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.
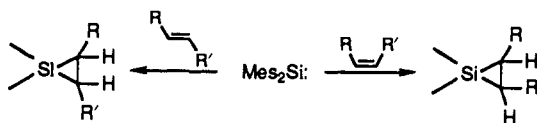

Recently, Ando and co-workers reported that the bulky dimesitylsilylene (**1**), photogenerated from trisilane **2**, reacted nonstereospecifically with *trans*-2-butene, yielding 23–55% of the air- and moisture-stable *cis*-2,3-dimethylsilirane product **3a**.[1]
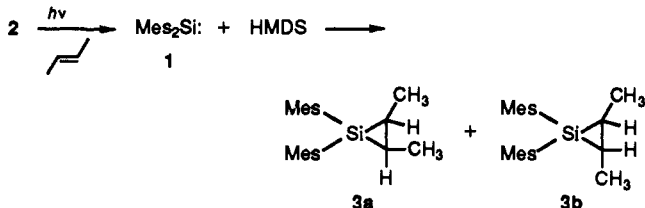
Curiously, addition of the silylene to the π bond of *cis*-2-butene showed significantly less loss of product stereochemistry, only 1–10% of the "wrong" isomer, the *trans*-2,3-dimethylsilirane **3b**.[2] This remarkable result stands in contrast to three earlier mechanistic studies of "normal" silylene 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

Chart I. ^{1}H NMR Spectral Data (CDCl$_3$)
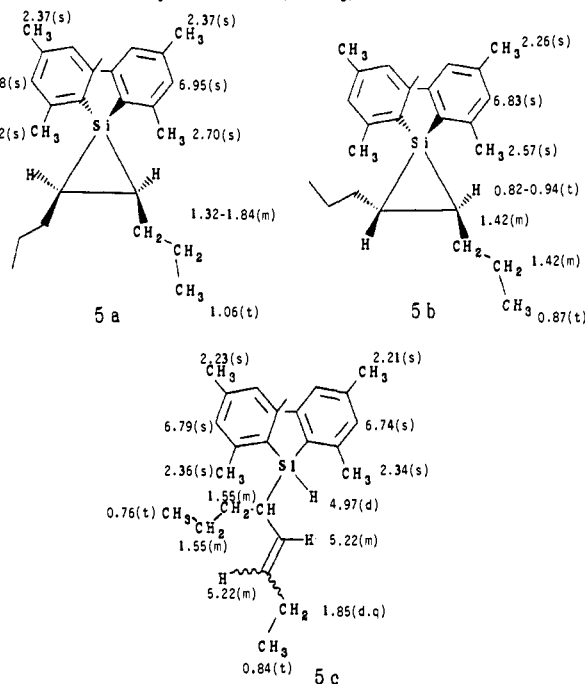
phenomenon of apparent nonstereospecific addition to *trans*-2-butene.

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:

(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.

δ −82.50) and hexamethyldisilane. The same experiment, but with *trans*-2-pentene as the trapping agent, also showed one silirane isomer **4b** (^{29}Si NMR: δ −78.33). At longer photolysis times, >3 h, two new acyclic isomers, dimesityl(1-ethylprop-2-enyl)silane (**4c**) and dimesityl(1-methylpent-2-enyl)silane (**4d**) were formed and isolated by preparative gas chromatography.
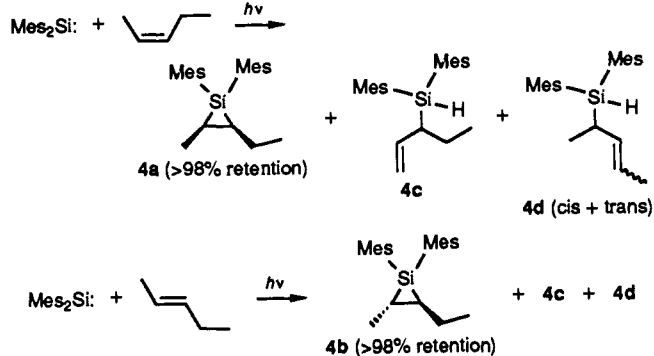
Structural assignments of siliranes **4a** and **4b** were based on the NMR spectra (^{1}H, ^{13}C, ^{29}Si) of solutions obtained at the shortest photolysis period required to record the complete spectrum (Charts I and II). Even at brief photolysis times, we note that small amounts of acyclic isomers **4c** and **4d**, ∼5%, were produced after >70% of the starting trisilane had been photolyzed (1.5 h). Although we have not been able to isolate purified siliranes using a variety of chromatographic methods, their role as photochemical precursors to **4c** and **4d** seems assured since there are no examples in which organic silylenes are known to insert *intermolecularly* into carbon–hydrogen bonds.[8] The spectra for the siliranes were obtained by subtracting signals of the previously determined acyclic products and the starting trisilane from the signals observed in the mixture. These tentative assignments were then confirmed by off-resonance ^{13}C spectra.

