a**, the product of addition to the less substituted π bond of the diene, was larger. Noteworthy is that both vinylsiliranes are thermally stable at room temperature over months, at least.

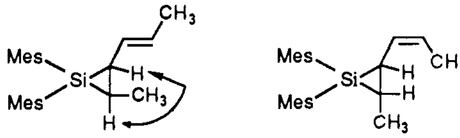
The stereochemistry of 2-vinylsilirane formation was studied by addition of **1** to each of the three configurational isomers of 2,4-hexadiene. Photolysis of pentane solutions of **2** (1.6 × 10^{-2} M) containing a 50-fold excess of *trans,trans*-2,4-hexadiene yielded two new products. The spectrum of the earliest detectable product, observed after 2-h irradiation, was assigned as the 2-vinylsilirane **7a**, on the basis of the ^{29}Si signal at δ −77.36, ^{13}C doublets at δ 118.05 and 133.03, and olefin multiplets of the propenyl group at δ 5.22 in the ^{1}H spectra. With longer photolysis time, >7 h, the upfield ^{29}Si resonance and carbon and proton signals of **7a** disappeared and both the small amount of dimesitylsilylene extrusion product, tetramesityldisilene, from silylene dimerization,[4,12] and the five-membered ring, *cis*-2,5-dimethyl-1,1-dimesitylsilacyclopent-3-ene (**7b**) were identified. The presence of the disilene was detected from its characteristic UV absorption, λ_{max} at 422 nm, and **7b** was isolated by vpc and then characterized by ^{29}Si, ^{13}C, and ^{1}H NMR spectra.



Under the same conditions but in a solution containing *cis,cis*-2,4-hexadiene, photolysis yielded a single product **8a** (^{29}Si: δ −78.16).

Stereospecificity of addition of the silylene to a π component of the conjugated diene might be indicated from the position of the ^{29}Si resonance, previously reported to be 5–10 ppm further upfield for the cis-2,3-disubstituted siliranes than trans isomers.[13] The differences, however, between the chemical shifts of the diastereomers in this study were relatively small compared to the larger influence, a ~30 ppm upfield displacement due to steric compression,[14] from the geminal mesityl groups on the silicon atom of the silirane.

The small variation between the ^{29}Si chemical shifts, δ <1.0, for the diastereomeric 2-vinylsiliranes **7a** and **8a** from silylene addition suggested caution before structural conclusions were drawn. This concern was no less diminished by the similarity of the ^{29}Si values for the two vinylsiliranes **9a** (δ −79.05) and **9b** (δ −77.50), produced in a 9:1 ratio,[15] respectively, from dimesitylsilylene addition to the different configurations of the π bonds in *cis,trans*-2,4-hexadiene. Unequivocal spectroscopic evidence that the favored addition path of the silylene is to the cis double bond was demonstrated by double-resonance proton NMR experiments on **9a**. The magnitude of the vicinal coupling between the nonequivalent ring protons of the silirane, 11.4 Hz, is characteristic of a cis orientation.[16] Noteworthy is that the major cis adduct **9a** again displayed a ^{29}Si resonance that was further upfield than that of the trans isomer **9b**.



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[9] For a discussion of factors influencing carbene 1,4-additions, see: Evanseck, J. D.; Mareda, J.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 73.

[10] At present, the mechanistic origin of the five-membered rings described here is unknown and we have not yet distinguished between (a) a unimolecular ring expansion process of the vinylsiliranes and (b) a silylene extrusion, followed by a bimolecular 1,4-addition of the silylene to the diene (see ref 1). Thermal gas-phase studies of dimethylsilylene reaction with *cis,cis*-2,4-hexadiene indicated a concerted rearrangement of the *cis,cis*-2-propenyl-1,1,3-trimethylsilirane to the acyclic *cis*-hexa-3-silahepta-1,4-diene.[12]

[11] Lei, D.; Gaspar, P. P. *J. Chem. Soc., Chem. Commun.* **1985**, *1149*.

[12] The rate of dimerization of **1** is known to proceed at about the diffusion-controlled limit. Conlin, R. T.; Netto-Ferreira, J. C.; Zhang, S.; Scaiano, J. C. *Organometallics* **1990**, *9*, 1332.

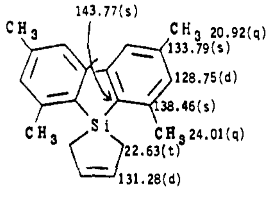
[13] (a) Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288. (b) Reference 7. (c) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355.

[14] The appearance of the silirane chemical shifts at a position considered to be further upfield than usually observed is likely due to additional steric compression imposed by the large mesityl groups. See: Macial, G. W. *Topics in Carbon-13 NMR Spectroscopy*; Levy, G. C., Ed.; Wiley-Interscience: New York, 1974.

[15] The product ratio, 9:1, for addition to the cis and trans Π bonds of *cis,trans*-2,4-hexadiene suggests that the rate constant for addition to the cis-substituted π bond is greater than that for addition to the trans-substituted π bond. We have obtained this ratio from the shortest irradiation times necessary to measure mesityl proton areas of **7a** and **7b** in order to minimize any secondary photolysis of the products. The average product ratio, **9a**:**9b** at 1, 2, and 3 h obtained from integration of the substituted vinylic carbon peaks was 9.1 ± 0.2.

[16] (a) Patel, D. J.; Howden, M. E. H.; Howden, M. E. H.; Roberts, J. D. *J. Am. Chem. Soc.* **1963**, *85*, 3218. (b) Williamson, K. L.; Lansford, C. A.; Nicholson, C. R. *J. Am. Chem. Soc.* **1964**, *86*, 762.

