Me_3NO in methanol at room temperature converted it to a mixture of osmium compounds of which **4** was the major constituent (IR). Other products were not identified except to note that **3** was not present. UV irradiation of a solution of **5** in CH_2Cl_2 in Pyrex led to general decomposition.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Council Canada through a Strategic Grant. Mass spectra by xenon fast atom bombardment were kindly carried out at the University of Alberta by Dr. A. M. Hogg.

Registry No. **1**, 65702-94-5; **3**, 86409-58-7; **4**, 86409-59-8; **5**, 86409-60-1; $Os_3(CO)_{10}(CH_3CN)_2$, 61817-93-4.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

Hexamethylsilirane. 5. Conversion to Five-Membered Ring Silicon Compounds by "Two-Atom" Insertion Reactions of Aryl Olefins, 1,3-Dienes, and Conjugated Acetylenes[1]

Dietmar Seyferth,* Don P. Duncan, Mark L. Shannon, and Emma W. Goldman

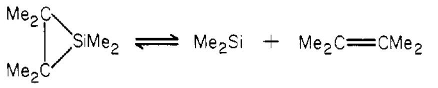
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received September 21, 1983

Hexamethylsilirane reacts, under mild conditions, with styrene, α-methylstyrene, terminal 1,3-dienes, conjugated terminal acetylenes, and benzyne with insertion of a C=C or C≡C bond into an Si—C bond of the silirane ring to give a silacyclopentane or silacyclopentene (in the case of the acetylenes). Byproducts derived from Me_2Si addition to these substrates also are obtained.

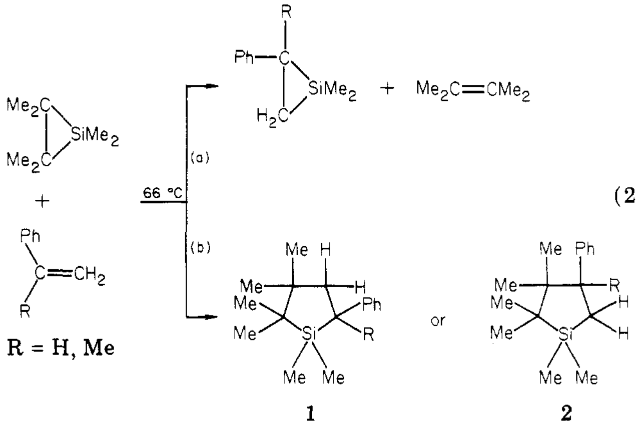
Introduction

In earlier papers of this series we have reported that hexamethylsilirane decomposes at temperatures as low as 65–75 °C with extrusion of dimethylsilylene (eq 1).[1,2] The



(1)

dimethylsilylene thus generated was found to insert into the Si—H bonds of organosilicon hydrides and into the Si—O bonds of methoxysilanes, hexamethylcyclotrisiloxane, and 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane and to add to the C=C bonds of internal olefins to give new siliranes.[1] During the course of an investigation of the scope of the formation of siliranes by the addition of hexamethylsilirane-derived dimethylsilylene to olefins we carried out the thermolysis of hexamethylsilirane in the presence of styrene and α-methylstyrene. The expected reaction was Me_2Si addition to the C=C bond of the styrene (eq 2a). However, what was found instead was that the major product was that of a ring expansion process: the insertion of both carbon atoms of the C=C bonds of styrene and α-methylstyrene into an Si—C bond of the silirane ring to give a silacyclopentane (eq 2b).[2] Such an apparent [3 + 2] cycloaddition, which we shall call a "two-atom insertion", was unexpected and very interesting in terms of mechanistic considerations and synthetic organosilicon chemistry, and thus we undertook to investigate the scope and, if possible, the mechanism of such two-atom insertions in more detail.



R = H, Me

1

2

(2)

Results and Discussion

We shall address ourselves first to the structure of the two-atom insertion products in the case of styrene and α-methylstyrene. In our initial report,[2] structure **1** was given; this assignment was based on proton NMR-based reasoning[3] which later considerations disputed.[4] The application of ^{13}C NMR spectroscopy allowed us to settle this question of structure.[5]

During the course of this investigation it was found that styrene reacts with hexamethylsilirane even at room temperature. An overnight reaction at 25 °C gave the same product (in 47% yield) as was obtained in the reaction carried out at 66 °C as well as a minor (6% yield) product

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(1) (a) Part 4: Seyferth, D.; Wiseman, G. H.; Annarelli, D. C.; Shannon, M. L. *J. Organomet. Chem.*, in press. (b) Preliminary communications: Seyferth, D.; Duncan, D. P.; Vick, S. C. *Ibid.* **1977**, *125*, C5. Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Duncan, D. P. *Ibid.* **1977**, *135*, C37.

(2) Seyferth, D.; Annarelli, D. C. *J. Organomet. Chem.* **1976**, *117*, C51.

(3) Annarelli, D. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1976.

