Tetrahedron Vol 45, No 7, pp 1929 to 1940, 1989
Printed in Great Britain

0040-4020/89 $3 00+ 00
Pergamon Press plc

NOVEL Si-C BOND CLEAVAGES OF ALKYLIDENESILIRANES IN THE REACTION WITH NUCLEOPHILES

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(*Received in Japan* 24 *October* 1988)

Abstract; 1,1,-Dimesityl-2-Z-neopentylidenesilirane(**1Z**) reacted with nucleophiles to give ring opening adducts inserting at unexpected Si-C2 bond. This behavior can be explained by the unique structural feature of **1Z** defined by its X-ray crystal analysis. A six electron participating concerted mechanism was suggested for the reaction with methanol and benzaldehyde. Palladium-catalyzed reaction of **1Z** with acetylene and allene gave ring expansion products.

Introduction

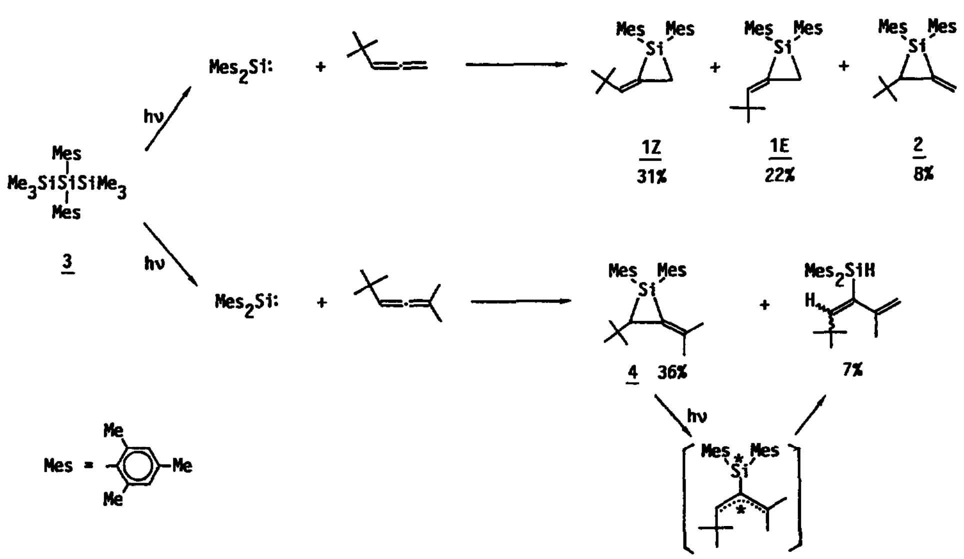
In the rapidly advancing field of silirane (silacyclopropane) chemistry, a topic of current interest is the reactivity of Si-C bond toward nucleophile.[1] The first isolation of a silirane was reported by Seyferth, who prepared 7-siladispiro[2.0.2.1]heptane from the magnesium-induced closure of α,α′-dibromosilane.[2a,e] These siliranes showed high reactivity toward atmospheric oxygen and a wide variety of nucleophiles.[2c,d] The reaction of silylene with olefin also gave silirane as an intermediate which easily reacted with methanol.[3] Ishikawa and Kumada reported that photolysis of tris(trimethylsilyl)phenylsilane in the presence of olefins afforded corresponding siliranes which were distilled under reduced pressure and detected spectroscopically.[3c] However, these siliranes were photochemically unstable to undergo rearrangement. Recently kinetically stable siliranes were isolated by protection with bulky substituents, however, there was no investigation of their reactivity.[4] Silirane with exocyclic π-bond has not been studied in detail for its isolation and characterization, although it is attractive in view of its higher strain than that of siliranes composed of two sp^3 carbons.

Methylenecyclopropane was known to have an extra strain than cyclopropane by 11 kcal/mol in calculation[5] and 13 kcal/mol in experiment.[6] We previously reported that dimesitylsilylene reacted with allene derivatives to give isolable alkylidenesiliranes.[7] Here, we wish to report the novel reactivity of alkylidenesiliranes toward various nucleophiles including palladium catalyzed ring expansion reaction.

Results and Discussion

Syntheses of Alkylidenesiliranes. Alkylidenesiliranes were prepared by a photolysis of 2,2-dimesitylhexamethyltrisilane(3) in the presence of allene derivatives (Scheme 1).

Scheme 1



Three kinds of alkylidenesiliranes: **1Z**, its E-stereoisomer (**1E**), and another structural isomer (**2**), were obtained in a reaction with tert-butylallene, and **1Z** was purified by recrystallization from hexane. **1Z**, **1E** and **2** were stable in air and in thermal conditions below 80 °C for at least one day, which is surprising in consideration of the extra strain by alkylidene substitution on inherently unstable silirane. This high stability arose from the protection by the bulky substituents.[4] It is noteworthy that a more crowded Z-stereoisomer was obtained as a main product. In a photochemical conditions, these siliranes were not stable, and the rate of decomposition of each alkylidenesilirane was in the following order, **2** >**1E** >**1Z**; photoisomerization among **1Z**, **1E** and **2**, however, was not observed. The above instability toward photolysis affects the yield of each alkylidenesilirane in the reaction of dimesitylsilylene with allene.

Photolysis of **3** in the presence of tert-butyldimethylallene gave single alkylidenesilirane **4** along with 3-silyl-1,3-hexadiene. Although **4** was found to be thermally stable enough to stand for GLC separation (200°C) and inert to methanol, it was photochemically sensitive to the latter product. In fact, photolysis of isolated **4** gave 3-silyl-1,3-hexadiene in 42% yield, which can be understood in terms of the intermediacy of silatrimethylenemethane; however, tautomerization to another alkylidenesilirane via such intermediate, which was general in carbon and hetero analogue,[8a-c,e] was not observed under our conditions.

X-Ray Crystal Analysis for 1Z. The structure of **1Z** was verified by X-ray crystal analysis. A stereoscopic view with the numbering scheme and bond distances and angles for **1Z** are given in Figure 1 and Table 1, respectively.