Chart II. ^{13}C NMR Spectral Data ($CDCl_3$)



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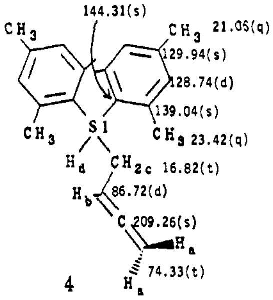

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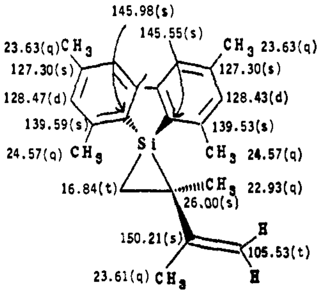
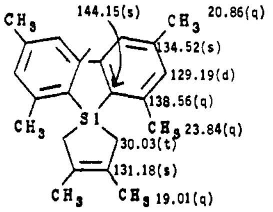
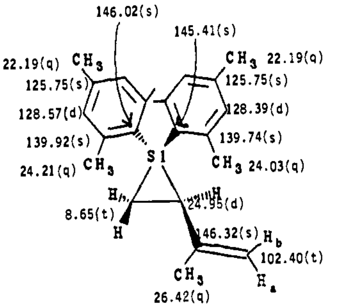


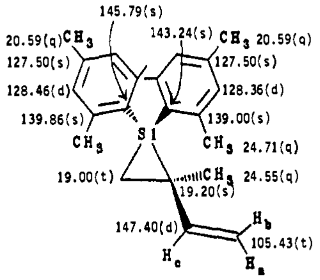
5a



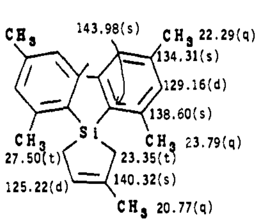
5b



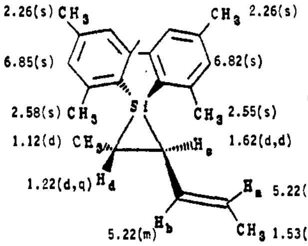
6a



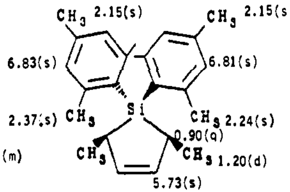
6b



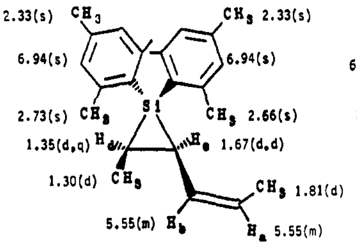
6c



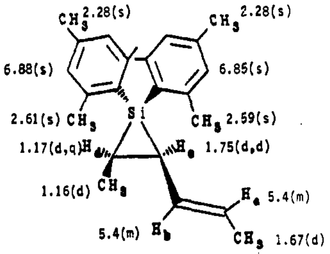
7a



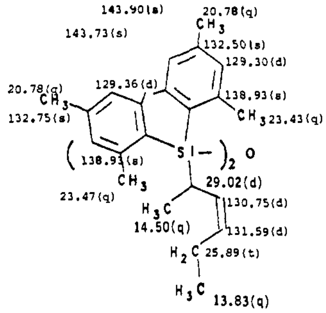
7b



8a

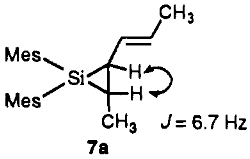


9a

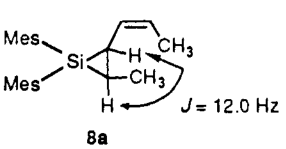


10

The vicinal coupling constant between ring protons in **7a**, from silylene addition to *trans*,*trans*-hexadiene, is 6.7 Hz expected for a *trans*-silirane. In **8a**, the product from silylene addition to *cis*,*cis*-hexadiene, the analogous vicinal coupling is 12.0 Hz, indicating the *cis*-silirane.



7a



8a

The very high stereospecificity of silylene addition to the various hexadienes is not in accord with the recently described addition of the dimesitylsilylene to *trans*-2-butene. A reinvestigation of that report follows.[17]

Experimental Section

General Procedures. Photolyses were carried out at room temperature in a Rayonet reactor equipped with a reduced number, typically seven, of medium-pressure Hg lamps to minimize over photolysis. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200 or Varian VXR 300 JEOL FX90Q spectrometers with C_6D_6 or $CDCl_3$ as a lock solvent. ^{29}Si NMR spectra were determined with use of the INEPT pulse sequence.[18]

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(17) See additional papers: Zhang, S.; Wagenseller, P. E.; Conlin, R. T. *J. Am. Chem. Soc.*, following paper in this issue. Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281.

FT-IR spectra were obtained on a Nicolet 20 SXB spectrometer. Mass spectra were determined on a HP 5970 mass-selective analyzer coupled to a HP 5790A gas chromatograph. High-resolution mass spectra were obtained at the Midwest Center for Mass Spectrometry, Rice University, and UCLA facilities. Attempts to isolate the vinylsiliranes by column chromatography resulted in reaction of the silirane ring with the stationary phase: silica gel, alumina, and Florisil that was previously dried for 24 h. However, after photolysis and removal of all volatile reactants, the colorless oily product contained only the reaction product(s) and unreacted starting trisilane. Vinylsiliranes did not survive the high temperatures necessary for elution on a gas chromatograph (programmed oven temperature 100–200 °C for 90 min, 20% OV-17 on Chromosorb W, 2 ft, flow rate 10 mL/s) unlike the five-membered rings and the dienylsilanes that did. Consequently, high-resolution mass spectra were recorded on mixtures enriched in the vinylsilirane components and may also reflect a contribution from the mass of its isomers.

Photolysis of 2,2-Dimesitylhexamethyltrisilane (2) in 1,3-Butadiene. A solution containing 200 mg of **2** (0.48 mmol), 1.5 mL (17 mmol) of 1,3-butadiene at -5 °C, and 3 mL of cyclohexane was placed in a 25-mm quartz tube. The degassed (three freeze/thaw cycles) solution was irradiated for 15 h by a Rayonet reactor equipped with five medium-pressure mercury lamps. Two adducts, dimesitylsilacyclopent-3-ene (**3**) and 2,3-butadienyldimesitylsilane (**4**), were formed in ~1:1 ratio as determined by ^{1}H NMR and gas chromatography. The combined product yield was 91%. Also, a small amount of mesityltrimethylsilane, ~5%, was produced. Experiments with shorter photolysis times, 1 and 3 h, and fewer lamps were carried out, and again, ^{1}H and ^{13}C NMR spectra of the less volatile product mixture indicated ~1:1 ratio of products **3** and **4** along with undecomposed **2**.