(4) Duncan, D. P. Ph.D. Thesis, Massachusetts Institute of Technology, 1979.

(5) Goldman, E. W. Ph.D. Thesis, Massachusetts Institute of Technology, 1983.

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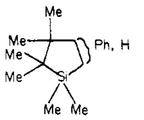
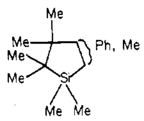
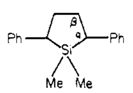
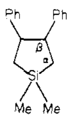
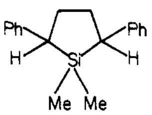
Table I. ^{13}C Chemical Shifts ($\delta_C{}^a$) of Ring Carbon Atoms

		 cis and trans 3/4	 5
16.38 (CH_2)	24.31 (CH_2)	Cα 35.74, 37.35	Cα 24.49
51.32 (CHPh)	52.46 (CHPh)	Cβ 31.71, 32.05	Cβ 52.94
45.84 (CMe_2)	48.56 (CMe_2)		
27.72 (CMe_2)	26.98 (CMe_2)		

[a] Parts per million of ring carbon atoms.

that was identified as an acyclic silane, the trans isomer of $Me_2CHCMe_2SiMe_2CH{=}CHPh$. At room temperature, the reaction of hexamethylsilirane and α-methylstyrene proceeded less well, giving the two-atom insertion product in only 5% yield. Closer examination of the reactions carried out at 66 °C showed that other, higher boiling products were formed. Thus, in another experiment, when an excess of styrene was heated with hexamethylsilirane at 66 °C for 15 h, the two-atom insertion product was produced in 67% yield. Also formed was a higher boiling product in 25% yield whose 270-MHz proton and ^{13}C NMR spectra suggested that it was a mixture of three isomeric silacyclopentanes, 3, 4, and 5. Similarly, the reaction of hexamethylsilirane with an excess of α-methylstyrene at 66 °C gave the two-atom insertion product in 53% yield and a mixture of 6 and 7 (identification tentative) in 20% yield. The silacyclopentane byproducts obtained in these reactions (3/4 and 5 and 6/7) contain only the Me_2Si unit of the hexamethylsilirane. Their presence indicates that extrusion of Me_2Si followed by its addition to the C=C bond of styrene and α-methylstyrene to give the originally expected phenyl-substituted siliranes (eq 2a) does indeed occur. The new siliranes produced, however, also undergo the two-atom insertion reaction very readily (even when a deficiency of the styrene is present) to give the observed silacyclopentanes, 3/4 and 5 in the styrene reaction and 6/7 in the α-methylstyrene reaction.



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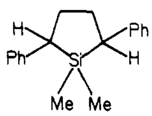

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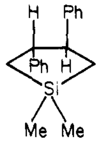

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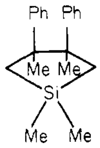

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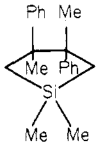
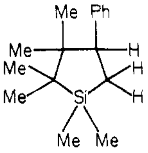


7

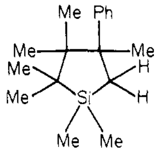
The 270-MHz proton NMR spectra of the styrene and α-methylstyrene two-atom insertion products were better resolved than the previously reported[3,4] 60-MHz spectra but provided no new information concerning structure. However, it was clear that only one of the two possible isomers, 1 or 2, was present.

Comparison of the ^{13}C NMR spectra of the two-atom insertion products with those of compounds 3, 4, and 5 yielded more information. The ^{13}C chemical shifts for the ring carbon atoms of 3/4 (mixture), 5, and the styrene and α-methylstyrene two-atom insertion products are given in Table I.

The ^{13}C NMR spectra of both two-atom insertion products show similar chemical shifts for their ring carbon atoms. The signals of the carbon atoms with the phenyl substituent are found at δ_C 51 and 52, respectively. A consideration of the ^{13}C NMR data for 3, 4, and 5 in Table I shows that the signal for the carbon atom bearing the phenyl group is found at δ_c 53 if it is β to the silicon atom (in 5) and at δ_C ~36–37 if it is α to the silicon atom (3, 4). Thus, we conclude that the two-atom insertion products of styrene and α-methylstyrene into hexamethylsilirane are 2a and 2b, respectively.

