by the Canadian Microanalytical Service, Vancouver, Canada, and the ^{1}H NMR spectra were recorded with a Bruker AM 300 spectrometer, with chemical shifts given in ppm relative to Me_4Si.

Synthesis of Complexes. $PdBrMe_2(CH_2COPh)(bpy)$. $PhCOCH_2Br$ (0.072 g, 0.36 mmol) was added to a stirred, filtered solution of $PdMe_2(bpy)$ (0.102 g, 0.35 mmol) in acetone at 0 °C (ca. 15 mL, warmed to dissolve if necessary). The yellow solution became decolorized immediately, hexane (10 mL) was added, and the solution was evaporated under reduced pressure at 0 °C to give a white crystalline solid at ca. half volume (yield 47%). The complex was washed with hexane and vacuum-dried. ^{1}H NMR ($CDCl_3$): δ 8.60 (d, ^3J = 4.7 Hz, 2, H6), 7.85 (m, 4, H3 and H4), 7.49 (m, 2 H5), 7.24 (t, 1, Ph(4)), 6.94 (m, 4, Ph(2,3,5,6)), 3.02 (s, 2, $PdCH_2$), 2.20 (s, 6, PdMe). Anal. Calcd for $C_{20}H_{21}BrN_2OPd$: C, 48.9; H, 4.3; N, 5.7. Found: C, 49.2; H, 4.3; N, 5.6.

The following complexes were obtained as pale yellow solids by using a similar procedure.

$PdBrMe_2(CH_2COPh)(phen)$: yield 46%; ^{1}H NMR ($CDCl_3$) δ 8.95 (dd, ^3J = 4.9 Hz, ^4J = 1.5 Hz, H2,9), 8.33 (dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz, H4,7), 7.82 (m, 2, H3,8), 7.75 (s, 2, H5,6), 6.87 (t(b), 1, Ph(4)), 6.65 (m, 2, Ph(3,5)), 6.54 (m, 2, Ph(2,6)), 3.12 (s, 2, $PdCH_2$), 2.35 (s, 6, PdMe). Anal. Calcd for $C_{22}H_{21}BrN_2OPd$: C, 51.2; H, 4.1; N, 5.4. Found: C, 50.6; H, 4.1; N, 5.7.

$PdBrMe_2(CH_2CO\text{-}p\text{-}C_6H_4Br)(bpy)$: yield 37%; ^{1}H NMR ($CDCl_3$) δ 8.61 (d, ^3J = 6 Hz, 2, H6), 7.92 (m, 4, H3 and H4), 7.53 (m, 2, H5), 7.05 (d, 2, Ph(3,5)) and 6.84 (d, ^3J = 8.5 Hz, 2, Ph(2,6)), 2.97 (s, 2, $PdCH_2$), 2.20 (s, 6, PdMe). Anal. Calcd for $C_{20}H_{20}Br_2N_2OPd$: C, 42.1; H, 4.2; N, 4.9. Found: C, 42.2; H, 3.6; N, 4.8.

$PdBrMe_2(CH_2CO\text{-}p\text{-}C_6H_4Br)(phen)$: yield 35%; ^{1}H NMR ($CDCl_3$) δ 8.97 (d(b), 2, H2,9), 8.38 (d(b), 2, H4,7), 7.85 (m(b), 4, H3,5,6,8), 6.58 (d, 2, Ph(3,5)) and 6.44 (d, ^3J = 8.5 Hz, 2, Ph(2,6)), 3.06 (s, 2, $PdCH_2$), 2.36 (s, 6, PdMe). Anal. Calcd for $C_{22}H_{20}Br_2N_2OPd$: C, 4.44; H, 3.4; N, 4.7. Found: C, 44.8; H, 3.5; N, 4.7.

X-ray Structure Determination. A unique data set was measured to $2\theta_{max}$ = 55° with an Enraf-Nonius CAD-4 diffractometer operating in the conventional 2θ-θ scan mode. A total of 4213 independent reflections were obtained at ca. 295 K, 2019 with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after Gaussian absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for non-hydrogen atoms; although hydrogen atoms of the methyl groups were located, all $(x, y, z, U_{iso})_H$ values were included constrained at estimated values. Residuals R and R_w on $|F|$ at convergence were 0.040 and 0.035; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were employed. Neutral-atom complex scattering factors were used;[14] computation was with the XTAL 3.0 program system implemented by Hall.[15] Crystal data and collection parameters: $PdBrMe_2(CH_2COPh)(bpy)$, $C_{20}H_{21}BrN_2OPd$, M_r = 491.7, orthorhombic, space group *Pbca*, a = 19.554 (3) Å, b = 15.007 (9) Å, c = 13.282 (4) Å, V = 3897.6 Å^3, $D_c(Z = 8)$ = 1.68 g cm^{-3}, $F(000)$ = 1952, specimen size 0.11 × 0.25 × 0.18 mm, monochromatic Mo Kα radiation, λ = 0.710 73 Å, μ = 28.9 cm^{-1}, $A^*_{min,max}$ = 1.36, 1.65.

Acknowledgment. We thank the Australian Research Council and the University of Tasmania for financial support and Johnson Matthey Ltd. for a generous loan of palladium salts.

Supplementary Material Available: Listings of thermal parameters, hydrogen atom parameters, and ligand and phenacyl geometries (3 pages). Ordering information is given on any current masthead page.

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Stable Silene Geometric Isomers

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Photolysis of the acylsilane $(Me_3Si)_2MesSiCOAd$ (**1**) at room temperature gave rise to two geometric isomers of $(Me_3Si)MesSi{=}C(OSiMe_3)Ad$ (**2a,b**) the first reported silene geometric isomers detectable and stable in solution at room temperature. Warming to 100 °C caused the slow decomposition of both isomers so that, at the end of 7 days, the minor isomer was completely decomposed while 60% of the major isomer remained. Addition of methanol to the silenes in the dark gave the pair of diastereomeric adducts **3a,b**, identical with the products of photolysis of **1** in the presence of methanol. Treatment of 1.4:1 mixtures of the silenes with phenylacetylene or (trimethylsilyl)acetylene gave rise to 1.4:1 mixtures of the anticipated silacyclobutenes **4a,b** and **5a,b**, indicating that the cycloaddition reactions were highly stereospecific. Crystal structures obtained for the major silacyclobutene derived from phenylacetylene, **4a**, and the major isomer derived from (trimethylsilyl)acetylene, **5a**, confirmed the regiochemistry and stereochemistry of their structures and indicated that the major silene isomer **2a** had *E* geometry. Silenes **2a,b** failed to react with 2,3-dimethylbutadiene or diphenylacetylene but reacted with butadiene, yielding only [2 + 2] cycloadducts **6**. Reaction of the silenes with oxygen gave the ester **8**. When the silenes **2a,b** were further photolyzed in inert solvent with ≥360 nm radiation, they were slowly converted to a complex mixture which contained the silaindanes **10a,b**. A crystal structure of the silacyclobutene adduct of the silene $(Me_3Si)_2Si{=}C(OSiMe_3)CMe_3$ with 1-phenylpropyne, **11**, indicated that the $=$CMe group of the silacyclobutene was adjacent to the ring silicon atom, consistent with the findings for **4** and **5** and contrary to a previous proposal.