Table 1. Selected Bond Distances(Å) and Angles(Deg.) for 1Z

Bond Distances

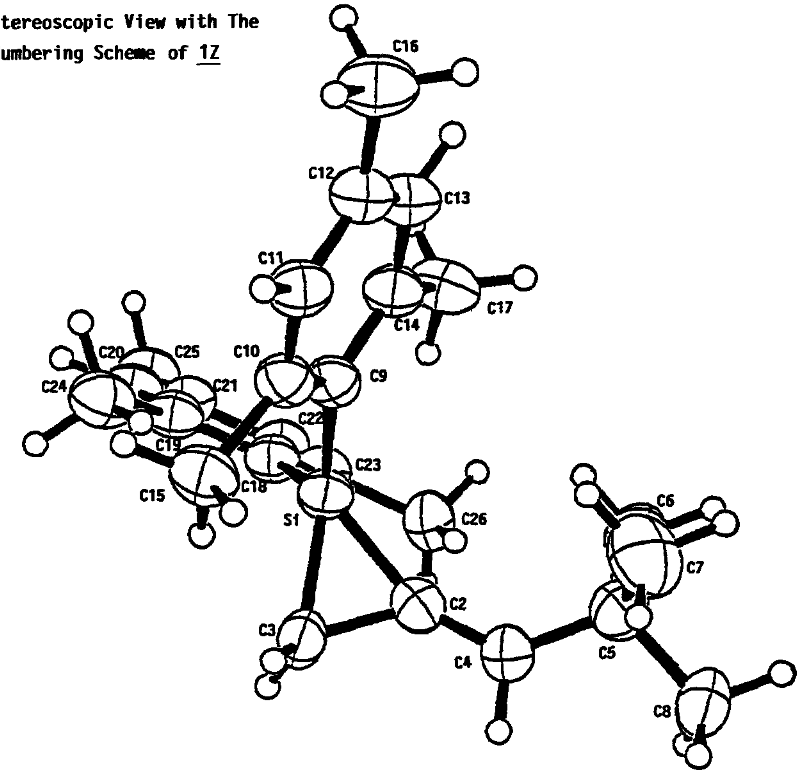
Si-C2	1.836(7)	C2-C3	1.516(11)
Si-C3	1.859(8)	C2-C4	1.310(11)
Si-C9	1.882(7)	C4-C5	1.507(13)
Si-C18	1.893(7)		

Bond Angles

C2-Si-C3	48.4(3)	Si-C3-C2	65.0(4)
C2-Si-C9	115.4(3)	Si-C2-C3	66.6(4)
C2-Si-C18	124.3(3)	Si-C2-C4	156.4(6)
C3-Si-C9	125.0(3)	C3-C2-C4	128.8(7)
C3-Si-C18	113.7(3)	C2-C4-C5	128.3(7)
C9-Si-C18	114.7(3)		

Although comparison of bond distances with other strained organosilicon compounds can not be recommended due to the poorly refined R value, there are two noteworthy structural features of **1Z** due to the introduction of Z-neopentylidene substituent: (a) the Si-C2 bond was slightly shorter than the Si-C3 bond and the bond angle ∠Si-C2-C3 was more extended than ∠ Si-C3-C2 similar to the methylenecyclopropane system; and (b) the bond angle ∠Si-C2-C4 was greatly extended to 156° in comparison with ∠ C3-C2-C4 at 129°. Result (b) strongly indicates that there is a steric repulsion between the tert-butyl group and the two mesityl groups, which probably causes a similar strain on the Si-C2 bond to Si-C3 bond. This abnormal strain was demonstrated in the following reactions.

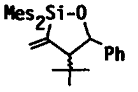
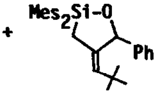
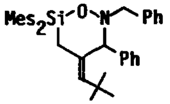
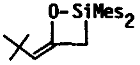
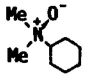
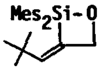
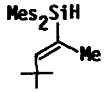
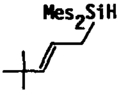
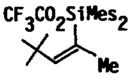
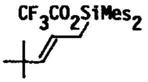
Figure 1. Stereoscopic View with The Numbering Scheme of 1Z



Reaction of Alkylidenesiliranes with Nucleophiles. Silirane was known to react with nucleophiles smoothly by a Si-C bond cleavage. **1Z** was also found to react with certain nucleophiles, and the results are listed in Table 2. **1Z** showed high reactivity toward oxygen-containing nucleophiles, and reactions with oxygen-transferable reagents gave the attractive product 1,2-oxasiletane whereas nitrone did not. Because of the high kinetic stability of **1Z** by steric protection, nucleophilic reagents were limited; therefore, ketones (acetophenone or mesityl oxide) and bulky alcohols (ethanol or *tert*-butyl alcohol) did not react, and the reaction with aliphatic aldehyde (propanal or 2-methylpropanal) afforded a complex mixture.

These reactions were initiated by nucleophilic attack on a silicon atom, but subsequent Si-C bond cleavage occurred on both bonds. The Si-C2 bond cleavage was unexpected, because methylenecyclopropane and its hetero

Table 2. Reactions of 1Z with Nucleophiles

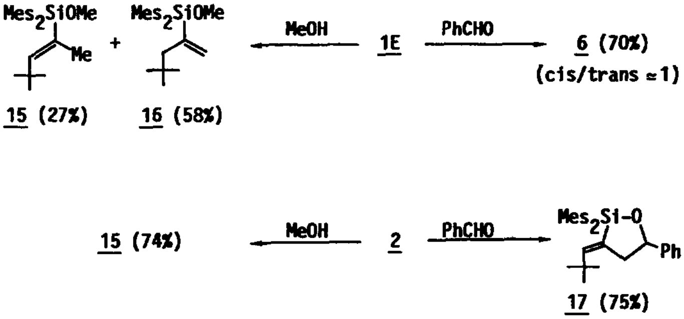
Run	Nucleophile	Conditions[a]	Products (Yields)
1	MeOH	r.t./ 12 h	$tBuCH{=}CHCH_2Si(OMe)Mes_2$ 5 (quant.)
2	PhCHO	r.t./ 18 h	 6 (40) (cis>95%) +  7 (30)
3	$PhCH{=}N(O)CH_2Ph$	80 °C/ 16 h	 8 (83)
4	Ph_2SO	80 °C/ 20 h	 9 (70)
5		80 °C/ 1 h	 10 (40)
6	$LiAlH_4$	r.t./ 2 h/ THF	 11 (20) +  12 (14)
7	CF_3CO_2H	r.t./ 5 min	 13 (40) +  14 (40)

a) Reaction was carried out under inert atmosphere in benzene unless otherwise noted.