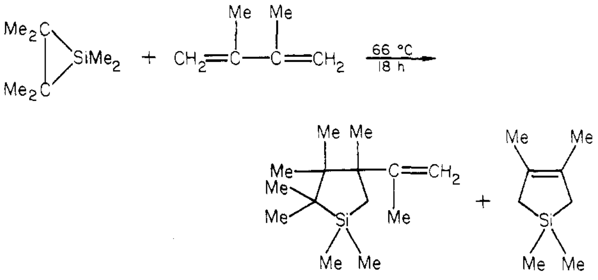


2a



2b

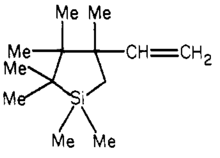
2,3-Dimethyl-1,3-butadiene also was found to undergo two-atom insertion into hexamethylsilirane at 70 °C but not at room temperature and not upon UV irradiation. As indicated in eq 3, the Me_2Si adduct of the diene 9 also was



(3)

8 (47%) 9 (15%)

produced in substantial quantity.[6,7] The presence of a diluent (pentane/benzene) favored formation of the Me_2Si addition product 9 at the expense of the two-atom insertion product 8. Isoprene reacted similarly, giving an inseparable ~2:1 mixture of 10 and 11, while the reaction of hexamethylsilirane with (*E*)-2,4-pentadienyltrimethylsilane,



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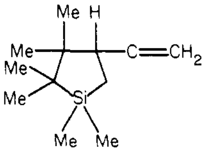

11

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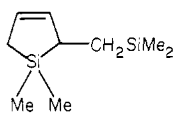
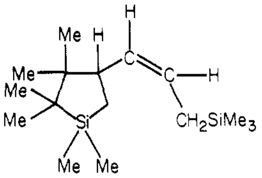
(6) Initial examination of this reaction[2,3] failed to detect the higher boiling two-atom insertion product.

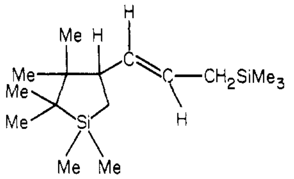
(7) For discussions of silylene addition to 1,3-dienes see: Gaspar, P. P. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A. Ed.; Wiley-Interscience: New York: 1978; Vol. 1, and 1981, Vol. 2.



12



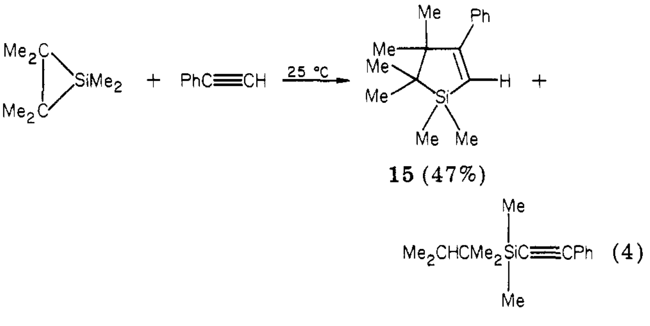
13



14

$Me_3SiCH_2CH{=}CHCH{=}CH_2$, resulted in formation of three products: the Me_2Si adduct **12** and two isomeric two-atom insertion products, **13** and **14**. In this case also, benzene diluent favored formation of the dimethylsilylene adduct **12** (10% yield in the absence, 29% yield in the presence of benzene) over the two-atom insertion product **13** + **14** (71% yield in the absence, 48% yield in the presence of benzene).

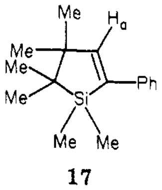
Conjugated acetylenes were found to be considerably more reactive toward hexamethylsilirane than conjugated olefins. Thus phenylacetylene and isopropenylacetylene both reacted at room temperature during an overnight reaction time. In the case of phenylacetylene the two-atom insertion product **15**, a silacyclopentene, was the major product, but an acyclic silane, **16**, was formed as well (eq 4). The yields of **15** and **16** were higher (52% and 34%, respectively) when the reaction was carried out at 70 °C for 18 h. The alternate structure for **15**, the 2-phenyl-1-silacyclopent-2-ene **17**, could be ruled out on the basis of the proton NMR spectrum. In silacyclopentenes of the latter type the olefinic proton signal (H_a) are found in the phenyl proton region (δ 6.85–7.30).[8] The olefinic proton resonance in the NMR spectrum of **15** was observed significantly upfield at δ 5.64. The reaction of isopropenylacetylene with an excess of hexamethylsilirane gave only one two-atom insertion product, **18**, in 92% yield. In the proton NMR spectrum of **18** $\delta(H_a)$ equals 5.53, which favors the structure indicated. No insertion involving the C=C of isopropenylacetylene occurred.



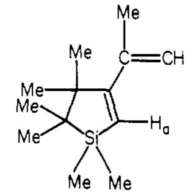
15 (47%)

(4)

16 (20%)

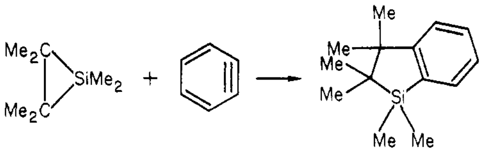


17



18

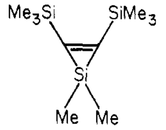
A two-atom insertion did not occur with $PhC{\equiv}CCH_3$, even though the C≡C bond is activated by the phenyl substituent. However, the highly reactive benzyne, generated in situ by the reaction of *o*-bromofluorobenzene with magnesium in refluxing THF, did insert into the Si—C bond of hexamethylsilirane (eq 5). These unusual and unexpected two-atom insertions are without precedent and are indicative of the already demonstrated[9,10] extremely high reactivity of the silirane ring. Hexamethylsilirane is easily prepared,[9] and thus the two-atom insertion reaction could be of preparative value. As a practical point, we note that at a reaction temperature of 65–70 °C both the known Me_2Si extrusion reaction and the two-atom insertion reaction can be competitive. For best results, reactions to prepare the two-atom insertion products should be carried out without the use of an inert diluent.