The 1,3-shift of a trimethylsilyl group from silicon to oxygen during the photolysis of acylpolysilanes under mild photochemical conditions ($\lambda \geq$ 360 nm) gives rise to silenes, as is now well-established.[1-3] For acylsilanes with the

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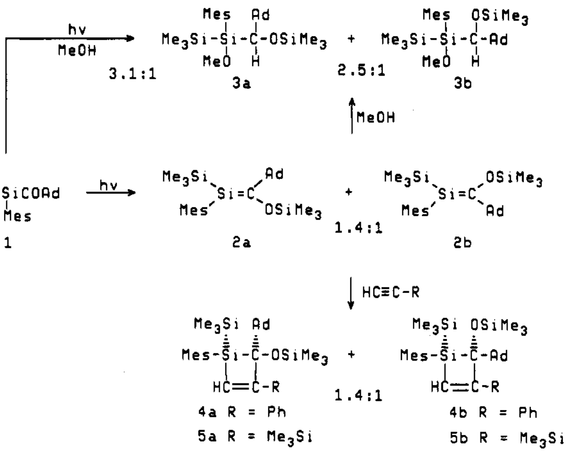
Scheme I



structure $(Me_3Si)_2RSiCOAd$ (1), where the R group is Me, Ph, or *t*-Bu, the potential for geometric isomers exists, but it was found that either the resulting silenes dimerized as rapidly as they were formed (R = Me, Ph) or else only one of the two possible geometric isomers was observed (R = *t*-Bu).[4] We have now observed that the acylsilane 1 (R = Mes), when photolyzed in deuteriobenzene, gives rise to the pair of geometric isomers **2a,b**, which have been characterized by ^1H, ^{13}C, ^{29}Si NMR spectroscopy as well as by their methanol adducts **3a,b**, their phenylacetylene adducts **4a,b**, and their (trimethylsilyl)acetylene adducts **5a,b**, as shown in Scheme I.

Numerous attempts to separate the silenes have not been successful to date, and attempts to establish the geometry of the silenes **2** using NOE techniques were inconclusive, because of multiple couplings in each isomer. However, their geometry can be inferred from the crystal structure obtained for the major phenylacetylene adduct **4a** (see below). This is the first time that stable silene geometric isomers have been reported, although they have previously been generated as transient species.[5] Stable geometric isomers from disilenes are well-known.[6]

The silenes **2a,b** are surprisingly stable. When their mixture was warmed at 65 °C for 16 h in C_6D_6, there was no change in the NMR spectra. When they were heated for 168 h in C_7D_8 at 100 °C in the presence of an NMR standard, it was observed that the initial ratio of major isomer to minor isomer to standard of 0.9:0.6:1 had changed to 0.9:0.2:1 after 24 h and to 0.8:0.08:1 after 72 h and was 0.6:0:1 after 168 h. Thus, the minor isomer thermally decomposed much more rapidly than the major isomer and there was no apparent interconversion of the gometrical isomers. Similar behavior was observed at 160 °C, when most of the minor isomer had decomposed after 40 min, and both isomers had been totally decomposed after 4 h. Attempts to isolate the major isomer from the products of decomposition are underway.

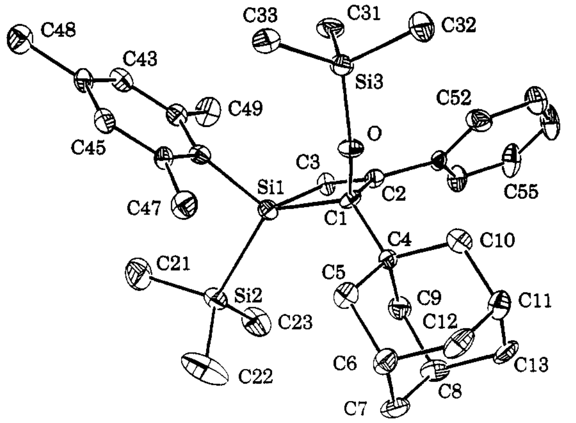


Figure 1. View of compound **4a** showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level.

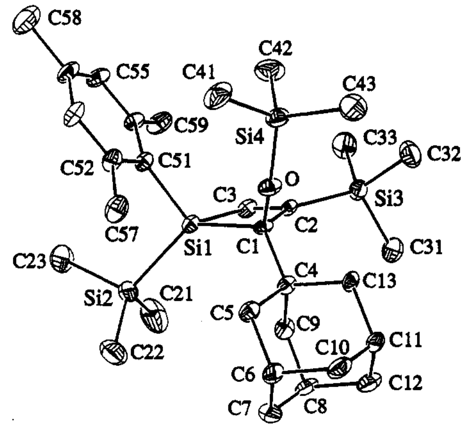


Figure 2. View of compound **5a** showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level.

When methanol was added in the dark to the 1.4:1 mixture of the preformed silenes **2a,b**, a 2.5:1 mixture of diastereomeric methanol adducts **3a,b** was formed. When 1 was photolyzed in deuteriobenzene containing methanol, a mixture of the same diastereomeric methanol adducts was obtained in varying proportions, depending on the methanol concentration: about 3:1 was typical. Since there is evidence that the addition of methanol to a single silene geometric isomer of this general structure is a nonstereospecific process which gives a mixture of isomers,[4,7] it is not possible to correlate a specific methanol adduct diastereomer with a particular silene.