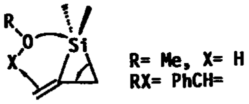
analogue have not previously been known to undergo such bond cleavage in their reaction with nucleophiles.[8a-d] This fission of 1Z can be explained by the results of X-ray study. The selectivity toward bond cleavage might depend on the nature of the nucleophile; it is especially interesting that the formation of 1,2-oxasiletanes (runs 4 and 5) was regiospecific depending on the oxidants.[9] It was noteworthy that in the reaction with benzaldehyde π-bond migration occurred and that with $LiAlH_4$ E-stereo product **11** was obtained, which implies that allyl intermediate may exist. Trifluoroacetic acid was known to undergo protodesilylation with allylsilanes; indeed, in the reaction with **1Z**, protonation on exomethylene with π-bond migration had been predicted.[3b] The formation of **13** with stereoretention, however, indicates that nucleophilic attack onto silicon is more significant than protonation, despite decreasing nucleophilicity in trifluoroacetic acid.

To investigate the inherent nature of alkylidenesilirane which has no additional strain as shown in **1Z**, **1E** and **2** were reacted with methanol and benzaldehyde (Scheme 2).

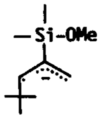
Scheme 2



All products in these reactions were the results of Si-C3 bond cleavage, which seems to be usual fission in consideration of the strain by alkylidene substitution. However, it should be noted that π-bond migrated products were preferentially obtained, which was also observed in the reaction of **1Z** with benzaldehyde. These results suggest that when alkylidenesilirane undergoes ring opening reaction, the six electron participating transition state such as **A** may be favorable and that it proceeds via a concerted mechanism. The concerted syn ring opening of silirane by methanol was demonstrated by Jones.[10] Although Seyferth speculated that hexamethylsilirane reacts with carbonyl compound in a stepwise mechanism via diradical intermediate,[11] concerted ring expansion reaction of alkylidenesilirane with benzaldehyde was supported by the selective formation of more sterically hindered cis-**6** from **1Z**. For this stereoselective reaction, it may be reasonable that **1Z** and benzaldehyde form only one conformation in a transient state **A** to go to cis-**6**. If the reaction of **1E** with benzaldehyde proceeded in same concerted mechanism as in **1Z**, trans-**6** should be formed stereoselectively via similar conformation. However, the reaction of **1E** to **6** resulted in lack of the stereoselectivity, consequently, the definitive conformation in the concerted reaction of alkylidenesilirane with benzaldehyde could not be suggested. In the case of **1E**, the reaction might partially involve a different mechanism via an intermediate such as **B**, because π-bond unmigrated product was obtained from the reaction with methanol, and the lack of stereoselective formation of oxasilacyclopentane **6** may be explained in terms of the diradical stepwise mechanism.



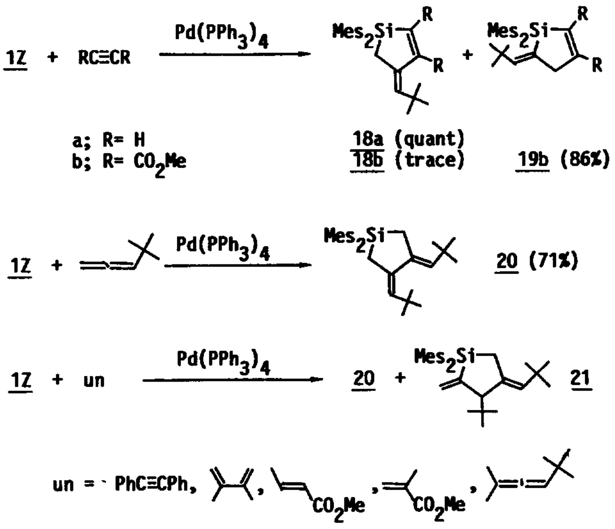
A



B

Although hexamethylsilirane easily underwent ring expansion reactions with not only carbonyl compounds but also olefins and acetylenes,[12] **1Z** was found to be inert toward C-C unsaturated compounds under thermal or photochemical conditions. However, **1Z** could react with acetylenes and tert-butylallene in the presence of a palladium catalyst to give ring expansion products (Scheme 3).[13]

Scheme 3



In the reaction with acetylenedicarboxylate, the insertion occurred at both of the Si-C bonds and its regioselectivity was varied according to the nature of the catalyst ($Pd(PPh_3)_4$, $PdCl_2L_2$: L= PPh_3, PEt_3, and PhCN); in going to the latter catalyst Si-C2 bond insertion was preferable. For other cases, insertion occurred exclusively on the more strained Si-C2 bond. In the reaction with slightly electron rich π-compounds, elimination of *tert*-butylallene occurred to afford adducts of **1Z**.

Experimental

^1H-, ^{13}C-, and ^{29}Si-NMR spectra were recorded on a JEOL JNM-PMX-60SI, a JEOL FX-100, a JEOL FX-90Q, and a Bruker AM-500 spectrometer. Chemical shifts were shown in parts per million (ppm) relative to internal or external tetramethylsilane as 0 ppm. IR and mass spectra were obtained on a Hitachi 260-50 and a Hitachi RMU-6M spectrometer, respectively. Elemental analyses were determined by our own analysis group. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-D300 mass spectrometer. Preparative HPLC was carried out on a LC-08 (Japan Analytical Ind. Co., LTD.). Preparative gas chromatographic separations were carried out on an Ohkura Model-802 using a 8 mm x 1 m glass column of 10% SF-96 on 60-80 mesh Celite 545. ^1H-NMR NOE spectra were observed on the JEOL FX-100. All melting points were uncorrected.