Irradiation of pentane solutions of **2** (0.055 M) with *cis*- or *trans*-4-octene (1.4 M) provided an even more demanding test of the steric congestion hypothesis. The reaction products, *cis*- and *trans*-2,3-di-*n*-propyl-1,1-dimesitylsiliranes (**5a** and **5b**, respectively), each retained the stereochemistry of the starting olefin
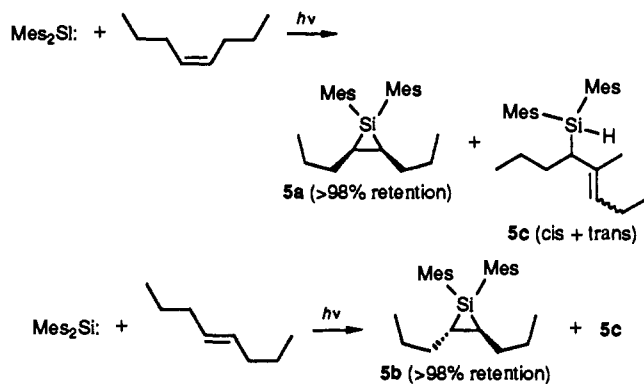
configuration (>98%).[9] Again, it was not possible to produce sufficient silirane for ^{29}Si characterization without formation of some acyclic isomer, (1-propylpent-2-enyl)dimesitylsilane (**5c**), ∼10%, from secondary photolysis of either **5a** or **5b**. When irradiation of reaction mixtures containing *cis*- or *trans*-4-octene and **2** proceeded more than 6 h, **5c** became the major product. These acyclic silanes may be considered as photochemical de-

Chart II. ^{13}C NMR Spectral Data (CDCl$_3$)

3 a

3 b

3 c

4 a

4 b

4 c

4 d
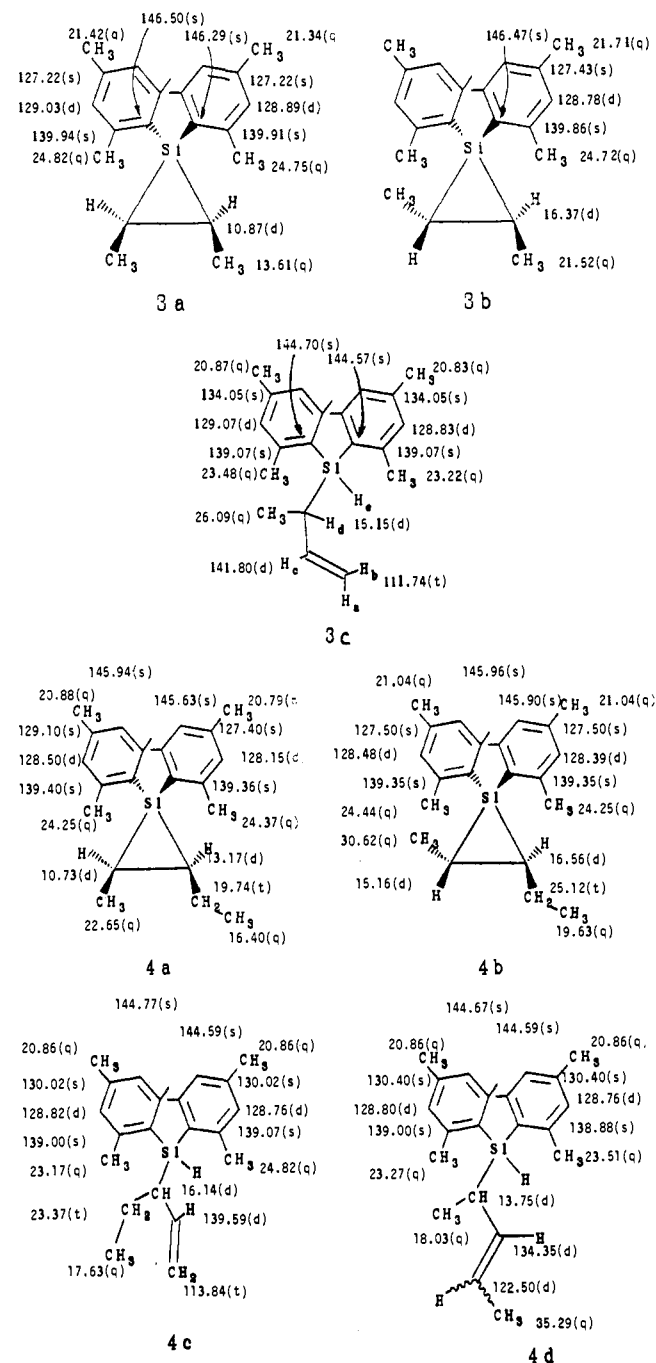
rivatives of the siliranes described herein.