However, reaction of phenylacetylene with a 1.4:1 mixture of the silenes (as established by ^1H NMR spectroscopy) gave rise to a 1.4:1 mixture of the related 1-silacyclobut-2-enes **4a,b** which could be separated and purified. A crystal structure of the major isomer **4a** was obtained, whose geometry is shown by the ORTEP diagram in Figure 1. These results not only show that the reaction of the silene with phenylacetylene is regiospecific but also indicate that the [2+2] cyclization reaction is highly stereospecific. On the assumption that the silene **2a** reacted with phenylacetylene suprafacially, the geometry of the major adduct indicates that the geometry of the major silene geometric isomer must be *E*. This had been anticipated on the basis that the preferred geometry would be that where there were minimal steric interactions between the bulky Ad and Mes groups. The silenes **2a,b** in the ratio 1.4:1 also reacted during 62-h heating at 50 °C in deuteriobenzene with (trimethylsilyl)acetylene to give a 1.4:1 mixture of two silacyclobutenes **5a,b**, which were separated by repeated liquid chromatography. A crystal structure

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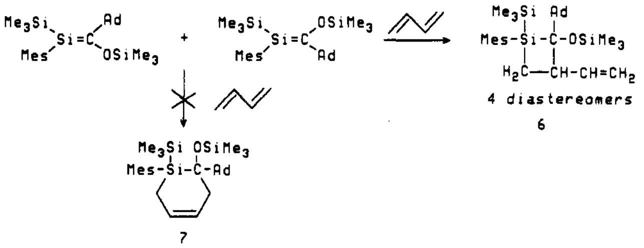
of the major isomer confirmed the *E* geometry of the parent major silene. The ORTEP diagram is shown in Figure 2.

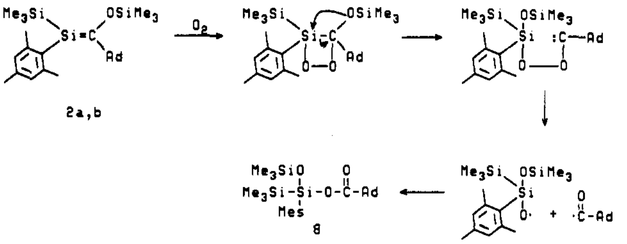
The silenes failed to react with 2,3-dimethylbutadiene over 7 h at room temperature or with heating to 50 °C for 1 h, possibly because of steric hindrance, since silenes of this general family normally react readily with this reagent.[1-3] No reaction with diphenylacetylene occurred either. In contrast, reaction with butadiene occurred at room temperature to give a mixture of four diastereomeric [2 + 2] 3-vinyl-1-silacyclobutane isomers **6** (see eq 1), on the



(1)

basis of comparison of the NMR spectra of the products with data for known related vinylsilacyclobutanes.[3] No evidence for the presence of any of the isomeric [2 + 4] adducts, the silacyclohexenes **7**, was found.

When the silenes were treated with dry air for 1 h, the ester **8** was formed in good yield. A possible mechanism for its formation involves the addition of oxygen to the silicon–carbon double bond followed by rearrangement, and homolysis of the O–O bond followed by radical recombination, as shown in eq 2.



(2)

Consistent with this proposal, when the oxidation was carried out at −78 °C, and the ^{29}Si NMR spectrum was run immediately at −70 °C, the spectrum indicated the presence both of the ester **8** and of a significant quantity (approximate ratio 1:1.5) of a new species which had three ^{29}Si NMR signals, including one at 57.5 ppm. This is the region (40–65 ppm) where the ring silicon atoms of siloxetanes and disiloxetanes (which carry an attached oxygen in a four-membered ring) are known to resonate.[8] Thus, the data are consistent with, but not proof for, the proposed siladioxetane intermediate. As the system was warmed to −30 °C, the intermediate completely isomerized to the ester **8**; thus, further characterization was not attempted.

When the silenes **2a,b** in inert solvent in the absence of any other reactant were photolyzed with λ ≥ 360 nm radiation, a slow change in the NMR spectra occurred over many hours to give a complex spectrum, after which there was no further change. The two major products, based on their NMR spectra, were the silaindanes **10a,b**. The photochemical isomerization of related silenes under similar conditions has been observed previously,[3] including one case where the silene contained mesityl groups, which led to the silaindane as the exclusive product via an intermediary silylcarbene.[9] Here the silaindanes are believed to be formed via the silylcarbene **9**, derived by photochemically induced migrations of the trimethylsiloxy groups of the silenes **2a,b** from carbon to silicon, as shown in eq 3. Attempts to separate the silaindanes from the mixture were not successful, but partial purification gave definitive NMR spectra, in particular the well-defined ABX pattern of doublets of doublets, associated with the $-CHCH_2$ protons.

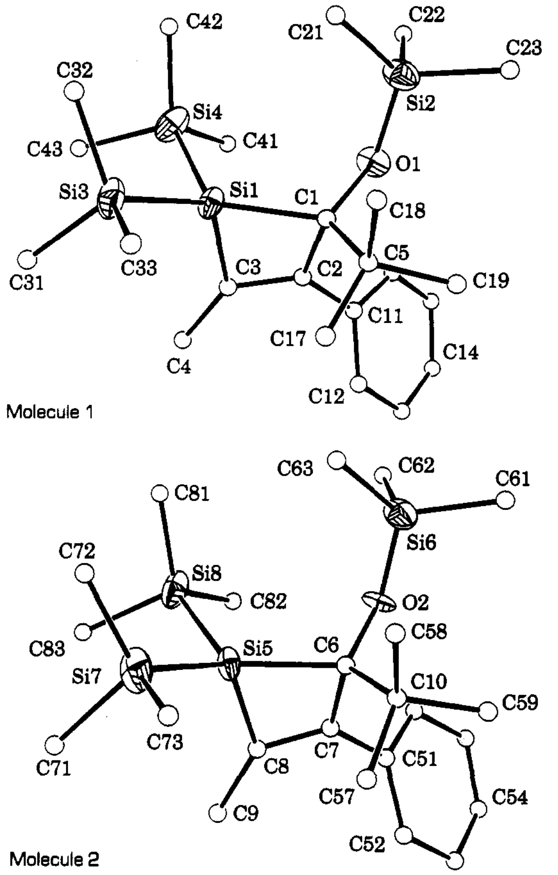
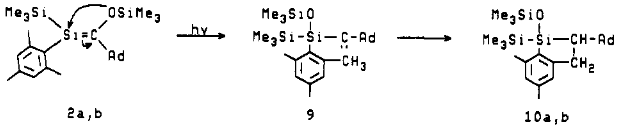


Figure 3. View of the two nonequivalent molecules of compound **11** showing the atomic labeling scheme. Thermal ellipsoids are at the 25% probability level.