Materials 2,2-Dimesitylhexamethyltrisilane (**3**),[14] 4,4-dimethyl-1,2-pentadiene (*tert*-butylallene), and 2,5,5-trimethyl-2,3-hexadiene (*tert*-butyldimethylallene)[15] were synthesized according to the literature procedures. Other materials were commercially available and purified before use.

Syntheses of Alkylidenesiliranes.

With *tert*-Butylallene. A cyclohexane solution of **3** (412 mg; 1.0 mmol) in the presence of exess amount of 4,4-dimethyl-1,2-pentadiene(2-3 ml), was irradiated with 80 W low pressure mercury lamp in quartz tube under argon atmosphere for 14 h. After concentrated, the reaction mixture was separated to two fractions through HPLC; the former fraction contained 1,1-dimesityl-2-*E*-neopentylidenesilirane (**1E**) in 22% yield, and the latter fraction contained 1,1-dimesityl-2-*Z*-neopentylidenesilirane (**1Z**) and 1,1-dimesityl-2-methylene-3-*tert*-butylsilirane (**2**) in a ratio of 15:4 (31% and 8% calculated yields, respectively). The ratio was determined by ^1H-NMR analysis. Pure **1Z** was obtained by recrystallization of the latter fraction from hexane or direct recrystallization of the irradiated reaction mixture in 15% yield. Crude **1E** and **2** were obtained by repeated HPLC purification of the residue of recrystallization and they were sufficient for a chemical reaction. **1Z**: Colorless crystals; m.p. 116-118 °C; ^1H-NMR ($CDCl_3$) δ 1.03(s,9H), 1.52(d,2H; J= 2.6 Hz), 2.24(s,6H), 2.46(s,12H), 6.46(t,1H; J= 2.6 Hz), 6.78(s,4H) ; ^{13}C-NMR ($CDCl_3$) δ 16.43(t), 21.15(q), 23.75(q), 29.65(q), 35.29(s), 128.41(d), 129.22(s), 139.30(s), 144.56(s), 148.43(d) ; ^{29}Si-NMR (C_6D_6) δ -77.76; Mass m/e 362 (M^+), 347 (M^+-Me) ; Elemental analysis, Calcd for $C_{25}H_{34}Si$: C; 82.80, H; 9.45, Found: C; 82.62, H; 9.53. **1E**: Colorless oil; ^1H-NMR (CCl_4) δ 1.15(s,9H), 1.69(d,2H; J= 3.0 Hz), 2.25(s,6H), 2.53(s,12H), 6.52(t,1H; J= 3.0 Hz), 6.85(s,4H) ; ^{13}C-NMR (C_6D_6) δ 15.01(t), 21.51(q), 24.66(q), 30.56(q), 37.28(s), 129.27(d), 133.38(s), 139.99(s), 145.84(s), 147.42(d) ; ^{29}Si-NMR (C_6D_6) δ -97.64 ; Mass m/e 362 (M^+). **2**: Colorless oil; ^1H-NMR (CCl_4) δ 0.95(s,9H), 1.81(brt,1H; J= 3.6 Hz), 2.24(s,12H), 2.58(s,6H), 6.24(brd,2H; J= 3.6 Hz), 6.69(s,4H) ; ^{13}C-NMR (C_6D_6) δ 21.07(q), 24.00(q), 24.81(q), 30.93(q), 34.73(s), 42.47(d), 121.51(t), 128.83(d), 139.39(s), 139.77(s), 144.86(s), 145.35(s), 154.02(s) ; ^{29}Si-NMR (C_6D_6) δ -88.73 ; Mass m/e 362 (M^+). The structures of **1E** and **2** were determined by their ^1H-, ^{13}C-, ^{29}Si-NMR, and Mass spectroscopic data in good agreement as alkylidenesilirane in comparison with that of **1Z**.

With *tert*-Butyldimethylallene. A cyclohexane solution of **3** (412 mg; 1.0 mmol) with exess amount of 2,5,5-trimethyl-2,3-hexadiene was irradiated in similar method as above for 5.5h. The products were separated by preparative GLC and yields were determined by GLC with triphenylmethane as internal standard. 1,1-Dimesityl-2-isopropylidene-3-*tert*-butylsilirane(**4**): colorless oil, ^1H-NMR ($CDCl_3$) δ 1.08(s,9H), 2.06(s,3H), 2.19(s,3H), 2.38(s,6H), 2.70(s,12H), 7.01(s,4H). A ring proton was obscured in methyl or mesityl region.; ^{13}C-NMR (CDCl$_3$) δ 21.14(q), 24.01(q), 24.19(q), 24.89(q), 26.83(q), 32.00(q), 34.70(s), 41.20(d), 128.34(d), 128.58(d), 129.40(s), 134.39(s), 138.79(s), 139.03(s), 141.90(s), 144.55(s), 145.13(s); UV (Cyclohexane) λ_{max} (shoulder)= 238 nm (logε= 4.35); Mass m/e 390(M$^+$). 3-(Dimethylsilyl)-2,5,5-trimethyl-1,3-hexadiene: colorless oil; ^{1}H-NMR (CCl$_4$) δ 1.07(s,9H), 1.83(brs,1H), 2.25(s,6H), 2.30(s,12H), 4.71(brs,1H), 4.81(brs,1H), 5.28(s,1H), 5.66(s,1H), 6.77(s,4H); IR(CCl$_4$) 2130 cm^{-1}; Mass m/e 390(M$^+$).