Other possible explanations for loss of the starting *trans*-2-butene configuration in the silirane products have been sought.[10]

First, the role of electronic spin states such as transient triplet states of either the 2,2-dimesityltrisilane **2** or the olefin merits scrutiny. Seemingly consistent with this notion are phosphorescence spectra of another polysilane, poly(methylpropylsilane), whose relaxed triplet-state energy appears in a range conducive for triplet energy transfer to *trans*-2-butene, 75–80 kcal/mol.[11] The rate of *possible* photosensitization by the trisilane, usually diffusion controlled,[12] might produce sufficient concentrations of

(8) Thermal intramolecular silylene insertions into carbon–hydrogen bonds are well established in the gas phase; see: Wulff, W. D.; Goure, W. F.; Barton, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6236. Boo, B. H.; Gaspar, P. P. *Organometallics* **1986**, *5*, 698. They have also been suggested in solution: Karatsu, T.; Miller, R. D.; Sooriyakumaran, R.; Michl, J. *J. Am. Chem. Soc.* **1989**, *111*, 1140.

(9) Silirane stereochemistry was established from the higher ^{29}Si chemical shift of the cis diastereomers. These values are δ −82.50 and −81.80 for *cis*-**4a** and -**5a** and δ −78.33 and −79.78 for *trans*-**4b** and -**5b**. For a discussion of this precedence, see the preceding paper in this issue.

(10) Among the possibilities we have not considered is a rapid photochemical cis/trans isomerization of siliranes which is described by Pae, D. H.; Xiao, M.; Chiang, M. Y.; Gaspar, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 1281.

(11) Michl, J.; Downing, J. W.; Karatsu, T.; Mckinley, A.; Poggi, G.; Wallraff, G.; Sooriyakumarin, R.; Miller, R. D. *Pure Appl. Chem.* **1988**, *60*, 959. For an overview of polysilane high polymers, see: Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

(12) Barltrop, J. A.; Coyle, J. D. *Excited States in Organic Chemistry*; Wiley: New York, 1974.

the *cis*-2-butene from the starting trans isomer to allow appreciable amounts of *cis*-silirane product. We have explored this possibility, repeatedly, but have not observed significant photosensitization of *trans*-2-butene to the cis isomer.

Second, the possibility that the silylene was initially produced in a triplet state and also reacted as that electronic isomer prior to intersystem crossing seemed unlikely. Since the triplet state of a divalent species is expected to react more rapidly with dienes than olefins,[13] it might be argued that a diene has a greater chance to capture a triplet silylene *before* it undergoes intersystem crossing to an undoubtedly singlet ground state. Nonetheless, no configuration of the silirane was lost from addition of **1** to a variety of stereolabeled dienes. This observation was especially relevant in view of kinetic studies of **1** that reported that a typical diene, 2,3-dimethylbutadiene, was >3 times more reactive than the *cis*-olefin cyclohexene. Furthermore, the relatively slow rate of reaction of **1** with triplet O_2 was consistent with a symmetry-imposed barrier for reactions between species of different spin states.[14]

The formalism of a transition state leading to formation of three-membered rings from addition of divalent species to π bonds is one in which steric factors,[15] such as olefin configuration, are usually less important than electronic factors, such as the multiplicity of reactants. That is, singlet states of reactive intermediates add to olefins with retention of stereochemistry. Consequently, a remaining interpretation of the Ando result is that the *trans*-butene used in the original experiments may have contained small amounts (<5%) of the cis isomer. In view of the higher reactivity (~9) of **1** toward the cis-substituted π bond of *cis*,-*trans*-2,4-hexadiene,[8] one might anticipate that *cis*-2-butene is significantly more reactive than *trans*-2-butene.