(3)

The regiochemistry found for the silacyclobutene adducts **4a** and **5a** led us to reexamine the structure of the adduct of the silene $(Me_3Si)_2Si{=}C(OSiMe_3)CMe_3$ with 1-phenylpropyne. In an earlier publication we proposed the structure **12** (eq 4) on the basis of mass spectrometric fragmentation.[1] However, the similarity of the chemical shifts of the ring atoms of **4a**, **5a**, and the phenylpropyne adduct suggested that the structure should be **11**, as has now been confirmed by a crystal structure, whose ORTEP diagrams (there were two nonequivalent molecules in the unit cell) are shown in Figure 3. Thus, in this cycloaddition, like those described above, the reaction is completely regiospecific, resulting in a single isomeric product.

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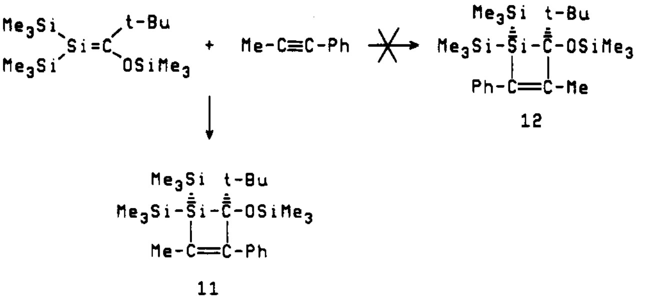

(4)

X-ray Structure Determinations

The crystal data for the three structures **4a**, **5a**, and **11** are summarized in Table I.

The four-membered silacyclobutene rings in **4a**, **5a**, and **11** each define a least-squares plane with maximum deviations from the planes of 0.016 (18) Å for C(2) in **4a**, −0.046 (10) Å for C(2) in **5a**, and 0.13 (3) and 0.12 (3) Å for C(3) and C(7) in each of the two molecules in **11**. In all of the molecules the substituents on the sp^2-hybridized ring atoms are essentially in the planes of the silacyclobutene rings. The dihedral angle in **4a** between the plane formed by the aromatic ring C(51)–C(56) and the silacyclobutene ring is 39.4 (7)°.

The interior angles of the four-membered rings at Si(1), C(1), C(2), and C(3), listed in Table II, are all much smaller than would be expected on the basis of hybridization principles: the angles at silicon are particularly small. Such distortions are the result of the strained ring and the steric repulsions of the bulky substituent groups. The bond lengths in the ring systems reflect the ring strain. The Si–C(sp^3) distances of 1.991 (13) Å in **4a**, 1.972 (7) Å in **5a**, and 1.981 (18) and 1.983 (17) Å in **11** are all considerably stretched compared to the normal silicon–carbon bond length of 1.872 (1) Å,[10] but the other ring bond lengths are fairly normal.

The effect of steric bulk is also illustrated by the angle widening of some exocyclic angles, namely Si(2)–Si(1)–C(1) = 130.9 (5)° (**4a**) and 132.93 (22)° (**5a**) and Si(1)–C(1)–C(4) = 120.9 (9)° (**4a**) and 119.4 (4)° (**5a**), indicating that the steric interaction is most pronounced between the adamantyl and the trimethylsilyl substituents in these compounds. In **11** the steric repulsions appear to be greatest between one of the trimethylsilyl groups and the *tert*-butyl group, illustrated by the wide angles Si(3)–Si(1)–C(1) = 131.0 (6)° (Si(7)–Si(5)–C(6) = 130.8 (6)°), and Si(1)–C(1)–C(5) = 117.3 (13)° (Si(5)–C(6)–C(10) = 117.1°).

Experimental Section

Experiments were performed with oven-dried glassware under argon using inert-atmosphere and vacuum-line techniques. Reaction solvents were dried and distilled before use: diethyl ether and tetrahydrofuran were dried over sodium benzophenone ketyl, pentanes were dried over lithium aluminum hydride, and toluene was dried over sodium. Photolyses were carried out using two or three 100-W PAR 38 mercury spot lamps, whose output is mainly at 360 nm and longer wavelengths.

All NMR spectra were obtained on either a Varian XL400 or a Gemini 200 spectrometer. The spectra were run in C_6D_6 unless otherwise specified. Where necessary, APT[11] and DEPT[12] pulse sequences were used in obtaining ^{13}C NMR spectra to allow unambiguous assignment of signals. Most ^{29}Si NMR spectra were obtained using the DEPT sequence.

Melting points are uncorrected.

Synthesis of Mesitylbis(trimethylsilyl)adamantoylsilane (1). Compound **1** was prepared by the cleavage of $(Me_3Si)_3SiMes$[13] in THF over 15 h with 1 equiv of MeLi, the resulting solution being added at −78 °C to 1 equiv of AdCOCl in THF. After the mixture was stirred at −78 °C for 2 h and then at room temperature for 5 h, workup gave 59% of **1** after recrystallization from MeOH; mp 112–114 °C. Anal. Calcd for $C_{26}H_{44}OSi_3$: C, 68.42; H, 9.73. Found: C, 68.20; H, 9.84. ^{1}H NMR: δ 0.33 (18 H, s, Me_3Si), 1.5–1.9 (15 H, m, Ad), 2.07 (3 H, s, *p*-Me), 2.43 (6 H, s, *o*-Me), 6.74 (2 H, CH Mes). ^{13}C NMR: δ 1.74 (Me_3Si), 21.02 (*p*-Me), 26.74 (*o*-Me), 28.68 (Ad CH), 36.96, 39.08 (Ad CH_2), 52.71 (Ad quat C), 129.02 (Mes CH), 131.72, 138.31, 143.65 (Mes quat C), 252.03 (C=O). ^{29}Si NMR: δ −13.99 (Me_3Si), −44.12 (central Si). IR: 1608 cm^{-1} (C=O). MS: calcd 456.270, found 456.268; *m/e* (%) 456 (7, M^+), 441 (23, $M^+ - Me$), 383 (12, $M^+ - Me_3Si$), 293 (54, M^+ − COAd), 219 (100, $Me_3SiSiHMes^+$), 135 (31, Ad), 73 (62, Me_3Si).