X-Ray Crystal Analysis for 1Z. The crystals were monoclinic, space group P2$_1$/c, with a = 15.230(5) Å, b = 23.649(7) Å, c = 12.776(5) Å, β = 92.04(3)° and D$_{calcd}$ = 1.0476 for Z = 8. The size of the crystal used for data collection was approximately 0.4x0.3x0.5 mm. The intensity data were measured on a Nicolet P3/F four circle diffractometer with graphite monochromated CuKα radiation (3°$\leq$2θ$\leq$120°). Because the intensities of five standard reflections were gradually reduced owing to crystal deterioration during data collection, following correction was made for crystal determination. I_0 = (1-N/12600)I_{0N} : I_{0N}; Observed intensity N; The number of measuring order. 6239 unique reflections measured of which 3745 has intensities greater than 3σ|F$_0$|, and were used for structure analysis. The structure was refined to an R value of 0.114.[16]

Reaction of Alkylidenesiliranes with Nucleophiles: General Procedure. In an NMR tube, to a benzene-d^6 solution of **1Z**, **1E**, or **2** and hexamethylcyclotrisiloxane as internal standard, in almost cases, three equivalents of nucleophile was added. After the reaction was completed, the yields were determined by ^{1}H- NMR. The products were separated on HPLC or preparative GLC. This procedure was performed on following reactions unless otherwise noted. Same products were obtained in similar yields by large scale performance in a flask.

Reaction of 1Z with Methanol. **1Z** (36 mg; 0.1 mmol) was reacted with methanol at r.t. for 12 h, to give 1-(dimesitylmethoxysilyl)-4,4-dimethyl-2-pentene (**5**) in quantitatively as colorless oil: ^{1}H-NMR (CCl$_4$) δ 0.80(s,9H), 2.04(dd,2H; J= 1.8 and 4.2 Hz), 2.21(s,18H), 3.30(s,3H), 5.06(m,2H), 6.62(s,4H) ; ^{13}C-NMR (CDCl$_3$) δ 20.96(q), 23.60(q), 25.36(t), 29.53(q), 32.82(s), 49.67(q), 119.30(d), 128.87(d), 131.75(s), 138.56(s), 141.67(d), 143.73(s), ; Mass m/e 394(M$^+$), 297([Mes$_2$SiOMe]$^+$); Elemental analysis, Calcd for $C_{26}H_{38}OSi$: C;79.12, H;9.70, Found: C;79.38, H;9.81 .

Reaction of 1E with Methanol. **1E** (36 mg; 0.1 mmol) was reacted at r.t. for 8 h, to give two kinds of adducts; 2-(dimesitylmethoxysilyl)-4,4-dimethyl-*E*-2-pentene (**15**) and 2-(dimesitylmethoxysilyl)-4,4-dimethyl-1-pentene (**16**) in 27 and 58% yields, respectively, after the separation by preparative GLC. **15:** Colorless oil; ^{1}H-NMR (CCl$_4$) δ 1.10(s,9H), 1.94(d,3H; J= 1.5 Hz), 2.24(s,18H), 3.40(s,3H), 5.90(q,1H; J= 1.5 Hz), 6.78(s,4H) ; ^{13}C-NMR (CDCl$_3$) δ 16.20(q), 21.08(q), 29.59(q), 30.18(q), 34.52(s), 51.43(q), 129.93(d), 131.69(s), 134.56(s), 138.50(s), 144.48(s), 151.65(d) ; Mass m/e 337(M$^+$-*tert*-Bu), 297([Mes$_2$SiOMe]$^+$). Stereochemistry was determined by ^{1}H-NMR NOE observation. **16:** Colorless oil; ^{1}H- NMR (CCl$_4$) δ 0.92(s,9H), 2.24(s,18H), 3.39(s,3H), 5.65(d,1H; J= 2.4 Hz), 5.82(d,1H; J= 2.4 Hz), 6.83(s, 4H) ; Mass m/e 362(M$^+$-MeOH), 337(M$^+$-*tert*-Bu), 297([Mes$_2$SiOMe]$^+$).

Reaction of 2 with Methanol. **2** (32 mg; 0.09 mmol) was heated with methanol at 70 °C for 7 h to give **15** in 74% conversion yield along with 31% of remained **2**. **15** was separated by preparative GLC.

Reaction of 1Z with Benzaldehyde. In a 5 ml of round bottomed flask, to a benzene solution of **1Z** (72 mg; 0.2 mmol), three equivalents of benzaldehyde was added through syringe under nitrogen atmosphere and the mixture was stirred at r.t. for 18 h to give **6** and **7** in 40 and 30% yields, respectively, after the separation on HPLC. The ratio of *cis* and *trans*-**6** was determined by ^{1}H-NMR. *cis*-**6** was purified by recrystallization from hexane, and its stereochemistry was shown by X-ray studies in reference 7. The spectroscopic data were as follow. 3,4-*cis*-4-*tert*-Butyl-2,2-dimesityl-3-methylene-5-phenyl-1-oxa-2-silacyclopentane (*cis*-**6**): colorless crystals; m.p. 165-166.5 °C; ^{1}H-NMR (CCl$_4$) δ 0.69(s,9H), 2.17(s,3H), 2.20(s,3H), 2.37(s,6H), 2.47(s,6H), 2.83(d,1H; J= 6.0 Hz), 5.24(d,1H; J= 6.0 Hz), 5.95(s,2H), 6.61(s,2H), 6.67(s,2H), 7.0-7.5(m,5H) ; ^{13}C- NMR ($CDCl_3$) δ 20.99(q), 21.08(q), 22.66(q), 23.31(q), 29.41(q), 33.29(s), 62.82(d), 80.37(d), 127.05(d), 127.58(d), 127.99(d), 128.93(d), 129.10(d), 130.86(s), 132.51(t), 138.91(s), 139.03(s), 142.02(s), 143.55(s), 143.90(s), 154.06(s) ; Elemental analysis, Calcd for $C_{32}H_{40}OSi$: C;81.99, H;8.60, Found: C;81.82, H;8.62. 3,4-trans-Isomer (trans-**6**): ^{1}H-NMR ($CDCl_3$) δ 0.85(s,9H), 2.18(s,6H), 2.21(s,6H), 2.43(s,6H), 2.84(d,1H; J= 5.4 Hz), 4.97(d,1H; J= 5.4 Hz), 5.88(d,1H; J= 2.4 Hz), 5.98(d,1H; J= 2.4 HZ), 6.62(s,2H), 6.77(s,2H). 2,2-Dimesityl-4-Z-neopentylidene-5-phenyl-1-oxa-2-silacyclopentane (**7**): colorless oil; ^{1}H- NMR ($CDCl_3$) δ 1.07(s,9H), 2.21(s,3H), 2.23(s,6H), 2.24(s,3H), 2.43(s,6H), 5.45(s,1H), 6.23(s,1H), 6.69(s,2H), 6.76(s,2H), 7.2-7.4(m,5H) ; Mass m/e 468 (M^+). The stereochemistry was determined by ^{1}H-NMR NOE observation.