(5)

19 (18%)

We will defer a more detailed discussion of the possible mechanism of these two-atom insertion reactions until a later paper in which similar reactions of silirene **20**[11] are presented. A preliminary discussion of our thoughts on the question of mechanism in which a radical mechanism was favored has already been published.[1b]



20

Experimental Section

General Comments. Infrared spectra were recorded by using a Perkin-Elmer Model 457A infrared spectrophotometer and proton magnetic resonance spectra by using either a Varian Associates T60 or a Perkin-Elmer R-20 or R-22 spectrometer. Chemical shifts are reported in δ units, parts per million downfield from internal tetramethylsilane. Chloroform and dichloromethane often were used as alternative internal standards. ^{13}C NMR spectra were obtained with a JEOL FNM HFX-60Q spectrometer, Gas–liquid chromatography (GLC) was used routinely for isolation of pure samples, for determination of purity of distilled samples, and for yield determinations by the internal standard method. All columns were packed on acid-washed, dimethyldichlorosilane-treated Chromosorb W.

All solvents used were rigorously dried. All reactions were carried out under an atmosphere of prepurified nitrogen or more

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(8) (a) Gilman, H.; Atwell, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 2678. (b) Atwell, W. H.; Weyenberg, D. R.; Gilman, H. *J. Org. Chem.* **1967**, *32*, 885.

(9) Seyferth, D.; Annarelli, D. C.; Vick, S. C.; Duncan, D. P. *J. Organomet. Chem.* **1980**, *201*, 179.

(10) (a) Seyferth, D.; Annarelli, D. C.; Shannon, M. L.; Escudie, J.; Duncan, D. P. *J. Organomet. Chem.* **1982**, *225*, 177. (b) Seyferth, D.; Duncan, D. P.; Haas, C. K. *Ibid.* **1979**, *164*, 305. (c) Seyferth, D.; Duncan, D. P.; Schmidbaur, H.; Holl, P. *Ibid.* **1978**, *159*, 137. (d) Hölderich, W.; Seyferth, D. *Ibid.* **1978**, *153*, 299.

(11) Seyferth, D.; Annarelli, D. C.; Vick, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 6382.

usually, argon. All glassware was flame-dried under a stream of nitrogen before use. Reactive reagents were transformed by syringe or cannula.

In part 1[9] the preparations of hexamethylsilirane and its precursors are described in detail, as are the methods used for the determination of the yield of hexamethylsilirane, for the preparation of solutions of hexamethylsilirane in solvents other than THF, and for the handling of hexamethylsilirane and its solutions. We stress again the high reactivity of hexamethylsilirane toward atmospheric oxygen and moisture and the absolute need to perform all operations involving this compound with complete exclusion of air in rigorously dried glassware using rigorously dried and degassed solvents.

For reactions that were carried out in benzene or neat trapping reagent, the following procedure was used. The reaction vessel, usually a 25-mL one-necked flask equipped with a magnetic stir-bar and a reflux condenser with an argon inlet tube, was purged with argon and flame dried. The substrate then was added to the flask by syringe, followed by a weighed amount of the concentrated hexamethylsilirane solution. The reaction vessel then was heated in a preheated oil bath. Reaction temperatures are uncorrected.

Reaction of Hexamethylsilirane with Styrene. A dry 50-mL one-necked flask equipped with a magnetic stir-bar, and a reflux condenser topped with a gas inlet tube was charged with 0.4138 g of a 36% by weight solution of the silirane in THF (1.06 mmol) and 2.0 mL (17.4 mmol) of freshly distilled styrene. The reaction mixture was stirred and heated at 66 °C under argon in an oil bath for 15 h. It then was cooled to room temperature, and volatiles were removed at reduced pressure. GLC analysis of the residue (4 ft 15% SE-30, 150–250 °C at 10°/min) showed the presence of two major products. The component of lower retention time was collected and identified as 1,1,2,2,3,3-hexamethyl-4-phenyl-1-silacyclopentane, **2a**: 55% yield; n^{25}_{D} 1.5270; 270-MHz ^{1}H NMR (CD_2Cl_2) δ 0.08 (s, 3 H, $SiCH_3$), 0.21 (s, 3 H, $SiCH_3$), 0.55, 0.64, 0.90, 0.94 (s, each 3 H, CCH_3), 0.84 (dd, *J* = 7 Hz, *J* = 14 Hz, 1 H, C*H*H), 1.14 (dd, *J* = 14 Hz, 1 H, CH*H*), 2.93 (dd, *J* = 7 Hz, *J* = 14 Hz, 1 H, CHPh), 7.16–7.29 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ_C −3.30, −1.19 (q, *J* = 120 Hz, $SiCH_3$), 16.38 (t, *J* = 123 Hz, CH_2), 19.53 (q, *J* = 125 Hz, CCH_3), 19.91 (q, *J* = 125 Hz, CCH_3), 20.71 (q, *J* = 125 Hz, CCH_3), 22.58 (q, *J* = 125 Hz, CCH_3), 27.72 (s, *C*Me$_2$), 45.84 (s, *C*Me$_2$), 51.32 (d, *J* = 125 Hz, *C*PhH), 125.15 (d, *J* = 165 Hz, phenyl C), 126.94 (d, *J* = 179 Hz, phenyl C), 127.96 (d, *J* = 163 Hz, phenyl C), 149 (s, ipso phenyl C). Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 77.63; H, 10.61.