Photolysis of Acylsilane 1. Formation of Silenes 2a,b. A solution of 0.25 g (5.5 mmol) of acylsilane **1** in 1 mL of deuteriobenzene was photolyzed for 4.5 h at about 10 °C. ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy revealed the presence of two sets of signals, attributed to silenes **2a,b**, present in the ratio 1.4:1. After the temperature was raised to 45 °C for 2 h, the NMR spectra were unchanged in chemical shift or intensity. Warming to 65 °C for 16 h also caused no change in the spectra. The deuteriobenzene was removed under vacuum to give a viscous oil. Numerous attempts to crystallize the silenes from ether, hexanes, pentanes, or THF failed. When a C_7D_8 solution of the silenes was heated at 100 °C in the presence of a small amount of 1,3-dimethoxybenzene (as an NMR standard), its ^{1}H NMR spectra taken periodically showed that the minor isomer slowly decomposed to unknown fragments, being totally decomposed after 168 h, at which time the concentration of the major isomer had fallen to 60% of its initial value. **2a** (major isomer): ^{1}H NMR δ −0.08, 0.24 (each 9 H, s, Me_3Si), 1.55–2.0 (m, Ad with **2b**), 2.11 (3 H, s, *p*-Me), 2.60 (6 H, s, *o*-Me), 6.79 (2 H, Mes CH); ^{13}C NMR δ 0.58 (Me_3Si), 2.05 (Me_3SiO), 21.34 (*p*-Me), 25.20 (*o*-Me), 29.22 (Ad CH), 37.60, 42.57 (Ad CH_2), 43.36 (Ad quat C), 127.86 (Mes CH), 132.28, 138.91, 144.74 (Mes quat C), 195.75 (C sp^2); ^{29}Si NMR δ −13.00 (Me_3Si), 14.05 ($OSiMe_3$), 41.84 (Si sp^2). **2b** (minor isomer): ^{1}H NMR δ 0.24, 0.38 (each 9 H, s, Me_3Si), 1.55–2.0 (m, Ad with **2a**), 2.05 (3 H, s, *p*-Me), 2.63 (6 H, s, *o*-Me), 6.77 (Mes CH); ^{13}C NMR δ 1.06 (Me_3Si), 1.98 (Me_3SiO), 21.32 (*p*-Me), 26.72 (*o*-Me), 29.11 (Ad CH), 37.33, 41.72 (Ad CH_2), 45.04 (Ad quat C), 128.00 (Mes CH), 134.55, 138.87, 143.08 (Mes quat C), 191.63 (C sp^2); ^{29}Si NMR δ −16.13 (Me_3Si), 13.56 ($OSiMe_3$), 44.05 (Si sp^2).

Reaction of Silenes 2a,b with Methanol. An excess of dry methanol was added to a 1.4:1 mixture of silenes **2a,b** prepared as described above. NMR spectroscopy showed the presence of two adducts in the ratio 2.5:1. After several recrystallizations from ethanol pure **3a** was isolated, together with **3b** slightly contaminated with **3a**. **3a**: mp 121–122 °C; ^{1}H NMR δ 0.05, 0.37 (each 9 H, s, Me_3Si), 1.67–1.97 (15 H, m, Ad), 2.10 (3 H, s, *p*-Me), 2.61 (6 H, s, *o*-Me), 3.28 (3 H, s, MeO), 3.76 (1 H, s, CH), 6.79 (2 H, s, Mes CH); ^{13}C NMR δ 1.17 (Me_3Si), 1.52 (Me_3SiO), 21.03 (*p*-Me), 24.39 (*o*-Me), 29.10 (Ad CH), 37.55, 40.71 (Ad CH_2), 38.45 (Ad quat C), 51.02 (MeO), 80.40 (CH-Ad), 129.47 (Mes CH), 132.39, 138.91, 144.94 (Mes C); ^{29}Si NMR δ −18.08 (Me_3Si), 15.72 ($OSiMe_3$), 1.31 (Si–OMe); MS calcd for M^+ − MeO 457.27783, found 457.27858; *m/z* (%) (EI) 488 (1, M^+), 473 (100, $M^+ - Me$), 457 (7, M^+ − MeO), 415 (28, $M^+ - Me_3Si$), 399 (4, $M^+ - OSiMe_3$), 369 (57, M^+ − Mes), 251 (100, $Me_3SiSi(OMe)Mes^+$), 237 (28, $Me_3SiOCHAd^+$). Anal. Calcd for $C_{27}H_{48}O_2Si_3$: C, 66.31; H, 9.92. Found: C, 65.81; H, 9.75. **3b** (with **3a**): ^{1}H NMR δ 0.06, 0.30 (9 H, s, Me_3Si), 1.6–2.0 (m, Ad), 2.09 (3 H, s, *p*-Me), 2.58 (6 H, s, *o*-Me), 3.51 (3 H, s, MeO), 3.82 (1 H, s, CH), 6.73 (Mes H); ^{13}C NMR δ 0.92 (Me_3Si), 1.03 (Me_3SiO), 21.03, 24.39 (Me, overlap), 29.05 (Ad CH), 37.50, 40.85 (Ad CH_2), 38.34 (Ad quat C), 52.48 (MeO), 82.57 (CH-Ad), 129.49 (Mes CH), 133.21, 138.60, 144.94 (Mes C); ^{29}Si NMR δ −17.66 (Me_3Si), 16.25 ($OSiMe_3$), −0.77 (Si–OMe). The same products were formed in a 3.1:1 ratio when 0.18 g of **1** was photolyzed in 0.8 mL of C_6D_6 containing 0.025 mL

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Table I. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters

compd	**4a**	**5a**	**11**
empirical formula	$C_{34}H_{50}OSi_3$	$C_{31}H_{54}OSi_4\cdot0.35C_3H_6O$	$C_{23}H_{44}OSi_4$
M_r	559.0	575.4	448.9
cryst size, mm	0.12 × 0.23 × 0.30	0.25 × 0.20 × 0.18	0.23 × 0.15 × 0.20
cryst class	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P\bar{1}$	$Pbn2_1$
a, Å	11.529 (5)	10.762 (5)	8.746 (2)
b, Å	18.486 (3)	11.976 (3)	21.178 (4)
c, Å	16.027 (3)	15.970 (3)	31.631 (7)
α, deg	90.0	109.75 (2)	90.0
β, deg	102.54 (1)	99.28 (2)	90.0
γ, deg	90.0	93.38 (3)	90.0
V, Å^3	3334 (1)	1898 (1)	5859 (2)
Z	4	2	8
D_{calc}, g cm^{-3}	1.11	1.01	1.02
μ(Mo Kα), cm^{-1}	1.6	1.7	2.1
F(000)	1216	630.4	1968
ω scan width, deg	0.6 + 0.35 tan θ	0.6 + 0.35 tan θ	0.7 + 0.35 tan θ
θ range collected, deg	1–22.5 ($\pm h,k,l$)	1–25 ($\pm h,\pm k,l$)	1–22.5 (hkl)
total no. of rflns	4527	4836	3893
av decline in std rflns, %	0	75.0	35.7
no. of unique rflns	4353	4836	3893
R_{int}	0.071		
no. of obsd data [$I > 2.5\sigma(I)$]	1559	3287	1908
weight modifier K	0.0004	0.0004	0.0004
R	0.061	0.080	0.085
R_w	0.059	0.121	0.088
goodness of fit	1.30	3.94	2.29
largest Δ/σ	0.001	0.160[a]	0.004
no. of params refined	343	342	275
max density in ΔF map, e Å^{-3}	0.34	0.77	0.27

[a] Associated with solvent molecule.