1,1-Dimesitylsilacyclopent-3-ene, Mes$_2$Si(CH$_2$CH=CHCH$_2$) (3). ^{1}H NMR (CDCl$_3$): δ 2.04 (4 H, d, *J* = 1.3 Hz, CH$_2$SiCH$_2$), 2.25 (6 H, s, *p*-CH$_3$), 2.34 (12 H, s, *o*-CH$_3$), 6.05 (2 H, t, *J* = 1.3 Hz, HC=CH), 6.79 (4 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 20.92 (q), 22.63 (t), 24.01 (q), 128.75 (d), 131.28 (d), 133.79 (s), 138.46 (s), 143.77 (s). ^{29}Si NMR (CDCl$_3$): δ 4.08. GC/MS, *m/e* (relative intensity): 320 (1), 305 (5), 266 (6), 251 (29), 200 (100), 172 (12), 160 (20), 146 (53), 119 (18), 105 (10). High-resolution mass obtained on the mixture of isomers: calcd for $C_{22}H_{28}Si$ 320.1960; found 320.2004. UV: $\epsilon_{214\mathrm{nm}} = 8.0 \times 10^4$, $\epsilon_{234\mathrm{nm}} = 5.4 \times 10^4$.

2,3-Butadienyldimesitylsilane, Mes$_2$SiH$_d$CH$_{c2}$CH$_b$=C=CH$_{a2}$ (4). ^{1}H NMR (CDCl$_3$): δ 2.03 (2 H, m, SiCH$_{c2}$), 2.23 (6 H, s, *p*-CH$_3$), 2.33 (12 H, s, *o*-CH$_3$), 4.58 (2 H, dt, J_{ab} = 6.9 Hz, J_{ac} = 2.7 Hz, H$_{a2}$C=), 5.06 (1 H, tt, J_{bc} = 8.1 Hz, J_{ab} = 6.9 Hz, H$_b$C=), 5.19 (1 H, t, J_{cd} = 4.8 Hz, SiH), 6.78 (4 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 16.82 (t), 21.05 (q), 23.42 (q), 74.33 (t), 86.72 (d), 128.74 (d), 129.94 (s), 139.04 (s), 144.31 (s), 209.26 (s). ^{29}Si NMR (CDCl$_3$): δ -21.76. GC/MS, *m/e* (relative intensity): 320 (2), 267 (100), 235 (10), 200 (28), 147 (14), 119 (15), 105 (10).

Mesityltrimethylsilane, MesSiMe$_3$. Previously unreported data. ^{13}C NMR (CDCl$_3$): δ 3.57 (q), 20.95 (q), 24.80 (q), 129.42 (d), 136.23 (s), 139.53 (s), 144.70 (s). ^{29}Si NMR (CDCl$_3$): δ -5.50. GC/MS, *m/e* (relative intensity): 192 (23), 177 (100), 161 (25), 149 (18), 119 (8), 105 (5), 91 (6), 73 (10), 43 (13).

Photolysis of 2 with 2,3-Dimethyl-1,3-butadiene. A solution containing 150 mg (0.36 mmol) of **2**, 4 mL (36 mmol) of 2,3-dimethylbutadiene, and 20 mL of cyclohexane was placed in a quartz vessel and deaerated by argon purging. The solution was irradiated at room temperature by a Rayonet reactor equipped with six medium-pressure Hg lamps. The photolysis was monitored by ^{1}H NMR at 30-min intervals and stopped at 2 h. ^{1}H, ^{13}C, and ^{29}Si NMR of the less volatile components of the reaction solution indicated that 75% of the trisilane had decomposed and three products were formed: 1,1-dimesityl-2-methyl-2-isopropenylsilirane (**5a**) (55%), 1,1-dimesityl-3,4-dimethylsilacyclopent-3-ene (**5b**) (40%), and mesityltrimethylsilane (~4%) based on conversion of the trisilane. If photolysis of the solution was continued more than 6 h, **2** and **5a** disappeared and **5b** became the major (>90%) product. Both **5b** and mesityltrimethylsilane (4%) were isolated by vpc as described previously.

1,1-Dimesityl-2-methyl-2-isopropenylsilirane, Mes$_2$SiCH$_2$CCH$_3$(C(CH$_3$)=CH$_a$H$_b$) (5a). ^{1}H NMR (CDCl$_3$): δ 1.31 (3 H, s, CH$_3$C), 1.60 (2 H, m, SiCH$_2$), 2.22 (3 H, br s, =CCH$_3$), 2.32 (6 H, s, *p*-CH$_3$C=), 2.55 (6 H, s, *o*-CH$_3$), 2.61 (6 H, s, o-CH$_3$), 4.47 (1 H, app d, $J_{H_aH_b}$ = 1.5 Hz, =CH$_b$), 4.55 (1 H, m, =CH$_a$), 6.78 (2 H, s, ArH), 6.87 (2 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 16.84 (t), 22.93 (q), 23.61 (q), 23.63 (q), 24.57 (q), 24.57 (q), 26.00 (s), 105.53 (t), 127.30 (s), the *p*-Me carbons and para aromatic carbons of nonequivalent mesityl groups usually show overlapping signals, 128.43 (d), 128.47 (d), 139.53 (s), 139.59 (s), 145.55 (s), 145.98 (s), 150.21 (s). ^{29}Si NMR (CDCl$_3$): δ -74.12. High-resolution mass obtained on the mixture of isomers: calcd for $C_{24}H_{32}Si$ 348.2273; found 348.2268. UV (cyclohexane): $\epsilon_{214\mathrm{nm}} = 6.7 \times 10^4$, $\epsilon_{234\mathrm{nm}} = 3.5 \times 10^4$.