The component with the longer GLC retention time was identified as a mixture of *cis*- and *trans*-2,5-diphenyl-1,1-dimethyl-1-silacyclopentane (**3**/**4**) and *trans*-3,4-diphenyl-1,1-dimethyl-1-silacyclopentane (**5**), 25% yield with a **3**:**4**:**5** ratio of approximately 1:1:1: ^{1}H NMR (270 MHz, CD_2Cl_2) δ −0.63 (**3**), −0.12 (**4**), 0.26 (**5**), 0.31 (**3**) (s, all $SiCH_3$), 0.10–2.95 (m, CH and CH_2), 6.8–8.0 (m, Ph) [lit.[12] for **3**/**4** δ −0.64, −0.14, 0.29 (s, $SiCH_3$), 2.3 (m, CH and CH_2), 7.1 (Ph)]. An authentic sample of **5**, mp 92–93 °C, was prepared by the procedure of Weyenberg et al.:[12] ^{1}H NMR (90 MHz, CCl_4) δ 0.25 (s, 6 H, $SiMe_2$), 0.75–1.31 (m, 4 H, CH_2), 2.82 (m, 2 H, C*H*Ph), 7.06 (s, 10 H, Ph) [lit.[12] δ 0.23 (s), 1.2 (m), 2.9 (m), 7.1 (m)]; ^{13}C NMR ($CDCl_3$) δ_C −1.10 (q, *J* = 119 Hz, $SiMe_2$), 24.49 (t, *J* = 123 Hz, CH_2), 52.94 (d, *J* = 128 Hz, *C*HPh), 125.4 (d, *J* = 163 Hz, Ph), 126.99 (d, *J* = 156 Hz, Ph), 127.84 (d, *J* = 166 Hz, Ph), 146.12 (s, ipso C).

A reaction in which an excess of the silirane (2.12 mmol) over the styrene (1.04 mmol) was used (66 °C for 15 h) gave **2a** in 37% yield, **3**/**4** in 5% yield, and octamethyl-1,2-disilacyclobutane[9] in 18% yield.

In another experiment, 3.9 g of a hexamethylsilirane solution in THF that contained 3.3 mmol of the silirane and 0.46 mL (4 mmol) of freshly distilled styrene were stirred under argon overnight. Subsequent GLC analysis showed the presence of two major products in 7.5:1 ratio. The major product (44% yield), of lower GLC retention time, was identified as the two-atom insertion product **2a**. The minor product, n^{25}_{D} 1.5267 (6% yield), was *trans*-$Me_2CHMe_2CSiMe_2CH{=}CHPh$: 60-MHz ^{1}H NMR ($CCl_4$) δ 0.16 (s, 6 H, $SiMe_2$), 0.90 (s, 6 H, CMe_2), 0.90 (d, *J* = 7 Hz, 6 H, CH*Me*$_2$), 1.42–1.90 (m, 1 H, C*H*Me$_2$), 6.44 (d, one-half of AB pattern, *J* = 19 Hz, 1 H, =CH), 6.78 (d, one-half of AB pattern, *J* = 19 Hz, 1 H, =CH), 7.12–7.42 (m, 5 H, Ph). The vinylic proton spin–spin coupling constant of 19 Hz is indicative of the trans geometry. Anal. Calcd for $C_{16}H_{26}Si$: C, 77.97; H, 10.63. Found: C, 77.92; H, 10.75.