Table II. Interior Angles (deg) of the Cyclobutene Rings

angle	**4a**	**5a**	**11** (molecule 1)	**11** (molecule 2)[a]
C(3)–Si(1)–C(1)	73.8 (6)	71.4 (3)	74.4 (8)	73.4 (8)
Si(1)–C(1)–C(2)	83.9 (8)	86.6 (4)	82.8 (10)	83.4 (10)
C(1)–C(2)–C(3)	106.0 (11)	103.8 (5)	103.9 (15)	106.2 (15)
Si(1)–C(3)–C(2)	96.3 (9)	97.7 (5)	95.5 (14)	94.1 (14)

[a] Equivalent angles quoted, although atomic labeling is different.

of MeOH (1:1.6 acylsilane:MeOH ratio) and a 1.3:1 ratio when the acylsilane:MeOH ratio was 1:29.

Synthesis of the Silacyclobutenes 4a,b from Phenylacetylene. A solution of 0.33 g (0.72 mmol) of acylsilane 1 in 0.8 mL of deuteriobenzene was photolyzed for 5 h, and NMR examination showed that the ratio **2a**:**2b** was 1.4:1. To the solution was added 0.084 g (0.82 mmol) of phenylacetylene, which resulted in an exothermic reaction. After 20 min the NMR spectra of the system were taken, which revealed the presence of two sets of signals attributable to **4a,b** in the ratio 1.4:1 (^{1}H NMR spectrum, Me_3Si signals). Column chromatography of the solution on silica gel using 100:1 hexane/ethyl acetate as eluent gave rise to pure **4a,b**. **4a** (major isomer, recrystallized from acetone): mp 138–140 °C; ^{1}H NMR δ 0.07 (9 H, s, Me_3Si), 0.21 (9 H, s, $OSiMe_3$), 1.6–2.0 (15 H, m, Ad), 2.10 (3 H, s, *p*-Me), 2.41, 2.58 (each 3 H, s, *o*-Me), 6.74–6.76 (2 H, m, CH of Mes), 6.90 (1 H, s, ring =CH), 7.05–7.20 (3 H, m, Ph), 7.62–7.72 (2 H, m, Ph); ^{13}C NMR ($CDCl_3$, also using $^{13}C\{^1H\}$ coupled spectrum) δ 0.63, 2.30 (Me_3Si), 21.14 (Mes *p*-Me), 24.78, 25.06 (Mes *o*-Me), 28.89 (Ad CH), 37.16, 39.81 (Ad CH_2), 40.50 (Ad quat C), 96.85 (ring C–Ad), 127.39, 127.91, 127.48 (2 CH), 128.02 (2 CH), 128.56 (Ar CH), 132.67 (Ph ipso), 138.35 (Mes *p*-C), 141.12 (Mes ipso), 141.36 (ring =CH), 143.54, 143.85 (Mes *o*-C), 166.36 (ring =C-Ph); ^{29}Si NMR δ 8.22 ($OSiMe_3$), −6.06 (ring Si), −16.26 (Me_3Si); MS calcd for $C_{34}H_{50}OSi_3$ 558.3169, found 558.3174; *m/e* (%) 558 (20, M^+), 543 (3, $M^+ - Me$), 485 (24, $M^+ - Me_3Si$), 439 (5, $M^+ - Mes$), 423 (10, $M^+ - Ad$), 365 (59), 309 (63, $(Me_3Si)MesSi{=}CPh^+$), 237 (64), 135 (78, Ad), 73 (100, Me_3Si). The ORTEP diagram of **4a** is shown in Figure 1. **4b** (minor isomer, recrystallized from acetone): mp 146–149 °C; ^{1}H NMR δ 0.22 (9 H, s, Me_3Si), 0.46 (9 H, s, $OSiMe_3$), 1.6–2.0 (15 H, m, Ad), 2.08 (3 H, s, *p*-Me), 2.55, 2.62 (each 3 H, s, *o*-Me), 6.74 (2 H, br, CH of Mes), 6.81 (1 H, s, ring =CH), 7.1–7.3 (3 H, m, Ph), 7.7–8.2 (2 H, m, Ph); ^{13}C NMR ($CDCl_3$) δ 0.00 (Me_3Si), 4.20 (Me_3SiO), 21.14 (*p*-Me), 24.39, 25.77 (*o*-Me of Mes), 28.88 (Ad CH), 36.86, 38.69 (Ad CH_2), 40.98 (Ad quat C), 95.96 (ring C-Ad), 126.93 (Ar CH), 126.98 (2 Ar CH), 127.79 (2 Ar CH), 127.85, 128.98 (Ar CH), 133.84 (Ar quat C), 138.13 (ring =CH), 138.48, 141.43, 142.17, 143.22 (Ar quat C), 160.83 (ring =CPh); ^{29}Si NMR δ 3.28 ($OSiMe_3$), −12.48 (Me_3Si), −18.10 (ring Si); MS calcd for $C_{34}H_{50}OSi_3$ 558.3169, found 558.3172; *m/e* (%) 558 (30, M^+), 485 (37, $M^+ - Me_3Si$), 365 (83), 309 (72, $(Me_3Si)MesSi{=}CPh^+$), 237 (69), 135 (83, Ad), 73 (100, Me_3Si).