1,1-Dimesityl-3,4-dimethylsilacyclopent-3-ene, Mes$_2$Si(CH$_2$CCH$_3$=CCH$_3$CH$_2$) (5b). ^{1}H NMR (CDCl$_3$): δ 1.74 (6 H, s, CH$_3$), 2.05 (4 H, s, CH$_2$), 2.25 (6 H, s, *p*-CH$_3$), 2.32 (12 H, s, *o*-CH$_3$), 6.78 (4 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 19.01 (q), 20.86 (q), 23.84 (q), 30.03 (t), 129.19 (d), 131.18 (s), 134.52 (s), 138.56 (s), 144.15 (s). ^{29}Si NMR (CDCl$_3$): δ -2.65. GC/MS, *m/e* (relative intensity): 348 (1), 265 (2), 251 (13), 229 (29), 228 (100), 213 (10), 186 (33), 146 (27), 119 (12), 105 (9). UV: $\epsilon_{214\mathrm{nm}} = 6.4 \times 10^4$, $\epsilon_{234\mathrm{nm}} = 3.1 \times 10^4$.

Photolysis of 2 with Isoprene. A quartz vessel containing 150 mg of **2** (0.36 mmol), 3 mL of isoprene, and 20 mL of cyclohexane was irradiated at room temperature by six medium-pressure Hg lamps. The photolysis was monitored by ^{1}H NMR until 90% of the trisilane had been photolyzed (~2.5 h). ^{1}H, ^{13}C, and ^{29}Si NMR indicated the formation of 1,1-dimesityl-2-isopropenylsilirane (**6a**) (27%), 1,1-dimesityl-2-methyl-2-vinylsilirane (**6b**) (16%), 1,1-dimesityl-3-methylsilacyclopent-3-ene (**6c**) (55%), 1,1-dimesityl(2-methyl-2,3-butadienyl)silane (**6d**) (trace), and mesityltrimethylsilane (3%). The photolysis was continued for an additional 2 h, and both **6a** and **6b** were converted to **6c** and **6d**. Isolation of **6c** was achieved by gas chromatography as previously described. Both **6a** and **6b** have remained unchanged for months, at least, under an inert atmosphere at room temperature. The proton NMR spectrum of **6a** was especially complex, exhibiting one of the many variations of an ABX spin system. In particular, the two geminal protons of the silirane ring display chemical shift differences arising from one being cis to the 2-ispropenyl group ring substituent and resonating at a higher field while the other geminal proton is trans to the alkenyl group. The remaining ring proton, H$_c$, resonates further upfield and is coupled to both the cis and trans geminal protons of the other ring carbon. This ABX system is especially interesting but presently beyond our full understanding. The structural assignment for **6a** is based on its characteristic features of the ^{1}H chemical shifts for the isopropenyl substituent (two nonequivalent hydrogens of the terminal olefin), the multiplicity and position of each ^{13}C signal, and the diagnostic ^{29}Si chemical shift.

1,1-Dimesityl-2-isopropenylsilirane, Mes$_2$SiCH$_2$CH$_c$(CH$_3$C=CH$_a$H$_b$) (6a). ^{1}H NMR (CDCl$_3$): δ 0.97 (1 H, m, H$_c$), 1.08–1.24 (2 H, ABX coupling pattern, CH$_2$Si), 1.78 (3 H, br s, CH$_3$C=), 2.25 (6 H, s, *p*-Me), 2.55 (6 H, s, *o*-CH$_3$), 2.63 (6 H, s, *o*-CH$_3$), 4.22 (1 H, d, $J_{H_aH_b}$ = 0.5 Hz, C=CH$_a$), 4.37 (1 H, dq, J_{H_bMe} = 0.5 Hz, $J_{H_aH_b}$ = 0.5 Hz, C=CH$_{H_b}$), 6.70 (2 H, s, HAr), 6.86 (2 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 8.65 (t), 22.19 (q), 24.03 (q), 24.21 (q), 24.95 (d), 26.42 (q), 102.40 (t, =CH$_2$), 125.75 (s), 128.39 (d), 128.57 (d), 139.74 (s), 139.92 (s), 145.41 (s), 146.02 (s), 146.32 (s); 147.40 (d). ^{29}Si NMR (CDCl$_3$): δ -84.91. GC/MS, *m/e* (relative intensity): 334 (3), 266 (3), 265 (4), 251 (22), 235 (10), 215 (22), 214 (100), 172 (23), 160 (17), 147 (43), 146 (46), 119 (19), 105 (12). High-resolution mass for mixture of isomers: calcd for $C_{18}H_{22}Si$ 334.2118; found 334.2114.

1,1-Dimesityl-2-methyl-2-vinylsilirane, Mes$_2$SiCH$_2$C(CH$_3$)CH$_c$=CH$_a$H$_b$ (6b). ^{1}H NMR (CDCl$_3$): δ 1.25 (3 H, s, SiCCH$_3$), 1.26 (2 H, m, SiCH$_2$), 2.40 (6 H, s, *p*-CH$_3$), 2.58 (6 H, s, *o*-CH$_3$), 2.60 (6 H, s, *o*-CH$_3$), 4.71 (1 H, dd, $J_{ac(cis)}$ = 10.5 Hz, J_{ab} = 1.6 Hz, C=CH$_a$), 4.74 (1 H, dd, $J_{bc(trans)}$ = 17.1 Hz, J_{ab} = 1.6 Hz, =CH$_b$), 5.57 (1 H, dd, J_{ac} = 10.5 Hz, J_{bc} = 17.1 Hz, CH$_c$=C), 6.73 (2 H, s, *p*-CH$_3$), 6.81 (4 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 19.00 (t), 19.20 (s), 20.59 (q), 24.55 (q), 24.71 (q), 24.74 (q), (diagnostic vinyl carbons) 105.43 (t), 147.40 (d), 127.50 (s), 128.36 (d), 128.46 (d), 139.00 (s), 139.86 (s), 143.24 (s), 145.79 (s), 147.40 (d). ^{29}Si NMR (CDCl$_3$): δ -73.95. GC/MS, *m/e* (relative intensity): 334 (3), 266 (3), 265 (4), 251 (22), 235 (10), 215 (22), 214 (100), 172 (23), 160 (17), 147 (43), 146 (46), 119 (19), 105 (12).