Reaction of 1E with Benzaldehyde. **1E** (52 mg; 0.14 mmol) was reacted with benzaldehyde in the general procedure at r.t. for 20 h to give stereoisomeric mixture of **6** in a ratio of 1:1 in 70% yield, after the separation on HPLC. The ratio was determined by ^{1}H-NMR.

Reaction of 2 with Benzaldehyde. **2** (50 mg; 0.14 mmol) was heated with benzaldehyde at 60 °C for 12 h to give 2,2-dimesityl-3-E-neopentylidene-5-phenyl-1-oxa-2-silacyclopentane (**17**) in 75% yield, after the separation on HPLC. **17**: Colorless oil; ^{1}H-NMR ($CDCl_3$) δ 1.13(s,9H), 2.27(s,6H), 2.34(s,6H), 2.39(s,6H), 2.43(ddd,1H; J= 2.6, 10.3, and 15.6 Hz), 3.46(ddd,1H; J= 1.7, 5.1, and 15.6 Hz), 5.07(dd,1H; J= 5.1 and 10.3 Hz), 6.01(dd,1H; J= 1.7 and 2.6 Hz), 6.79(s,4H), 7.2-7.3(m,5H) ; HRMS m/e Calcd for $C_{32}H_{40}OSi$: 468.2848, Found: 468.2873. The stereochemistry was determined by ^{1}H-NMR NOE observation.

Reaction of 1Z with N-Benzylphenylimine N-Oxide. **1Z** (40 mg; 0.11 mmol) was reacted with nitrone (25 mg; 0.12 mmol) in o-dichlorobenzene at 80 °C for 16 h to give 2-benzyl-6,6-dimesityl-4-E-neopentylidene-3-phenyl-1-oxa-2-aza-6-silacyclohexane (**8**) in 83% yield after the separation by HPLC. **8**: White crystals, m.p.= 122-129 °C; ^{1}H-NMR ($CDCl_3$) δ 0.94(s,9H), 1.78(d,1H; J= 13.8 Hz), 2.18(s,12H), 2.32(s,6H), 3.11(d,1H; J= 13.8 Hz), 3.70 (q_{AB}, 2H;J_{AB}= 13.8 Hz, $\Delta\nu_{AB}$= 22.2 Hz), 4.89(s,1H), 5.04(s,1H), 6.49(s,2H), 6.63(s,2H), 6.7-6.8(m,4H), 7.1-7.6(m,6H); ^{13}C-NMR ($CDCl_3$) δ 21.00(q), 23.64(q), 29.31(t), 31.36(q), 33.52(s), 61.19(t), 69.85(d), 126.25(d), 127.30(d), 127.42(d), 129.36(d), 128.65(d), 128.82(d), 129.00(d), 132.39(s), 132.57(s), 134.32(s), 136.60(d), 137.25(s), 138.36(s), 143.68(s), 143.92(s); IR (NaCl) 1140 cm^{-1}(-O-N<); Mass m/e 573(M^+); Elemental analysis, Calcd for $C_{39}H_{47}ONSi$: C;81.62, H;8.26, N;2.44, Found: C;81.86, H;8.29, N;2.27. The stereochemistry was determined by ^{1}H-NMR NOE observation.

Reaction 1Z with Diphenyl Sulfoxide. **1Z** (30 mg; 0.083 mmol) was heated with diphenyl sulfoxide (24 mg; 0.12 mmol) in benzene-d_6 in an NMR tube at 80 °C for 20 h to give 2,2-dimesityl-4-Z-neopentylidene-1,2-oxasiletane (**9**) in 70% yield. **9**: ^{1}H-NMR (C_6D_6) δ 1.32(s,9H), 2.05(s,6H), 2.41(s,12H), 2.66(d,2H; J= 1.8 Hz), 4.32(t,1H; J= 1.8 Hz), 6.60(s,4H); ^{13}C-NMR (C_6D_6) δ 21.52(q), 23.50(q), 28.77(t), 31.70(q), 32.28(s), 112.52(d), 129.80(d), 136.82(s), 140.80(s), 144.61(s), 151.22(s); IR (NaCl) 1675 cm^{-1}(Si-O-C=C); Mass m/e 378(M^+), 363(M^+-Me). The stereochemistry was determined by ^{1}H-NMR NOE observation.

Reaction of 1Z with Cyclohexyldimethylamine N-Oxide. A benzene solution of **1Z** (80 mg; 0.22 mmol) was heated with amine N-oxide (100 mg; 0.70 mmol) at 80 °C under argon atmosphere for 1 h, 2,2-dimesityl-3-Z-neopentylidene-1,2-oxasiletane (**10**) was obtained in 40% yield after the separation by silica gel followed by HPLC. **10**: Colorless oil; ^{1}H-NMR (CCl_4) δ 0.93(s,9H), 2.23,2.31(2s,18H), 4.77(d,2H; J= 2.0 Hz), 5.83(t,1H; J= 2.0 Hz), 6.68(s,4H); ^{13}C-NMR (C_6D_6) δ 21.13(q), 23.67(q), 28.93(q), 34.67(s), 74.49(t), 129.53(d), 133.27(s), 139.99(s), 143.83(s), 145.62(d), 149.90(s); HRMS m/e Calcd for $C_{25}H_{34}OSi$: 378.2379, Found: 378.2411. The stereochemistry was determined by ^{1}H-NMR NOE observation.