Reaction of Hexamethylsilirane with α-Methylstyrene. The standard apparatus was charged with 0.4138 g of a 36% by weight solution of the silirane in THF (1.06 mmol) and 3.0 g (23.08 mmol) of freshly distilled α-methylstyrene. The mixture was stirred and heated under argon at 66 °C for 15 h. After it had cooled to room temperature, volatiles were removed at reduced pressure. GLC examination of the high-boiling residue (4 ft 15% SE-30, 150–250 °C at 10°/min) showed the presence of two products. The major product (53% yield) was **2b**: n^{25}_{D} 1.5302; 90-MHz ^{1}H NMR (CD_2Cl_2) δ 0.19 and 0.22 (s, 3 H each, $SiCH_3$), 0.45, 0.82, 0.83, 1.08, 1.41 (s, 3 H each, CCH_3), 0.71 (d, *J* = 14 Hz, 1 H, C*H*H), 1.64 (d, *J* = 14 Hz, 1 H, CH*H*), 6.99–7.44 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ_C −1.54 and −0.74 (q, *J* = 120 Hz, $SiCH_3$), 17.85 (q, *J* = 125 Hz, CCH_3), 23.85 (q, *J* = 125 Hz, CCH_3), 24.31 (t, *J* = 125 Hz, CH_2), 24.79 (q, *J* = 125 Hz, CCH_3), 25.92 (q, *J* = 125 Hz, CCH_3), 26.98 (s, *C*Me$_2$), 28.25 (q, *J* = 125 Hz, CCH_3), 48.56 (s, *C*Me$_2$), 52.46 (s, *C*PhMe), 125.12 (d, *J* = 165 Hz, PhC), 126.94 (d, *J* = 179 Hz, PhC), 127.96 (d, *J* = 163 Hz, PhC), 149 (s, ipso C). Anal. Calcd for $C_{17}H_{28}Si$: C, 78.38; H, 10.83. Found: C, 78.32; H, 11.00.

The second component of longer GLC retention time was present in 20% yield and was *tentatively* identified as a mixture of the cis and trans isomers **6** and **7**: 90-MHz ^{1}H NMR (CD_2Cl_2) δ 0.37 (s, $SiMe_2$ of trans isomer), 0.39 and 0.50 (s, $SiMe_2$ of cis isomer), 0.92 (dd, *J* = 15 Hz, *J* = 4 Hz, CH_2), 1.18 (s, CCH_3), 1.53 (s, CCH_3), 1.70 (dd, *J* = 15 Hz, *J* = 4 Hz, CH_2), 6.83–7.17 (m, 20 H, Ph); ^{13}C NMR (decoupled) ($CDCl_3$) δ_C 0.23, 0.60, 1.65 ($SiCH_3$), 25.79, 26.50, 26.67, 27.28 (CH_2 and CH_3 groups), 52.77 and 53.24 (*C*PhMe), 125.24, 125.54, 126.56, 126.89, 127.81, 128.25, 128.49, 146.17, 147.52 (phenyl C). Anal. Calcd for $C_{20}H_{26}Si$: C, 81.57; H, 8.90. Found: C, 81.23; H, 8.63.

A reaction between hexamethylsilirane (1.41 mmol, THF concentrate) in 15 mL of pentane with 4 mmol of α-methylstyrene, carried out overnight at room temperature, gave **2b** in only 5% yield.

Reaction of Hexamethylsilirane with 2,3-Dimethyl-1,3-butadiene. The standard apparatus was charged with 2.73 mmol of the silirane (THF concentrate) and 2.0 mL (~17.7 mmol) of the diene (Chemical Samples Co.) in 2.5 mL of benzene. The solution was stirred and heated under argon at 66 °C for 18 h. GLC analysis showed the presence of two products (4 ft. 10% UCW-98 100–200 °C program), samples of which were collected. The first was the Me_2Si-derived derived product **9**: n^{25}_{D} 1.4564 (lit.[13] n^{25}_{D} 1.4570); present in 31% yield; 60-MHz ^{1}H NMR (CCl_4) δ 0.13, 1.27, 1.67 (singlets) (lit.[13] singlets at 0.15, 1.30, 1.68 ppm). The second product was **8**: n^{25}_{D} 1.4929; present in 28% yield: 60-MHz ^{1}H NMR (CCl_4) δ 0.11, 0.13 (s, $SiCH_3$), 0.72, 0.86, 0.91, 1.03, 1.18 (s, ring CCH_3), 1.82 (s, $=CCH_3$), 4.75–4.90 (m, $=CH_2$).[14] Anal. Calcd for $C_{14}H_{28}Si$: C, 74.91; H, 12.57. Found: C, 75.10; H, 12.63.

Another experiment was carried out by using 1.24 mmol of the silirane (THF concentrate) and 2.5 mL of the diene without a diluent (18 h at 68 °C). The yields of **8** and **9** were 58% and 24%, respectively. Thus the absence of a diluent favors the two-atom insertion reaction.

Reaction of Hexamethylsilirane with Isoprene. The standard apparatus was charged with 2.87 mmol of the silirane (THF concentrate) and 2.0 mL (~20 mmol) of isoprene (Eastman). The solution was stirred and heated under argon at 66 °C for 18 h. GLC analysis (as in the previous experiment) showed the presence of only one product (74% yield); n^{25}_{D} 1.4826. The ^{1}H NMR spectrum showed this to be a 2:1 mixture of **10** and **11**: ^{1}H NMR (mixture of **10** and **11**, in CCl_4) δ −0.02, 0.06, 0.09 (3s, $SiCH_3$), 0.66, 0.71, 0.79, 0.82, 0.91, 1.02 (7s, ring CCH_3), 1.74 (s,

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[14] In this spectrum as well as in those of the other diene two-atom insertion products the ring $SiCH_2$ proton multiplet is obscured by the closely spaced CMe_2 signals.