1,1-Dimesityl-3-methylsilacyclopent-3-ene, Mes$_2$SiCH$_2$C(CH$_3$)=CHCH$_2$ (6c). ^{1}H NMR (CDCl$_3$): δ 1.80 (3 H, app d, *J* = 1.3 Hz, =CCH$_3$), 1.95 (2 H, br s, CH$_2$), 2.03 (2 H, br m, CH$_2$), 2.23 (6 H, s, *p*-CH$_3$), 2.31 (12 H, s, *o*-CH$_3$), 5.64 (1 H, m, C=CHC), 6.77 (4 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 20.77 (q), 22.29 (q), 23.35 (t), 23.79 (q), 27.50 (t), 125.22 (d), 129.16 (d), 134.31 (s), 138.60 (s), 140.32 (s), 143.98 (s). ^{29}Si NMR (CDCl$_3$): δ 5.33. GC/MS, *m/e* (relative intensity): 334 (3), 266 (3), 265 (4), 251 (22), 235 (10), 215 (22), 214 (100), 172 (23), 160 (17), 147 (43), 146 (46), 119 (19), 105 (12). UV: $\epsilon_{214\mathrm{nm}} = 8.1 \times 10^4$, $\epsilon_{234\mathrm{nm}} = 6.3 \times 10^4$.

1,1-Dimesityl(2-methyl-2,3-butadienyl)silane, Mes$_2$SiH(CH$_2$CCH$_3$C=C=CH$_2$) (6d). The identification of **6d** at this time, must be regarded as tentative since it is based primarily on the uniqueness of the ^{13}C NMR signals for the allenic carbons (δ 207.50 (s), 95.78 (s), 73.25 (t)) and the ^{29}Si NMR (δ -21.72) (compare to the other 2,3-butadienylsilanes **4** (δ -21.76) and **7c** (δ -21.83).

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

The ^{29}Si signals from δ −73 to −85 are indicative of 1,1-dimesitylsiliranes. Similarly, one of the sp^2 carbons of the unreacted vinyl group (the one away from the three-membered ring) displays an alkene ^{13}C chemical shift at an unusually low-field position, δ 105.53 (t), for an unsubstituted alkene carbon as in **5a**. Compare to the similar low-field positions of the two analogously unsubstituted and vinylic C atoms of **6a**, δ 102.40 (t) and **6b**, δ 105.43 (t), from **1** and isoprene.

Photolysis of 2 with *trans,trans*-2,4-Hexadiene. A solution of **2** (150 mg, 0.36 mmol), 2 mL (18.2 mmol) of *trans,trans*-2,4-hexadiene, and 20 mL of *n*-pentane was irradiated with a Rayonet reactor equipped with seven medium-pressure Hg lamps for 3 h. ^{1}H NMR of the solution indicated that 60% of the trisilane had decomposed with formation of *trans*-2-methyl-3-(*trans*-1-propenyl)-1,1-dimesitylsilirane (**7a**) and *cis*-2,5-dimethyl-1,1-dimesitylsilacyclopent-3-ene (**7b**) in 90% and 7% yields, respectively. Again, mesityltrimethylsilane, 3%, was found. The photolysis was continued, monitored by ^{1}H NMR, and stopped when nearly all **2** had been photolyzed. The initially formed product **7a** disappeared and was replaced by **7b** as the major product, >90%, isolated by gas chromatography. In addition to **7b**, a small amount of dimesityl(1-methyl-2,3-pentadienyl)silane (**7c**), <3%, was tentatively identified from the position of the ^{13}C allenic carbons and the ^{29}Si chemical shift. ^{13}C NMR ($CDCl_3$): δ 204.81 (s), 94.45 (d), 87.16 (d). ^{29}Si NMR ($CDCl_3$): δ −21.83.

***trans*-2-Methyl-3-(*trans*-1-propenyl)-1,1-dimesitylsilirane, $Mes_2SiCH_d(CH_3)CH_c(CH_b{=}CH_aCH_3)$ (7a).** ^{1}H NMR ($CDCl_3$): δ 1.12 (3 H, d, $J_{H_dMe} = 6.9$ Hz, CH_3C), 1.22 (1 H, dq, $J_{H_dH_c(trans)} = 6.7$ Hz, $J_{HMe} = 6.9$ Hz, $SiCCH_dC$), 1.53 (3 H, d, $J_{H_aMe} = 4.5$ Hz, $CH_3C{=}$), 1.62 (1 H, dd, $J_{H_cH_d} = 6.7$ Hz, $J_{H_bH_c} \approx 6.7$ Hz, H_c), 2.26 (6 H, s, *p*-CH_3), 2.55 (6 H, s, *o*-CH_3), 2.58 (6 H, s, *o*-CH_3Ar), 5.22 (H, m, $SiCC{=}CH_a$), 5.22 (H, m, $SiCCH_b{=}C$), 6.82 (2 H, s, HAr), 6.85 (2 H, s, ArH). ^{13}C NMR ($CDCl_3$): δ 15.43 (d), 17.78 (d), 19.08 (q), 20.76 (q), 20.95 (q), 24.15 (q), 24.32 (q), 32.42 (q), 118.05 (d), 126.41 (s), 126.50 (s), 128.26 (d), 128.40 (d), 133.03 (d), 139.66 (s), 139.71 (s), 145.92 (s), 145.97 (s). ^{29}Si NMR ($CDCl_3$): δ −77.36. High-resolution mass obtained on the mixture of isomers: calcd for $SiC_{24}H_{32}$ 348.2273; found 348.2268. UV (cyclohexane): $\epsilon_{214nm} = 8.7 \times 10^4$, $\epsilon_{234nm} = 4.6 \times 10^4$.

NMR Double Resonance of 7a: A Trans Adduct. The proton H_c of **7a**, bonded to the ring carbon atom carrying the vinyl substituent, is coupled to both the vicinal H_d also attached to the ring and to the vicinal H_b on the vinyl group. In the ^{1}H NMR, the signal for H_c appeared as a doublet of doublets at δ 1.62. The olefinic methyl showed a doublet at δ 1.53 due to coupling with the vicinal sp^2 H. When both olefinic hydrogens at δ ~5.22 are irradiated, the multiplicity of the ring H_c on C2 became a doublet since it was, then, coupled only to H_d on the ring. Correspondly, the olefinic methyl doublet became a singlet. The coupling constant between H_c on C2 and H_d on C3 was 6.7 Hz, in the region expected for trans-vicinal hydrogens attached to a three-membered ring.