At the start of this study of the addition of **1** to *trans*-2-butene, the reinvestigation, we used a supply containing 97.7% trans isomer and 2.3% cis isomer. The stereochemistry of the silirane adducts was 40% cis and 60% trans as indicated from integration of ortho methyl peaks in the ^{13}C spectra. We also observed formation of the acyclic dimesityl(1-methylprop-2-enyl)silane (**3c**) (5–10%) from photolysis of **2** with either 2-butene diastereomer. In an identical experiment, but with a new source of *trans*-2-butene, 99.5% trans and 0.5% cis, the relative amount of *cis*-silirane decreased to 11% and the *trans*-silirane increased to 89%. From a third experiment in which a mixture of 1.3% *cis*-2-butene and 98.7% *trans*-2-butene was prepared for quantitative trapping studies, NMR integration showed 75% *trans*-silirane and 25% *cis*-silirane.

Since the ratios of cis- and *trans*-silirane products from the different cis/trans-2-butene compositions were known, it was possible to calculate the relative reactivity, k_{cis}/k_{trans}, of dimesitylsilylene addition in each mixture of 2-butene diastereomers. Thus, $k_{rel} = k_{3a}/k_{3b}$(% *trans*-butene/% *cis*-butene) = 28, 25, and 25, respectively, from the three butene mixtures above.

The high stereospecificity of silylene addition that we report for other olefins and dienes deserves further comment. In each case, except *trans*-2-butene, the trapping agents were easily purified and/or nearly free of the other configurational isomer (>99.8%). Furthermore, it is likely that the preferred addition of the bulky silylene **2** to the π bond of a *cis*-dialkyl isomer relative to trans is maximized when the alkyl substituent is smallest, i.e., methyl.

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 overphotolysis. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian Gemini 200 or Varian VXR 300 spectrometer with use of C_6D_6 or $CDCl_3$ as lock solvents. Mass

spectra were determined on an HP 5970 mass-selective analyzer coupled to a HP 5790A gas chromatograph. FT-IR measurements were made on a Nicolet 20 SXB spectrometer. High-resolution mass spectra were obtained at Duke University and UCLA. Attempts to isolate siliranes by column chromatography, using previously dried silica gel or alumina, resulted in reaction of the ring. However, after photolysis and removal of all volatile reactants, the typically colorless oily product contained only the reaction product(s) and unreacted starting trisilane depending on the irradiation time. These siliranes 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 acyclic products that did.

Photolysis of 2 with *cis*-2-Pentene. A solution of *cis*-2-pentene (purity >99.8%) (2 mL, 18.6 mmol) and 5 mL of cyclohexane was passed through a column of alumina (dried at 200 °C overnight) and placed in a quartz vessel containing **2** (170 mg, 0.41 mmol). After being purged with argon at 0 °C for 15 min, the solution was irradiated by six medium-pressure Hg lamps for 1.5 h. The volatiles were removed by vacuum, 10^{-3} Torr, and NMR spectra were obtained on the involatile, usually colorless, and oil products. NMR spectra indicated that ~70% of **2** had been photolyzed and the new products, 90%, were *cis*-2-ethyl-3-methyl-1,1-dimesitylsilirane (**4a**) and the acyclic isomers (1-ethylprop-2-enyl)-1,1-dimesitylsilane (**4c**) as well as (1-methylbut-2-enyl)-1,1-dimesitylsilane (**4d**). As with all our photolyses of **2**, a small amount (~5%) of mesityltrimethylsilane was formed. From the ^{29}Si NMR spectra, no evidence of the *trans*-silirane could be found. A faint yellow color, λ_{max} = 422 nm, due to trace amounts of tetramesityldisilene was sometimes noted when the olefin trapping agents were not present in very large excess. When the solution was photolyzed for longer than 4 h with six Hg lamps, nearly all **2** disappeared as well as silirane **4a**. The photostable products **4c** and **4d** (in 5:4 ratio) were isolated by preparative GC in 80% yield.

cis-2-Ethyl-3-methyl-1,1-dimesitylsilirane, $Mes_2SiCH(CH_3)CH-(CH_2CH_3)$ (**4a**). ^{1}H NMR ($CDCl_3$): δ 1.08 (3 H, app t, J = 7.4 Hz, CH_3 of ethyl), 1.18 (3 H, d, J - 7.3 Hz, CH_3 attached to ring), 1.36 (2 H, br m, CH_2 of ethyl), 1.57 (2 H, br m, 2 ring CH), 2.27 (6 H, s, *p*-CH_3), 2.60 (12 H, s, *o*-CH_3), 6.80 (2 H, s, ArH), 6.84 (2 H, s, ArH). ^{13}C NMR ($CDCl_3$: δ 10.73 (d), 13.17 (d), 16.40 (q), 19.74 (t), 20.79 (q), 20.88 (q), 22.65 (q), 24.25 (q), 24.37 (q), 127.40 (s), 128.15 (d), 128.50 (d), 129.10 (s), 139.36 (s), 139.40 (s), 145.63 (s), 145.94 (s). ^{29}Si NMR ($CDCl_3$): δ -82.50. High-resolution mass obtained on the mixture of isomers: calcd for $SiC_{23}H_{32}$ 336.2273; found 336.2266.