=CCH$_3$ of **11**), 2.30 (dd, J = 11 Hz, J^2 = 8 Hz, ring H of carbon 4 of **11**), 4.62–5.08 (m, =CH$_2$), 6.05 (dd, J(trans) = 18 Hz, J(cis) = 10 Hz, CH=CH$_2$ of **10**). Anal. Calcd for $C_{13}H_{26}Si$: C, 74.19; H, 12.45. Found: C, 74.17; H, 12.38.

Reaction of Hexamethylsilirane with (*E*)-2,4-Pentadienyltrimethylsilane. The standard apparatus was charged with 1.50 mL (ca. 8.2 mmol) of the diene,[15] 3.31 mmol of the silirane (THF concentrate, 2.91 mmol/g), and 2.50 mL of benzene. The solution was stirred and heated under argon at 75 °C for 18 h. Workup as above and GLC analysis (10% SE-30, 140–220 °C program) of the higher boiling portion showed the presence of three products, samples of which were collected.

(1) 1,1-Dimethyl-2-((trimethylsilyl)methyl)-1-silacyclopent-3-ene, **12**: $n^{25}{}_D$ 1.4611; in 29% yield; 90-MHz ^{1}H NMR (CCl$_4$) δ 0.05 (s, 9 H, Me$_3$Si), 0.10 (s, 3 H, ring SiMe), 0.19 (s, 3 H, ring SiMe), 0.58 (dd, J^1 = 7 Hz, J^2 = 4 Hz, 2 H, Me$_3$SiCH_2), 1.27 (br s, 2 H, ring CH$_2$), 1.38–1.85 (complex m, 1 H, CHCH$_2$), 5.68 (br s, 2 H, vinyl H). Anal. Calcd for $C_{10}H_{22}Si_2$: C, 60.51; H, 11.17. Found: C, 60.59; H, 11.20.

(2) Two-atom insertion product, cis isomer **13**: $n^{25}{}_D$ 1.4685; in 10% yield; mass spectrum, M$^+$ at m/z 282; 250-MHz ^{1}H NMR (CCl$_4$) δ –0.02 (s, 9 H, SiMe$_3$), 0.00 (s, 3 H, ring SiMe), 0.09 (s, 3 H, ring SiMe), 0.66 (2s, in 1:1 ratio, 6 H, CMe$_2$), 0.82 (s, 6 H, CMe$_2$), 1.52–1.54 (m, 2 H, Me$_3$SiCH_2), 2.52–2.58 (m, 1 H, ring CH), 5.18–5.40 (AB multiplet, 2 H, vinyl H). Anal. Calcd for $C_{16}H_{34}Si_2$: C, 67.99; H, 12.13. Found: C, 68.08; H, 12.32.

(3) Two-atom insertion product, trans isomer **14**: $n^{25}{}_D$ 1.4692; in 38% yield; mass spectrum, M$^+$ at m/z 282; 250-MHz ^{1}H NMR (CCl$_4$) δ –0.04 (s, 12 H, Me$_3$Si and ring SiMe), 0.07 (s, 3 H, ring SiMe), 0.60 (s, 3 H, CMe), 0.66 (s, 3 H, CMe), 0.77 (s, 3 H, CMe), 0.81 (s, 3 H, CMe), 1.30–1.47 (m, 2 H, Me$_3$SiCH_2), 1.80–2.30 (m, 1 H, ring CH), 5.13–5.42 (AB multiplet, 2 H, vinyl H). Anal. Calcd for $C_{16}H_{34}Si_2$: C, 67.99; H, 12.13. Found: C, 67.94; H, 12.03.

Detailed analysis of the AB multiplets due to the vinyl protons in **13** and **14** was carried out,[16] and it was determined that J_{AB} = 10.8 Hz for **13** and 15.1 Hz for **14**, thus leading to the isomer assignments shown.

When hexamethylsilirane (1.46 mmol, THF concentrate) was heated with the neat diene (8.2 mmol) for 18 h at 75 °C, the yields of **12**, **13**, and **14**, were 10%, 15%, and 56%, respectively (a total yield of 81%).

Reaction of Hexamethylsilirane with Phenylacetylene. To 9.0 g of a THF solution of hexamethylsilirane (containing 4.24 mmol of the silirane) was added 0.55 mL (5 mmol) of phenylacetylene, and the reaction mixture was stirred under argon at room temperature overnight. Subsequent GLC analysis (10% DC-710 at 170 °C) showed the presence of two major products, samples of which were collected. The ratio of these was found to be 70:30 by NMR integration of the Si–Me peaks.