***cis*-2,5-Dimethyl-1,1-dimesitylsilacyclopent-3-ene, $Mes_2SiCH(CH_3)$-$CH{=}CHCH(CH_3)$ (7b).** ^{1}H NMR ($CDCl_3$): δ 0.90 (2 H, app q, $J = 7.4$ Hz, $CHCH_3$), 1.20 (6 H, d, $J = 7.4$ Hz, CH_3CH), 2.15 (6 H, s, *p*-CH_3), 2.24 (6 H, s, *o*-CH_3), 2.37 (6 H, s, *o*-CH_3), 5.73 (2 H, br s, $HC{=}$), 6.81 (2 H, s, HAr), 6.83 (2 H, s, HAr). ^{13}C NMR ($CDCl_3$): δ 16.03 (d), 20.58 (q), 20.63 (q), 25.00 (q), 25.11 (q), 28.86 (q), 128.77 (d), 129.23 (d), 136.55 (d), 138.04 (s), 138.42 (s), 138.50 (s), 143.50 (s), 145.31 (s). ^{29}Si NMR ($CDCl_3$): δ 12.11. GC/MS, *m/e* (relative intensity): 348 (14), 303 (39), 302 (26), 301 (100), 266 (29), 265 (23), 251 (25), 235 (22), 228 (11), 181 (6), 160 (19), 147 (38), 146 (41), 119 (15). UV (cyclohexane): $\epsilon_{214nm} = 5.7 \times 10^4$, $\epsilon_{234nm} = 3.4 \times 10^4$.

Photolysis of 2 with *cis,cis*-2,4-Hexadiene. A solution of **2** (150 mg, 0.36 mmol), 2 mL (18 mmol) of *cis,cis*-hexadiene, and 20 mL of dry *n*-pentane was placed in a quartz vessel and degassed by Ar. Photolysis of the solution with six medium-pressure Hg lamps was monitored by ^{1}H NMR hourly until about 90% of **2** had decomposed (~6 h). A new product, **8a**, was formed in about 90% yield (based on conversion of **2** along with ≤5% trimethylmesitylsilane). In addition, very small amounts of allenylsilane **8c** were detected.

***cis*-2-Methyl-3-(*cis*-propenyl)-1,1-dimesitylsilirane, Mes_2SiCH_d-$(CH_3)CH_c(CH_b{=}CH_aCH_3)$ (8a).** ^{1}H NMR ($CDCl_3$): δ 1.30 (3 H, d, $J = 7.5$ Hz, CCH_3), 1.35 (1 H, dq, $J_{H_dH_c} = 12.0$ Hz, $J_{H_dMe} = 7.5$ Hz, H_d), 1.67 (1 H, dd, $J_{H_cH_d} = 12.0$ Hz, $J_{H_cH_b} = 7.4$ Hz, H_c), 1.81 (3 H, d, $J_{H_aMe} = 5.0$ Hz, $=CCH_3$), 2.33 (6 H, s, *p*-CH_3), 2.66 (6 H, s, *o*-CH_3), 2.73 (6 H, s, *o*-CH_3), 5.55 (2 H, m, $H_bC{=}CH_a$), 6.94 (4 H, s, ArH). ^{13}H NMR ($CDCl_3$): δ 11.67 (d), 13.02 (d), 14.45 (q), 20.86 (q), 20.93 (q), 21.60 (q), 24.39 (q), 24.46 (q), 119.43 (d), 126.45 (s), 128.23 (d), 128.60 (d), 129.63 (d), 139.76 (s), 139.84 (s), 146.14 (s), 145.75 (s). ^{29}Si NMR ($CDCl_3$): δ −78.16. High-resolution mass obtained on the mixture of isomers: calcd for $SiC_{24}H_{32}$ 348.2273; found 348.2299. UV (cyclohexane): $\epsilon_{214nm} = 6.2 \times 10^4$, $\epsilon_{236nm} = 3.0 \times 10^4$.

Attempted Florisil Column Chromatography of 8a. A mixture (400 mg) containing **8a** (>80%) and the two impurities, unphotolyzed **2** and small amounts (5%) of mesityltrimethylsilane, was placed on column packed with Florisil previously dried for 24 h at 100 °C. The mixture was separated with hexane as the eluent initially, and both the trisilane and trimethylmesitylsilane were eluted as indicated by ^{1}H NMR. Methylene chloride was then employed for further elution. A sticky oil (250 mg) was obtained after removal of the solvent. The product **10**, whose retention time on both analytical and preparative vpc columns was approximately twice that of **7b** (a structure of the same molecular weight as **8a**), appeared to contain two units of silirane **8a** plus one of H_2O. The evidence for destruction of the silirane ring was the disappearance of the upfield ^{29}Si signal at δ −78.16 and formation of new and strong Si–O–Si vibrations[19] from 1060 to 1080 cm^{-1} in the infrared spectrum of **10**. Interestingly, the *cis*-propenyl group of **8a** isomerized to the cis internal olefin in water/Forisil-promoted decomposition. Efforts to obtain the high-resolution mass spectrum of the large disiloxane, MW 714, at the Midwest Center for Mass Spectrometry were unsuccessful despite lowering the ionization voltage to 30 eV. The largest peak was observed at 283 amu, the same as recorded in the GC/MS spectrum.