Reaction of 1Z with $LiAlH_4$. To a THF suspension of $LiAlH_4$ (15 mg; 0.40 mmol) was added a benzene solution of **1Z** (29 mg; 0.08 mmol) at r.t. under nitrogen atmosphere. The mixture was stirred at r.t. for 2 h and subjected in preparative GLC to give 2-(dimesitylsilyl)-4,4-dimethyl-2-E-pentene (**11**) and 1-(dimesitylsilyl)-4,4-dimethyl-2-E-pentene (**12**) in 20 and 14% yields, respectively. The yields were determined by GLC with n-eicosane as internal standard. **11**: Colorless oil; ^{1}H- NMR (CCl_4) δ1.09(s,9H), 1.91(d,3H; J= 1.8 Hz), 2.22(s,18H), 5.09(s,1H), 5.71(q,1H; J= 1.8 Hz), 6.63(s,4H) ; IR (NaCl) 2120 cm^{-1} (Si-H) ; HRMS m/e Calcd for $C_{25}H_{36}Si$: 364.2585, Found: 364.2572. **12**: Colorless oil; ^{1}H-NMR ($CDCl_3$) δ 0.87(s,9H), 2.13(dd,2H; J= 4.8 and 5.5 Hz), 2.24(s,6H), 2.32(s,12H), 5.12(t,1H; J= 4.8 Hz), 5.26(t,1H; J= 5.5 Hz), 5.26(s,1H), 6.77(s,4H) ; IR (NaCl) 2130 cm^{-1} (Si-H) ; HRMS m/e Calcd for $C_{25}H_{36}Si$: 364.2585, Found: 364.2610. The stereochemistry of **11** and **12** were determined by ^{1}H-NMR NOE observation.

Reaction of 1Z with Trifluoroacetic acid. In the general procedure, **1Z** (36 mg; 0.10 mmol) was reacted with trifluoroacetic acid (11.3 mg; 0.099mmol) at r.t. for 5 min to afford 1:1 mixture of **13** and **14** in 80% yield after the HPLC separation. These isomers were separated by preparative GLC. 2-(Dimesityltrifluoroacetoxysilyl)-4,4-dimethyl-2-Z-pentene (**13**): colorless oil; ^{1}H-NMR (CCl_4) δ 0.88(s,9H), 2.02(d,3H; J= 1.8 Hz), 2.26(s,18H), 6.20(q,1H; J=1.8 Hz), 6.69(s,4H) ; IR (NaCl) 1760 cm^{-1} (C=O) ; HRMS m/e Calcd for $C_{27}H_{35}O_2SiF_3$: 476.2357, Found: 476.2357. The sterechemistry was determined by ^{1}H-NMR NOE observation. 1-(Dimesityltrifluoroacetoxysilyl)-4,4-dimethyl-2-E-pentene (**14**): colorless oil; ^{1}H- NMR ($CDCl_3$) δ 0.88(s,9H), 2.25(s,6H), 2.30(2,12H), 2.45(d,2H; J= 7.3 Hz), 5.06(dt,1H; J= 7.3 and 15.5 Hz), 5.34(d,1H; J= 15.5 Hz), 6.78(s,4H) ; ^{13}C-NMR ($CDCl_3$) δ 21.07(q), 23.57(q), 25.19(t), 29.42(q), 30.01(s), 117.18(d), 129.53(d), 140.20(s), 143.67(s), 143.94(d), 144.70(s) ; IR (NaCl) 1760 cm^{-1} (C=O) The stereochemistry was assumed from the J value (15.5 Hz).

Reaction of 1Z with Propanal or 2-Methylpropanal. In an NMR tube, **1Z** (36 mg; 0.1 mmol) was reacted with aldehyde at r.t. for 70 h. Both of aldehydes afforded a complex mixture and the separation by routine method was not be successful.

Attempted Reaction of 1Z with Acrolein, Mesityl Oxide, or Acetophenone. In the general procedure, no reaction had occurred in spite of heating at 70 °C for 20 h, in each case.

Pd-Catalyzed Reaction of 1Z: General Procedure. To a benzene or toluene solution of **1Z** (72 mg; 0.20 mmol) and 5-10 mol% of Pd catalyst, unsaturated compound was added and heated at 80 °C for 0.5-40 h. The reaction was monitored by TLC. The separation by preparative TLC gave products. 1,1-Dimesityl-4-E-neopentylidene-1-silacyclopent-2-ene (**18a**): white crystals m.p.= 91-93 °C; ^{1}H-NMR ($CDCl_3$) δ 1.14(s,9H), 2.14(d,2H; J= 1.2 Hz), 2.21(s,6H), 2.28(s,12H), 5.54(dd,1H; J= 1.2 and 1.8 Hz), 6.51(dd,1H; J= 1.8 and 10.2 Hz), 6.71(s,4H), 7.60(d,1H; J= 10.2 Hz); ^{13}C-NMR ($CDCl_3$) δ21.00(q), 23.81(q), 26.50(t), 32.00(q), 33.41(s), 128.82(d), 133.44(s), 137.19(d), 137.48(d), 138.53(s), 138.83(s), 143.51(s), 146.78(d); Mass m/e 388(M^+); Elemental analysis, Calcd for $C_{27}H_{36}Si$: C;83.44, H;9.34, Found: C;83.61, H;9.46. The stereochemistry was determined by ^{1}H-NMR NOE observation. Characterization for **18b** and **19b** were described in reference 13. 3-E-4-Z-Bis(neopentylidene)-1-silacyclopentane (**20**): white crystals m.p.= 146-147.5 °C; ^{1}H-NMR ($CDCl_3$) δ 1.09(s,9H), 1.12(s,9H), 2.12(d,2H; J= 1.5 Hz), 2.23(s,6H), 2.31(s,12H), 2.41(brs,2H), 5.16(brs,1H), 5.51(t,1H; J= 1.5 Hz), 6.74(s,4H); ^{13}C-NMR ($CDCl_3$) δ 20.97(q), 23.95(q), 24.27(t), 29.69(t), 31.00(q), 31.69(q), 33.32(s), 33.64(s), 128.83(d), 134.14(d), 134.62(s), 136.09(s), 136.30(d), 138.42(s), 142.42(s), 143.29(s); Mass m/e 458(M^+); Elemental analysis Calcd for $C_{32}H_{46}Si$: C;83.77, H;10.11, Found: C;83.96, H;10.34. 3-tert-Butyl-2-methylene-4-Z-neopentylidene-1-silacyclopentane (**21**): colorless oil; ^{1}H-NMR ($CDCl_3$) δ 0.86(s,9H), 1.03(s,9H), 2.16(s,6H), 2.21(s,3H), 2.24(s,3H), 2.40(s,6H), 2.82(brs,1H), 5.25(d,1H; J= 3.0 Hz), 5.71(dd,1H; J= 3.0 and 1.5 Hz), 5.90(d,1H; J= 1.5 Hz), 6.72(s,2H), 6.77(s,2H); ^{13}C-NMR ($CDCl_3$) δ 21.57(q), 21.72(q), 25.18(q), 25.48(q), 25.98(t), 30.01(q), 31.69(q), 33.77(s), 35.54(s), 70.72(d), 129.52(d), 129.77(d), 131.50(t), 133.11(s), 136.46(s), 138.22(d), 138.82(s), 139.01(s), 139.09(s), 143.98(s), 145.49(s), 155.72(s); HRMS m/e Calcd for $C_{32}H_{46}Si$: 458.3368, Found: 458.3383. The stereochemistry was determined by ^{1}H-NMR NOE observation.