(1-Ethylprop-2-enyl)dimesitylsilane, $Mes_2SiHCH(CH_2CH_3)(CH_c=CH_bH_a)$ (**4c**). ^{1}H NMR ($CDCl_3$): δ 0.95 (3 H, t, J = 7.3 Hz, CH_3CCSi), 1.60 (H, m, CHSi), 1.60 (2 H, m, CCH_2CSi), 2.25 (6 H, s, *p*-CH_3), 2.37 (12 H, s, *o*-CH_3), 4.97 (H, dd, $J_{H_aH_b}$ = 0.8 Hz, $J_{H_aH_c}$ = 10.6 Hz, =CH_a), 4.98 (H, dd, $J_{H_bH_a}$ = 0.8 Hz, $J_{H_bH_c}$ = 16.5 Hz, =CH_b), 5.08 (H, d, J_{HSiCH} = 5.7 Hz, SiH), 5.65 (H, m, =CH_c), 6.78 (2 H, s, ArH), 6.80 (2 H, s, ArH). ^{13}C NMR ($CDCl_3$): δ 16.14 (d), 17.63 (q), 20.86 (q), 23.17 (q), 23.37 (t), 24.82 (q), 113.84 (t), 128.76 (d), 128.82 (d), 130.02 (s), 139.07 (s), 139.00 (s), 139.59 (d), 144.59 (s), 144.77 (s). ^{29}Si NMR ($CDCl_3$): δ -25.82.

All the acyclic dimesitylalkenylsilanes, **3c**, **4c**, **4d**, and **5c**, reported here contain an asymmetric CH group α to Si, which renders the two mesityl groups diastereotopic. Thus, slight differences in the ^{1}H and ^{13}C chemical shifts of the two mesityls were noted.

(1-Methylbut-2-enyl)-1,1-dimesitylsilane, $Mes_2SiH(CH[CH_3]CH=CHCH_3)$ (**4d**). ^{1}H NMR ($CDCl_3$): δ 1.20 (3 H, d, J = 7.1 Hz, $SiCCH_3$), 1.58 (3 H, d, J_{HCCH_3} = 6.2 Hz, CH_3C=) 1.60 (1 H, m, SiCH), 2.25 (6 H, s, *p*-CH_3), 2.37 (12 H, s, *o*-CH_3), 5.08 (1 H, d, J_{HCSiH} = 5.7 Hz, SiH), 5.46 (2 H, m, CH=CH), 6.78 (2 H, s, HAr), 6.80 (2 H, s, HAr). ^{13}C NMR ($CDCl_3$): δ 13.75 (d), 18.03 (q), 20.86 (q), 23.27 (q), 23.51 (q), 35.29 (q), 122.50 (d), 128.76 (d), 128.80 (d), 130.40 (s), 134.35 (d), 138.88 (s), 139.00 (s), 144.59 (s), 144.67 (s). ^{29}Si NMR ($CDCl_3$): δ -22.95. GC/MS, m/e (relative abundance): 267 (100, M – 69), 235 (2), 220 (3), 207 (1), 159 (2), 147 (5), 119 (5). High-resolution mass for mixture: calcd for $SiC_{23}H_{32}$ 336.2273; found 336.2274.

The FT-IR spectrum of **4d** showed an absorption at 970 cm^{-1}, suggesting that some of the double bond of the butenyl group is in the trans configuration. Although definitive evidence for the acyclic *cis*-butenyl isomer was not obtained, we assume that a photostationary state of cis/trans configurations was achieved.

Photolysis of 2 with *trans*-2-Pentene. The experiment was carried out by the same method as above. A solution containing 2 mL of *trans*-2-pentene (purity >99.8%), 5 mL of cyclohexane, and **2** (170 mg) was irradiated with six medium-pressure Hg lamps for 1.5 h. The ^{1}H NMR of the nonvolatile products indicated that 70% of the **2** had been photolyzed and yielded the following products: *trans*-2-ethyl-3-methyl-1,1-dimesitylsilirane (**4b**) (90%) and the acyclic isomers **4c** and **4d** (less than 5% based on decomposition of **2**).