[*cis*-$Mes_2Si(CH_f(CH_{e3})CH_d{=}CH_cCH_{b2}CH_{a3})]_2O$ (10). ^{1}H NMR ($CDCl_3$): δ 0.91 (3 H, t, $J_{ab} = 7.5$ Hz, CH_3CH_2), 1.19 (3 H, d, $J_{ef} = 7.3$ Hz, $CHCH_3$), 1.99 (2 H, app pent, $J = 7.5$ Hz, CH_2CH_3), 2.24 (6 H, s, *p*-CH_3), 2.36 (6 H, s, *p*-CH_3), 2.37 (6 H, s, *o*-CH_3), 2.42 (1 H, m, CH), 5.42 (1 H, ddt, $J_{cd} = 15.5$ Hz, $J_{cf} = 1.1$ Hz, $J_{bc} = 6.1$ Hz, $CH_2CH{=}$), 5.60 (1 H, ddt, $J_{dc} = 15.5$ Hz, $J_{db} = 1.0$ Hz, $J_{df} = 7.1$ Hz, $CH{=}$), 6.77 (4 H, s, ArH). ^{13}C NMR ($CDCl_3$): δ 13.83 (d), 14.50 (q), 20.78 (q), 23.43 (q), 23.47 (q), 25.89 (t), 29.02 (q), 129.30 (d), 129.36 (d), 130.75 (d), 131.59 (d), 132.50 (s), 132.75 (s), 138.93 (s), 143.73 (s), 143.90 (s). ^{29}Si NMR ($CDCl_3$): δ −3.98. GC/MS, *m/e* (relative abundance): 283 (100), 265 (11), 235 (2), 220 (3), 163 (10), 105 (3), 91 (3), 45 (4). (parent ion not observed).

Photolysis of 2 with *cis,trans*-2,4-Hexadiene. A solution containing 150 mg (0.36 mmol) of **2**, 3 mL of *cis,trans*-2,4-hexadiene (27 mmol, which had been passed previously through an alumina column), and 20 mL of *n*-pentane was placed in a quartz vessel. After argon purging, the solution was irradiated by six medium-pressure Hg lamps at room temperature. The photolysis was monitored by ^{1}H NMR every 0.5 h and stopped at 3 h. By that time, about 60% of the trisilane had decomposed and silylene adducts in >90% yield were formed: *cis*-2-(*trans*-1-propenyl)-3-methyl-1,1-dimesitylsilirane (**9a**) and *trans*-2-(*cis*-1-propenyl)-3-methyl-1,1-dimesitylsilirane (**9b**) in 9:1 ratio. After 3-h photolysis, only 1% of *cis,trans*-hexadiene isomerized to the trans,trans isomer and no silacyclopentene was detected.

***cis*-2-Methyl-3-(*trans*-1-propenyl)-1,1-dimesitylsilirane, $(Mes)_2SiCH_d(CH_3)CH_c(CH_b{=}CH_aCH_3)$ (9a).** ^{1}H NMR ($CDCl_3$): δ 1.16 (3 H, d, $J = 7.3$ Hz, CCH_3), 1.17 (1 H, dq, $J_{H_dH_c} = 11.4$ Hz, $J_{H_dMe} = 7.3$ Hz, H_d), 1.67 (3 H, d, $J = 5.7$ Hz, $=CCH_3$), 1.75 (1 H, dd, $J_{cd(cis)} = 11.4$ Hz, $J_{cb} = 6.7$ Hz, CH_c), 2.28 (6 H, s, *p*-CH_3), 2.59 (6 H, s, *o*-CH_3), 2.61 (6 H, s, *o*-CH_3), 5.2–5.6 (2 H, m, $CH{=}CH$), 6.85 (2 H, s, HAr), 6.88 (2 H, s, HAr). ^{13}C NMR ($CDCl_3$): δ 11.77 (d), 14.63 (d), 18.05 (q), 20.89 (q), 20.97 (q), 24.43 (q), 24.50 (q), 25.77 (q), 121.13 (d), 126.51 (s), 128.50 (d), 131.02 (d), 137.24 (s), 139.75 (s), 145.82 (s), 146.20 (s). ^{13}C NMR (C_6D_6): δ 12.03 (d), 15.05 (d), 18.15 (q), 20.83 (q), 24.54 (q), 26.20 (q), 121.41 (d), 126.90 (s), 128.72 (d), 128.99 (d), 131.28 (d), 139.66 (s), 139.73 (s), 145.77 (s), 146.15 (s). The resolution of peaks for the aliphatic carbons of **9a** was achieved in $CDCl_3$, but resolution of aromatic carbons was unsatisfactory. However, when C_6D_6 was the solvent, good resolution of the aromatic carbons was obtained. ^{29}Si NMR ($CDCl_3$): δ −79.05.

***trans*-2-Methyl-3-(*cis*-1-propenyl)-1,1-dimesitylsilirane, $(Mes)_2SiCH_d(CH_3)CH_c(CH_b{=}CCH_aCH_3)$ (9b).** The spectroscopic evidence for **9d** is limited due to its low yield. The ^{13}C NMR spectrum displayed a characteristic peaks at δ 116.84 (d) for the methyl-substituted vinyl carbon and in the ^{29}Si spectrum, a peak at δ −77.50.

Distinction between the *trans*- and *cis*-Propenyl Groups of the Vinylsiliranes 7a, 8a, and 9a by FT-IR. To determine whether the structure of unreacted vinyl group of **7a** (trans,trans adduct), **8a** (cis,cis adduct), and **9a** (major cis,trans adduct) was retained after the photogeneration and reaction silylene **1**, IR spectra of **7a**, **8a**, and **9a** have been obtained and compared. Diastereomers **7a** and **8a** display weak C=C stretching vibrational bands centered at 1652 and 1635 cm^{-1}, respectively. A characteristic feature that indicates olefin stereochemistry is the olefin H out-of-plane vibration.[18] Only the trans-disubstituted alkenes gave rise to an absorption within 980–965 cm^{-1} as was observed also for **7a** at 964 cm^{-1} but not for **8a**. Similarly, IR spectra for **9a** revealed an intense absorption at 969 cm^{-1} indicative of the *trans*-alkene as well as a weak absorption at 1652 cm^{-1}.

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(19) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975; Vol. 1, p 379.

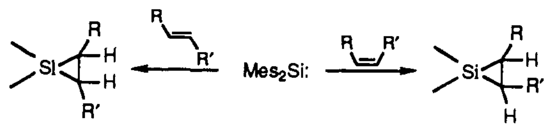
Acknowledgment. We gratefully acknowledge the Robert A. Welch Foundation for financial support of this work. We thank Dr. J. C. Scaiano (National Research Council of Canada) for a generous gift of 2,2-dimesitylhexamethyltrisilane. High-resolution mass spectra were provided by the facilities at the Midwest Center for Mass Spectrometry, a National Science Foundation Facility, Rice University (Dr. T. D. Marriott) and UCLA (Dr. M. Namavari).