(1) 1,1,2,2,3,3-Hexamethyl-4-phenyl-1-silacyclopent-4-ene, **15**: $n^{25}{}_D$ 1.5281; in 47% yield; ^{1}H NMR (CCl$_4$) δ 0.14 (s, 6 H, Me$_2$Si), 0.93 (s, 6 H, CMe$_2$), 0.96 (s, 6 H, CMe$_2$), 5.64 (s, 1 H, =CH), 7.02–7.25 (m, 5 H, Ph). The alternate structure, **17**, was ruled out on the basis of the NMR spectrum, as noted in the Results and Discussion.

(2) Me$_2$CHCMe$_2$SiMe$_2$C≡CPh, **16**: $n^{25}{}_D$ 1.5248; in 20% yield; ^{1}H NMR (CCl$_4$), δ 0.20 (s, 6 H, Me$_2$Si), 0.95 (s, 6 H, Me$_2$C), 0.97 (d, J = 5 Hz, 6 H, CHCH_3), 1.49–1.86 (m, 1 H, CHCH$_3$), 7.15–7.49 (m, 5 H, Ph); IR (film) $\nu_{C≡C}$ 2185 cm^{-1}. Anal. Calcd for $C_{16}H_{24}Si$: C, 78.61; H, 9.90. Found (mixture of **15** and **16**): C, 78.82; H, 9.87.

Reaction of Hexamethylsilirane with Isopropenylacetylene. A mixture of 76 g of a THF solution of hexamethylsilirane (containing 10.6 mmol of the silirane) and 1.0 g (5 mmol) of isopropenylacetylene was stirred under argon at room temperature overnight. Subsequent GLC analysis (10% DC 200, 150 °C) showed the presence of the two-atom insertion product **18**: $n^{25}{}_D$ 1.4802; in 92% yield; ^{1}H NMR (CCl$_4$) δ 0.14 (s, 6 H, SiMe$_2$), 0.92 (s, 6 H, CMe$_2$), 1.00 (s, 6 H, CMe$_2$), 1.90 (s, 3 H, MeC=), 4.66–4.85 (m, 2 H, =CH$_2$), 5.53 (s, 1 H, ring =CH). Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 74.59; H, 11.69.

Reaction of Hexamethylsilirane with in Situ Generated Benzyne. A 50-mL three-necked flask equipped with a magnetic stir-bar, two no-air septa, and a reflux condenser topped with an argon inlet tube was charged with 0.246 g (10.1 mmol) of 99.99% magnesium (Alfa) and flame dried under a stream of argon. Subsequently, the silirane (3.90 mmol) in 11 mL of THF was added. The flask was immersed in an oil bath at 65 °C, and *o*-fluorobromobenzene (1.1 mL, ca. 10 mmol) was added dropwise over a 1-h period to generate the benzyne.[17] The reaction mixture was stirred under argon at 65 °C for 18 h. Subsequently, the mixture was filtered and the filtrate trap-trap-trap distilled at 0.05 mm with mild heating into a receiver cooled to –78 °C. GLC analysis of the distillate showed the presence of one product, 1,1,2,2,3,3-hexamethyl-1-silaindan, **19**: $n^{25}{}_D$ 1.5270; in 18% yield; mass spectrum, M$^+$ at m/z 219; ^{1}H NMR (CCl$_4$) δ 0.27 (s, 6 H, Me$_2$Si), 0.95 (s, 6 H, CMe$_2$ α to Si), 1.15 (s, 6 H, CMe$_2$ β to Si), 7.46 and 6.96 (m, 4 H, benzo H). Anal. Calcd for $C_{14}H_{22}Si$: C, 76.98; H, 10.15. Found: C, 76.99; H, 10.06.

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Registry No. **2a**, 88296-41-7; **2b**, 88296-42-8; **3**, 26436-15-7; **4**, 26436-16-8; **5**, 88296-43-9; **6**, 88296-44-0; **7**, 88296-45-1; **8**, 68945-34-6; **9**, 16109-39-0; **10**, 88296-46-2; **11**, 88296-47-3; **12**, 88296-48-4; **13**, 88296-49-5; **14**, 88296-50-8; **15**, 62346-58-1; **16**, 62346-59-2; **18**, 88296-51-9; **19**, 88296-52-0; *trans*-Me$_2$CHMe$_2$CSiMe$_2$CH=CHPh, 88296-53-1; (*E*)-Me$_3$SiCH$_2$CH=CHCH=CH$_2$, 72952-73-9; PhC≡CH, 536-74-3; hexamethylsilirane, 55644-09-2; styrene, 100-42-5; octamethyl-1,2-disilacyclobutane, 62346-42-3; α-methylstyrene, 98-83-9; 2,3-dimethyl-1,3-butadiene, 513-81-5; isoprene, 78-79-5; isopropenylacetylene, 78-80-8; *o*-fluorobromobenzene, 1072-85-1; benzyne, 462-80-6.

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