(13) Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013, 4015.

(14) Conlin, R. T.; Netto-Ferreira, J. C.; Zhang, S.; Scaiano, J. C. *Organometallics* **1990**, *9*, 1332.

(15) The significance of steric factors in the approach of a divalent silicon atom, dimethylsilylene, to a π bond has been discussed previously by: Baggot, J. E.; Blitz, M.; Frey, H. M.; Lightfoot, P. D.; Walsh, R. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 515.

***trans*-2-Ethyl-3-methyl-1,1-dimesitylsilirane, Mes$_2$SiCH(CH$_3$)CH-(CH$_2$CH$_3$) (4b).** ^{1}H NMR (CDCl$_3$): δ 0.84 (2 H, app dq, J = 7.4 Hz, J = 6.2 Hz, 2 ring CH), 0.98 (3 H, t, J = 7.4 Hz, CH$_3$ of ethyl), 1.08 (3 H, d, J = 6.2 Hz, CH$_3$), 1.40 (2 H, br m, CH$_2$), 2.26 (6 H, s, *p*-CH$_3$), often overlapping signals were observed for the nonequivalent *p*-methyl protons of the *syn*- and *anti*-mesityl substituents, 2.58 (12 H, s, *o*-CH$_3$), 6.84 (4 H, s, ArH). The strongest evidence in the proton NMR spectra that **4b** is the trans isomer was the relatively upfield position of the ring protons, δ 0.84, compared to the ring protons of the cis isomer **4a**, δ 1.57. The shielding influence of the *cis*-alkyl groups is well-known as the "γ effect" and has been used to establish stereochemistry in other cyclic silanes.^{16} Although the two ring methine protons of **4b** are nonequivalent due to differences resulting from adjacent methyl and ethyl groups, this difference was not resolvable. ^{13}C NMR (CDCl$_3$): δ 15.16 (d), 16.56 (d), 19.63 (q), 21.04 (q), often the nonequivalent *p*-methyl and ipso carbons of the two mesityl substituents show overlapping signals, 24.25 (q), 24.44 (q), 25.12 (t), 30.62 (q), 127.50 (s), 128.39 (d), 128.48 (d), 139.35 (s), 145.90 (s), 145.96 (s). ^{29}Si NMR (CDCl$_3$): δ −78.33. High-resolution mass obtained on the mixture of isomers: calcd for SiC$_{23}$H$_{32}$ 336.2273; found 336.2274.

Photolysis of 2 with *cis*-4-Octene. A solution containing **2** (150 mg, 0.36 mmol), *cis*-4-octene (purity >99.8%) (1.5 mL, 8.5 mmol), and 5 mL of *n*-pentane was irradiated with five Hg lamps for 3 h. The volatiles were removed under vacuum, and a colorless sticky oil was obtained. NMR spectra indicated that 90% of **2** decomposed. The major product, *cis*-1,1-dimesityl-2,3-di-*n*-propylsilirane (**5a**) was formed in ∼90% yield based on the decomposition of **2**, along with the acyclic product **5c** (<∼5%), which likely arises from secondary photolysis of **5a**. No *cis*-silirane was detected by NMR. If the above solution was photolyzed longer than 6 h, the major product became (1-propylpent-2-enyl)dimesitylsilane (**5c**), isolated by GC. The stereochemistry of the 1-propylpent-2-enyl group has been explored by FT-IR. The presence of an absorption at 966 cm^{-1} for **5c** indicated a trans configuration for at least some of the acyclic 2-pentenyl group, and presumably the cis configuration was also present. The structural assignments for the *trans*-silirane as well as for the cis isomer were based on the ^{13}C chemical shifts and peak multiplicities and the diagnostic ^{29}Si chemical shifts. The complex ^{1}H chemical shifts of the *n*-propyl substituents did not permit extraction of all the coupling constants.

***cis*-2,3-Di-*n*-propyl-1,1-dimesitylsilirane, Mes$_2$SiCH(CH$_2$CH$_2$CH$_3$)-CH(CH$_2$CH$_2$CH$_3$) (5a).** ^{1}H NMR (CDCl$_3$): δ 1.06 (6 H, t, J = 7.4 Hz, CH$_3$), 1.32−1.84 (10 H, m, CH$_2$ of propyls and ring CH), 2.37 (6 H, s, *p*-CH$_3$), 2.70 (6 H, s, *o*-CH$_3$), 2.72 (6 H, s, *o*-CH$_3$), 6.95 (2 H, s, ArH), 6.98 (2 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 14.19 (d), 20.63 (q), 20.78 (q), 20.90 (q), 24.05 (q), 24.36 (q), 24.71 (t), 29.19 (t), 127.90 (s), 128.19 (d), 128.45 (d), 139.24 (s), 145.27 (s), 145.76 (s). ^{29}Si NMR (CDCl$_3$): δ −81.80. High-resolution mass obtained on the mixture of isomers: calcd for SiC$_{26}$H$_{38}$ 378.2743; found 378.2741.