Addition of Dimesitylsilylene to Olefins. A Reinvestigation

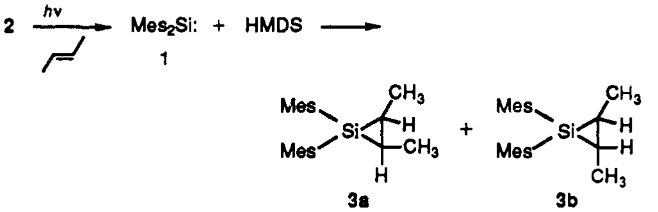
S. Zhang, P. E. Wagenseller, and R. T. Conlin*

Contribution from the Center for Organometallic Research and Education, Department of Chemistry, University of North Texas, Denton, Texas 76203. *Received June 4, 1990. Revised Manuscript Received February 1, 1991*

Abstract: We have reinvestigated the report that dimesitylsilylene adds nonstereospecifically to *cis*- and *trans*-2-butene. Stereospecific addition of dimesitylsilylene to *cis*- and *trans*-2-pentenes and -4-octenes produced the corresponding siliranes. A photoisomerization pathway is also reported for these siliranes. A probable explanation for the earlier and spurious interpretation is given.



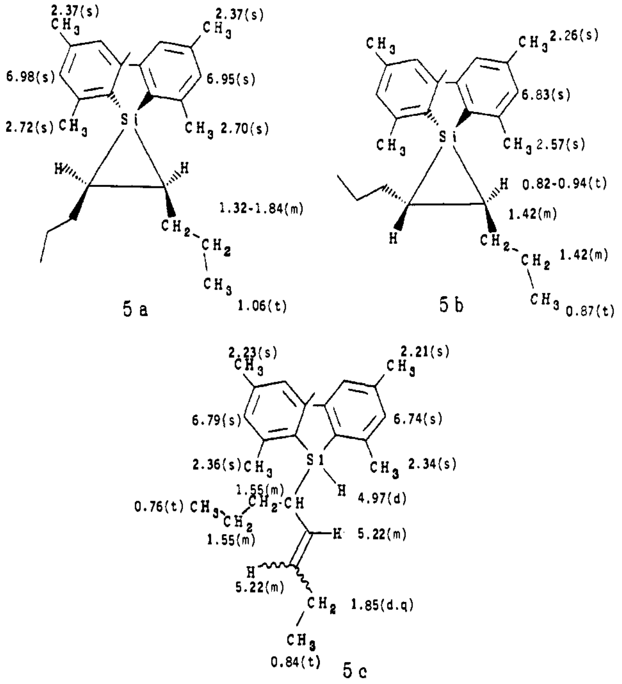
Recently, Ando and co-workers reported that the bulky dimesitylsilylene (**1**), photogenerated from trisilane **2**, reacted nonstereospecifically with *trans*-2-butene, yielding 23–55% of the air- and moisture-stable *cis*-2,3-dimethylsilirane product **3a**.[1]



Curiously, addition of the silylene to the π bond of *cis*-2-butene showed significantly less loss of product stereochemistry, only 1–10% of the "wrong" isomer, the *trans*-2,3-dimethylsilirane **3b**.[2] This remarkable result stands in contrast to three earlier mechanistic studies of "normal" silylene addition to alkenes where, in the absence of direct spectral characterization of the highly air- and moisture-sensitive siliranes, less direct and more subtle arguments were required to develop the case for stereospecific addition.[3-6]

In this and the preceding paper, we demonstrate that photogenerated **1** adds *stereospecifically* to the four different π bonds of *cis,cis*-, *cis,trans*-, and *trans,trans*-2,4-hexadienes as well as the four different π bonds of two olefins, *cis*- and *trans*-2-pentenes and -4-octenes, and also offer a different interpretation for the phenomenon of apparent nonstereospecific addition to *trans*-2-butene.

Chart I. ^{1}H NMR Spectral Data (CDCl$_3$)



If steric congestion in the transition state for silirane formation altered the course of simple ring closure, as implied by the Ando result, such an effect might be exacerbated by increasing the size of the substituents that define the stereochemistry. Yet, we observe that the addition of dimesitylsilylene (**1**) to *cis*-2-pentene is >98% stereospecific,[7] yielding *cis*-2-ethyl-3-methylsilirane **4a**. Photolysis of cyclohexane solutions containing **2** (0.058 M) and *cis*-pentene (2.7 M) for 1.5 h produced a single silirane isomer (^{29}Si NMR:

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(1) Ando, W.; Fujita, M.; Hitoaki, Y.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310.

(2) We observed no loss of stereochemistry in formation of the *cis*-silirane from *cis*-2-butene.

(3) Ishikawa, M.; Nakagawa, K.-I.; Kumada, M. *J. Organomet. Chem.* **1979**, *178*, 105.

(4) (a) Tortorelli, V. J.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 1425. (b) Tortorelli, V. J.; Jones, M., Jr.; Wu, S.; Li, Z. *Organometallics* **1983**, *2*, 759.

(5) Seyferth, D.; Annarelli, D. C.; Duncan, D. P. *Organometallics* **1982**, *1*, 1288.

(6) The experimental observation, vaguely supported by theory, that singlet divalent states add to olefins stereospecifically is often described as the Skell postulate and has been critically reviewed: Gaspar, P. P.; Hammond, G. S. In *Carbene Chemistry*; Kirmse, W., Ed.; Academic Press: New York, 1964. More recently: Gaspar, P. P.; Hammond, G. S. In *Carbenes Vol. II*; Moss, R.A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975. Among the several recent challenges, none have been maintained.

(7) Assiduous precautions were taken to eliminate possibilities for misleading effects such as photosensitization from O$_2$ or Hg by three freeze/thaw cycles on a Hg-free vacuum line plus addition and removal of the reaction mixture under Ar.

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