Reactions of Silenes 2a,b with (Trimethylsilyl)acetylene. Synthesis of 5a,b. A solution of 1 (0.34 g, 0.75 mmol) in 0.8 mL of C_6D_6 was photolyzed in a capped NMR tube for 5.5 h, at which point no further starting material was present, and the silenes **2a,b** were present in the ratio 1.4:1. To this was added 0.20 mL (1.4 mmol) of (trimethylsilyl)acetylene, and the reaction mixture was warmed at 50 °C for 62 h, by which time all the silene isomers had reacted. After removal of the solvent, attempted recrystallization from hexanes, acetone, or THF failed; therefore, successive column chromatographs (six repetitions) on silica gel (hexane eluent) were used to separate the mixture of adducts **5a,b**, which were present in the ratio 1.4:1. **5a** eluted first and when partially separated could be purified by crystallization from acetone. Later fractions contained **5b**, which were combined and crystallized from acetone to give pure **5b**. **5a**: mp 112–114 °C; ^{1}H NMR δ −0.01, 0.17, 0.32 (each 9 H, s, Me_3Si), 1.6–2.15 (15 H, m, Ad), 2.10 (3 H, s, *p*-Me), 2.39, 2.50 (each 3 H, s, *o*-Me), 6.72, 6.74 (each 1 H, s, CH–Mes), 7.52 (1 H, s, ring =CH); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 0.44, 1.74, 2.49 (Me_3Si), 21.14 (*p*-Me), 24.41, 25.03 (*o*-Me), 28.95 (Ad CH), 37.21, 39.10 (Ad CH_2), 39.88 (Ad quat C), 98.51 (ring C-Ad), 127.82, 128.41 (CH Mes), 133.58 (Mes ipso), 138.11 (Mes *p*-C), 143.22, 143.34 (Mes *o*-C), 159.98 (ring =CH), 179.35 (ring =$CSiMe_3$); ^{29}Si NMR ($CDCl_3$) δ 5.94 ($OSiMe_3$), 4.89 (ring Si), −12.60 (Me_3Si), −17.37 (Me_3Si); MS calcd for $C_{31}H_{54}OSi_4$ 554.325 18, found 554.322 02; *m/e* 554 (2, M^+), 539 (3, $M^+ - Me$), 481 (56, $M^+ - Me_3Si$), 177 (100, $MesMe_2Si^+$), 135 (37, Ad), 73 (61, Me_3Si). The ORTEP diagram for **5a** is shown in Figure 2. **5b**: mp 139–140 °C (from acetone); ^{1}H NMR δ 0.21, 0.33, 0.38 (each 9 H, s, Me_3Si), 1.5–2.0 (15 H, m, Ad), 2.07 (3 H, s, *p*-Me), 2.45, 2.55 (each 3 H, s, *o*-Me), 6.70 (2 H, br s, CH Mes), 7.32 (1 H, s, ring =CH); ^{13}C NMR ($CDCl_3$) δ 0.11, 0.78, 4.03

(Me_3Si), 21.13 (*p*-Me), 24.14, 25.53 (*o*-Me), 28.93 (Ad CH), 36.90, 38.78 (Ad CH_2), 40.46 (Ad quat C), 98.54 (ring C–Ad), 127.70, 127.77 (CH Mes), 135.05 (ipso-C Mes), 138.20 (*p*-C Mes), 141.49, 143.08 (*o*-C Mes), 155.43 (ring =CH), 173.98 (ring =$CSiMe_3$); ^{29}Si NMR ($CDCl_3$) δ 1.84 ($OSiMe_3$), −10.30 (ring Si), −12.35 (Me_3Si–C), −13.95 (Me_3Si); MS calcd for $C_{31}H_{54}OSi_4$ 554.325 18, found 554.323 50; *m/e* 554 (2, M^+), 539 (3, $M^+ - Me$), 481 (61, $M^+ - Me_3Si$), 419 (3, $M^+ - Ad$), 177 (100, $MesMe_2Si^+$), 135 (34, Ad), 73 (49, Me_3Si).

Reaction of Silenes 2a,b with Butadiene. 3-Vinyl-1-silacyclobutanes 6. A solution of 0.40 g of acylsilane 1 in 0.8 mL of deuteriobenzene was photolyzed for 7 h, by which time most of the acylsilane had been converted to silenes **2a,b**, and the formation of small amounts of silaindanes **10** could be detected. A slow stream of butadiene was passed through the solution for 20 min, causing a mild exothermic reaction. After excess butadiene was pumped off and the solution was cleaned up by flash chromatography (no major signals were altered), the ^1H NMR spectrum showed several signals definitive for vinylsilacyclobutanes:[3] δ −0.1 to +0.4 (Me_3Si, eight major signals, two for each of four isomers), 2.9–3.5 (m, ring CH), 5.1–5.3 (m, vinyl =CH_2), 6.2–6.6 (m, vinyl =CH) (there were no signals in the region 5.4–6.1, characteristic of silacyclohexenes 7[3]); ^{13}C δ 0.0–5.0 (8 Me_3Si signals), 93.11, 95.29, 95.42, 97.14 (typical for ring C quat), 112.49, 112.71, 113.58, 114.14 (typical of vinyl =CH). No attempts were made to separate the complex mixture.

Reaction of Silenes 2a,b with Oxygen. Isolation of Ester 8. When dry air was passed through a solution of silenes **2a,b** in C_6D_6, the silene concentrations disappeared during 1 h and a new set of signals appeared. On isolation, a viscous oil was obtained, which was found to be the ester **8**: ^1H NMR δ 0.24, 0.27 (each 9 H, s, Me_3Si), 1.55–2.05 (15 H, m, Ad), 2.09 (3 H, s, *p*-Me), 2.57 (6 H, s, *o*-Me), 6.75 (2 H, s, Mes CH); ^{13}C NMR δ −1.25 (Me_3Si), 2.22 (Me_3SiO), 21.04 (*p*-Me), 24.51 (*o*-Me), 28.37 (Ad CH), 36.72, 39.41 (Ad CH_2), 41.66 (Ad quat C), 129.60 (Mes CH), 130.60, 139.40, 143.88 (Mes quat C), 177.59 (C=O); ^{29}Si NMR δ 9.70 ($OSiMe_3$), −17.14 (*Si*–$SiMe_3$, assigned using $^{29}Si\{^1H\}$ coupled spectrum), −20.22 (Me_3Si); IR 1703 cm^{-1} (C=O); MS *m/e* (%) 488 (6, M^+), 487 (13, $M^+ - H$), 473 (31, $M^+ - Me$), 415 (60, $M^+ - Me_3Si$), 369 (100, $M^+ - Mes$), 309 (23, $MesSi(OSiMe_3)Me_3Si^+$), 135 (57 (Ad^+), 73 (42, Me_3Si^+).