(1-Propylpent-2-enyl)dimesitylsilane, Mes$_2$SiH[CH(CH$_2$CH$_2$CH$_3$)-CH=CHCH$_2$CH$_3$] (5c). ^{1}H NMR (CDCl$_3$): δ 0.76 (3 H, t, J_{HH} = 7.5 Hz, CH$_3$), 0.84 (3 H, t, J_{HH} = 7.1 Hz, CH$_3$CC=), 1.20 (H, m, SiCH), 1.55 (4 H, m, CH$_2$CH$_2$), 2.21 (3 H, s, *p*-CH$_3$), 2.23 (3 H, s, *p*-CH$_3$), 2.34 (6 H, s, *o*-CH$_3$), 2.36 (6 H, s, *o*-CH$_3$), 4.97 (1 H, d, J_{HSiCH} = 5.8 Hz, SiH), 5.22 (2 H, m, CH=CH), 6.74 (2 H, s, HAr), 6.79 (2 H, s, HAr). ^{13}C NMR (CDCl$_3$): δ 13.73 (d), 20.84 (q), 22.03 (t), 23.29 (q), 23.52 (q), 25.72 (t), 27.61 (q), 31.41 (q), 33.22, 128.65 (d), 129.02 (d), 130.08 (d), 130.50 (s), 131.63 (d), 138.70 (s), 138.93 (s), 144.46 (s), 144.77 (s). ^{29}Si NMR (CDCl$_3$): δ −25.87. GC/MS, *m/e* (relative abundance): 267 (100, M − 111), 235 (5), 220 (3), 207 (2), 159 (3), 147 (8), 119 (7).

Photolysis of 2 with *trans*-4-Octene. A solution containing 150 mg of **2**, 1.5 mL of *trans*-4-octene (purity >99.8%), and 5 mL of *n*-pentane was photolyzed for 3 h with five Hg lamps. About 90% of **2** was pho-

tolyzed, and the major product, ∼90%, was *trans*-1,1-dimesityl-2,3-di-*n*-propylsilirane (**5b**) (no cis isomer was observed). A minor product, the acyclic isomer **5c**, was observed in less than 5% yield.

***trans*-2,3-Di-*n*-propyl-1,1-dimesitylsilirane, Mes$_2$SiCH-(CH$_2$CH$_2$CH$_3$)CH(CH$_2$CH$_2$CH$_3$) (5b).** ^{1}H NMR (CDCl$_3$): δ 0.82−0.94 (2 H, t, J = 7.1 Hz, 2 ring CH groups partially hidden by methyls), 0.87 (6 H, t, J = 7.3 Hz, 2 CH$_3$ of 2 propyls), 1.42 (8 H, m, CH$_2$), 2.26 (6 H, s, *p*-CH$_3$), 2.57 (12 H, s, *o*-CH$_3$), 6.83 (4 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 13.98 (d), 20.95 (q), 23.64 (t), 24.29 (q), 26.40 (q), 34.27 (t), 127.56 (s), 128.37 (d), 139.28 (s), 140.83 (s). ^{29}Si NMR (CDCl$_3$): δ −79.78. High-resolution mass obtained on the mixture of isomers: calcd for SiC$_{26}$H$_{38}$ 378.2743; found 378.2729.

Photolysis of 2 in *cis*-2-Butene. A solution of 5 mL of cyclohexane, *cis*-2-butene (purity >99.5%) (3.2 mL (0 °C), 36 mmol), and **2** (150 mg, 0.36 mmol) was irradiated for 1.5 h with seven medium-pressure Hg lamps. Nearly 80% of **2** reacted. After the volatiles were removed under vacuum, the colorless oily mixture was dissolved in CDCl$_3$ for NMR analysis. Both ^{13}C and ^{1}H NMR indicated that two products, *cis*-2,3-dimethyl-1,1-dimesitylsilirane (**3a**) (major, 90%) and (1-methylprop-2-enyl)dimesitylsilane (**3c**) (minor, 10%), were formed. No *trans*-2,3-dimethyl-1,1-dimesitylsilirane (**3b**) was observed. While we do agree with the overall structural assignments of Ando et al., the simplicity of the NMR spectra deserves more careful consideration of the chemical shifts and multiplicities of the signals than previously reported. For that reason, they are reported below.