Acknowledgment. We thank Shin-etsu Chemical Co., Ltd. for a gift of organochlorosilanes. This work was supported by a Grant-in-Aid for Special Project Research (No. 62115003) from the Ministry of Education, Science, and Culture of Japan.

References

(1) (a) T. J. Barton, "Carbacyclic Silanes" in Comprehensive Organometallic Chemistry, Pergamon, New York, 1982, vol. 2, pp 206-226. and references cited therein. (b) S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, and J. F. Blount, J. Am. Chem. Soc., 104, 1150-1153 (1982). (c) S. Masamune, S. Murakami, H. Tobita, and D. J. Williams, J. Am. Chem. Soc., 105, 7776-7778 (1983). (d) W. Ando, A. Sekiguchi, and Y. Hamada, Tetrahedron Lett., 23, 5323-5326 (1982).

(2) (a) R. L. Lambert, Jr. and D. Seyferth, J. Am. Chem. Soc., 94, 9246-9248 (1972). (b) D. Seyferth and D. C. Annarelli, J. Am. Chem. Soc., 97, 2273-2275 (1975). (c) D. Seyferth, J. Organomet. Chem., 100, 237-256 (1975). (d) D. Seyferth, C. K. Haas, R. L. Lambert, Jr., and D. C. Annarelli, J. Organomet. Chem., 152, 131-154 (1978). (e) G. L. Delker, Y. Wang, G. D. Stucky, R. L. Lambert, Jr., C. K. Haas, and D. Seyferth, J. Am. Chem. Soc., 98, 1779-1784 (1976).

(3) (a) M. Ishikawa and M. Kumada, J. Organomet. Chem., 81, C3-C6 (1974). (b) M. Ishikawa, K. Nakagawa, M. Ishiguro, F. Ohi, and M. Kumada, J. Organomet. Chem., 152, 155-174 (1978). (c) M. Ishikawa, K. Nakagawa, and M. Kumada, J. Organomet. Chem., 178, 105-118 (1979). (d) D. Seyferth and D. C. Annarelli, J. Organomet. Chem., 117, C51-C54 (1976). (e) R-. J. Hwang, R. T. Conlin, and P. P. Gasper, J. Organomet. Chem., 94, C38-C42 (1975). (f) V. T. Tortorelli, M. Jones, Jr., S-. H. Wu, and Z-. H. Li, Organometallics, 2, 759-764 (1983).

(4) (a) M. Ishikawa, S. Matsuzawa, H. Sugisawa, F. Yano, S. Kamitori, and T. Higuchi, J. Am. Chem. Soc., 107, 7706-7710 (1985). (b) W. Ando, M. Fujita, H. Yoshida, and A. Sekiguchi, J. Am. Chem. Soc., 110, 3310-3311 (1988).

(5) N. C. Baird and M. J. S. Dewar, J. Am. Chem. Soc., 89, 3966-3970 (1967).

(6) K. B. Wiberg and R. A. Fenoglio, J. Am. Chem. Soc., 90, 3395-3397 (1968).

(7) W. Ando and H. Saso, Tetrahedron Lett., 27, 5625-5628 (1986).

(8) (a) P. Dowd, Acc. Chem. Res., 5, 242-248 (1972). and references cited therein. (b) N. J. Turro, Acc. Chem. Res., 2, 25-32 (1969) (c) T. H. Chan and B. S. Ong, Tetrahedron, 36, 2269-2289 (1980). (d) T. Furuhata and W. Ando, Tetrahedron, 42, 5301-5308 (1986). (e) W. Ando, A. Itami, T. Furuhata, and N. Tokitoh, Tetrahedron Lett., 28, 1787-1790 (1987).

(9) H. Saso, H. Yoshida, and W. Ando, Tetrahedron Lett., 29, 4747-4750 (1988).

(10) V. J. Tortorelli, M. Jones, Jr., S. Wu, and Z. Li, Organometallics, 2, 759-764 (1983).

(11) D. Seyferth, D. P. Duncan, and M. L. Shannon, Organometallics, 3, 579-583 (1984).

(12) D. Seyferth, D. P. Duncan, M. L. Shannon, and E. W. Goldman, Organometallics, 3, 574-578 (1984).

(13) H. Saso and W. Ando, Chem. Lett., 1988, 1567-1570.

(14) Y. Hamada, PH. D. Thesis, The University of Tsukuba (1985).

(15) L. Brandsma and H. D. Verkruijsse, Synthesis of Acetylenes, Allenes and Cumulenes, Elsevier, New York, 1981, pp157-158.

(16) The atomic co-ordinates, bond distances, and bond angles for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.