Reaction of Silenes 2a,b with Oxygen at −70 °C. A solution of 0.20 g of acylsilane 1 with 0.8 mL of toluene-d_8 in an NMR tube was irradiated for 9 h, at which time only a trace of starting material remained, and some silaindanes **10a,b** were starting to form. The solution was cooled to −78 °C (dry ice/MeOH), and a slow stream of dry air was bubbled through it for 1 h. The ^{29}Si NMR spectrum was immediately run at −70 °C, which showed the presence of the ester 8 (δ 9.80 ($OSiMe_3$), −16.77 (central silicon), and −20.54 (Me_3Si)), three other, stronger signals due to an intermediate (approximate ratio 1:1.5 for 8:intermediate) at δ 57.51 (central silicon), 13.07 ($OSiMe_3$), and −18.48 (Me_3Si), and other weak signals due to the silaindanes **10a,b**. No silene remained. When the solution was warmed up to −30 °C over about 2 h, the ^{29}Si NMR spectrum run at −30 °C revealed that all the intermediate had been converted into 8.

Extended Photolysis of Silenes 2a,b. A solution of the silenes **2a,b** in deuteriobenzene was photolyzed for a total of 96 h, after which no further changes occurred. Attempts to separate the complex mixture by column chromatography removed some products and led to the isolation of a mixture of the silaindanes **10a,b** in the ratio 1.5:1, which were not separable. **10a** (major isomer mixed with **10b**): ^1H NMR δ 0.12, 0.20 (s, Me_3Si), 1.7–2.1 (m, Ad), 2.17 (s, *p*-Me), 2.50 (s, *o*-Me), 1.53 (d × d, H_A of CH_A), 2.9 (d × d, H_B of CH_BH_C, overlapped with **10b**, J = 7.8, 16.5 Hz observed), 3.19 (d × d, H_C, J = 8.6, 16.6 Hz observed, overlapped with **10b**), 6.77 (2 H, br s, Mes CH); ^{13}C NMR δ −0.42 (Me_3Si), 2.41 ($OSiMe_3$), 21.52 (*p*-Me), 24.44 (*o*-Me), 29.49 (Ad CH), 33.75 (ring CH_BH_C), 37.64, 43.15 (Ad CH_2), 41.12 (ring CH_A), 124.26, 127.89 (CH Mes), 136.08, 139.73, 141.53, 152.49 (Mes quat C); ^{29}Si NMR δ 7.98 ($OSiMe_3$), 7.40 (ring Si), −22.67 (Me_3Si). **10b** (minor isomer mixed with **10a**): ^1H NMR δ 0.16, 0.23 (Me_3Si), 1.7–2.1 (Ad), 1.53 (d × d, H_A of CH_A), 2.9 (d × d, H_B of CH_BH_C, overlapped with **10a**, J = 7.8, 16.5 Hz observed), 3.19 (d × d, H_C, J = 8.6, 16.6 Hz observed, overlapped with **10a**), 2.17 (*p*-Me, accidental overlap), 2.49 (*o*-Me), 6.84, 6.88 (each 1 H, Mes CH); ^{13}C NMR δ −0.33 (Me_3Si), 2.48 ($OSiMe_3$), 21.54 (*p*-Me), 23.33 (*o*-Me), 29.44 (Ad CH), 30.60 (ring CH_BH_C), 37.51, 44.14 (Ad CH_2), 52.48 (ring CH_A), 124.56, 128.26 (Mes CH), 135.58, 139.14, 142.17, 150.56 (Mes quat C); ^{29}Si NMR δ 7.74 ($OSiMe_3$), 3.51 (ring Si), −21.96 (Me_3Si). MS (mixture): *m/e* (%) 456 (5, M^+), 441 (18, $M^+ - Me$), 383 (100, $M^+ - Me_3Si$), 294 (8, $M^+ - Me_3Si - OSiMe_3$), 247 (57), 221 (29), 135 (70, Ad), 73 (37, Me_3Si).

Silacyclobutene 11 from $(Me_3Si)_2Si{=}C(OSiMe_3)CMe_3$ and 1-Phenylpropyne. The silacyclobutene 11 was prepared according to published procedures[1] and recrystallized from methanol: mp 67–69 °C; ^1H NMR δ 0.29, 0.30, 0.34 (s, each 9 H, Me_3Si), 1.01 (s, 9 H, *t*-Bu), 1.85 (s, 3 H, Me–C ring), 7.0–7.25 (m, 3 H, Ph), 7.45–7.52 (m, 2 H, Ph); ^{13}C NMR δ 1.62, 1.81 (Me_3Si), 3.57 ($OSiMe_3$), 15.43 (*Me*C=), 29.56 (*Me*$_3$C), 39.36 (Me_3*C*), 92.13 (ring C–$OSiMe_3$), 126.67 (*p*-CH Ph), 128.11, 128.70 (*o*-, *m*-CH Ph), 139.03 (ipso-C Ph), 143.52 (Me*C*=), 156.81 (Ph*C*=); ^{29}Si NMR δ 6.92 ($OSiMe_3$), −11.69 (ring Si), −16.24, −17.52 (Me_3Si). The ORTEP diagram defining the regiochemistry is shown in Figure 3.

X-ray Structural Determination. Intensity data for all compounds were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo Kα radiation (λ = 0.709 30 Å). The ω–2θ scan technique was applied with variable scan speeds. The intensities of three standard reflections were measured every 2 h. The data for compounds **5a** and **11** were corrected for linear intensity decay. Data for all compounds were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved by direct methods (compound 11 has two independent molecules in the asymmetric unit). Non-hydrogen atoms were refined anisotropically (except for compound 11, for which the carbon atoms were refined with isotropic thermal parameters) by least squares to minimize $\sum w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + KF^2$. Hydrogen atoms were positioned on geometric grounds (C–H = 0.95 Å, $U_{iso}(H) = U_{iso}(C) + 0.01$ Å^2). The structure of **5a** contains a partial-occupancy, disordered solvent molecule (acetone), and these atoms (excluding hydrogens) were refined with isotropic thermal parameters. Crystal data, data collection, and least-squares parameters are listed in Table I. All calculations were performed using NRCVAX[14] and SHELXS86[15] on an IBM-compatible 486-33 personal computer and an Apollo computer. ORTEP[16] diagrams of the structures are presented in Figures 1–3.

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Supplementary Material Available: For **4a**, **5a**, and **11**, tables of atomic coordinates, complete bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, torsion angles, and least-squares planes (29 pages). Ordering information is available on any current masthead page.

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