***cis*-2,3-Dimethyl-1,1-dimesitylsilirane, Mes$_2$SiCH(CH$_3$)CH(CH$_3$) (3a).** ^{1}H NMR (CDCl$_3$): δ 1.28 (6 H, d, J = 7.1 Hz, CH$_3$C), 1.41 (2 H, q, J = 7.1 Hz, CCH$_3$), 2.35 (6 H, s, *p*-CH$_3$), 2.71 (12 H, s, *o*-CH$_3$), 6.91 (2 H, s, HAr), 6.95 (2 H, s, HAr). ^{13}C NMR (CDCl$_3$): δ 10.87 (d), 13.61 (q), 21.34 (q), 21.42 (q), 24.75 (q), 24.82 (q), 127.22 (s), 128.89 (d), 129.03 (d), 139.91 (s), 139.94 (s), 146.29 (s), 146.50 (s). ^{29}Si NMR (CDCl$_3$): δ −83.16.

(1-Methylprop-2-enyl)dimesitylsilane, Mes$_2$Si(H$_a$)CH$_d$(CH$_3$)CH$_c$= CH$_b$H$_a$) (3c). ^{1}H NMR (CDCl$_3$): δ 1.26 (3 H, d, $J_{H_dCCH_3}$ = 6.8 Hz, CH$_3$CSi), 1.52 (H, m, CH$_d$), 2.24 (6 H, s, *p*-CH$_3$), 2.37 (6 H, s, *o*-CH$_3$), 2.38 (6 H, s, *o*-CH$_3$), 4.94 (1 H, d, J_{HSiCH_d} = 5.4 Hz, SiH), 4.90 (1 H, dd, J_{ab} = 1.6 Hz, J_{ac} = 10.4 Hz, =CH$_a$), 4.98 (1 H, dd, J_{ba} = 1.6 Hz, J_{bc} = 17.2 Hz, =CH$_b$), 5.96 (1 H, ddd, J_{cb} = 17.2 Hz, J_{ca} = 10.4 Hz, J_{cd} = 6.8 Hz, CH$_c$=), 6.79 (2 H, s, ArH), 6.80 (2 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 15.15 (d), 20.83 (q), 20.87 (q), 23.22 (q), 23.48 (q), 26.09 (q), 111.74 (t), 128.83 (d), 129.07 (d), 134.05 (s), 139.07 (s), 141.80 (d), 144.57 (s), 144.70 (s). ^{29}Si NMR (CDCl$_3$): δ −22.47. GC/MS, *m/e* (relative abundance): 267 (100, M-55), 235 (4), 220 (3), 207 (3), 159 (4), 147 (8), 119 (7).

Photolysis of 2 in *trans*-2-Butene. The photolysis was carried out in the same way as for *cis*-butene. A solution containing 5 mL of cyclohexane, 3.2 mL of *trans*-2-butene (36 mmol), and **2** (150 mg, 0.36 mmol) was photolyzed for 1.5 h. A mixture of *trans*-2,3-dimethyl-1,1-dimesitylsilirane (**3b**), *cis*-silirane **3a**, and the acyclic isomer **3c** was obtained. The purity of *trans*-butene was determined by GC with a 10% silver nitrate/Chromsorb P column (10 ft × $^1/_8$ in.) at 40 °C and, also, with a picric acid on graphite column (5 ft × $^1/_8$ in.) at 30 °C.

***trans*-2,3-Dimethyl-1,1-dimesitylsilirane, Mes$_2$SiCH(CH$_3$)CH(CH$_3$) (3b).** ^{1}H NMR (CDCl$_3$): δ 0.92 (2 H, q, J = 6.9 Hz, ring HC), 1.18 (6 H, d, J = 6.9 Hz, CH$_3$), 2.32 (6 H, s, ArCH$_3$), 2.68 (12 H, s, ArCH$_3$), 6.90 (4 H, s, ArH). ^{13}C NMR (CDCl$_3$): δ 16.37 (d), 21.52 (q), 21.71 (q), 24.72 (q), 127.43 (s), 128.78 (d), 139.86 (s), 146.47 (s). ^{29}Si NMR (CDCl$_3$): δ −77.27.

(16) Conlin, R. T.; Namavari, M.; Chickos, J. S.; Walsh, R. *Organometallics* **1989**, *8*, 168.