Stereo- and Regioselectivity of Reactions of Siliranes with Aldehydes and Related Substrates

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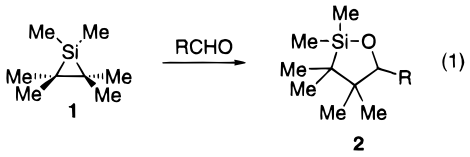
Siliranes undergo stereoselective and regioselective insertions of benzaldehyde to provide oxasilacyclopentane products. The thermal reaction (>100 °C) leads to more decomposition and side products, whereas the catalyzed variant (*t*-BuOK, <25 °C) proceeds more cleanly with a high degree of inversion (>95%). Treatment of siliranes with enolizable aldehydes leads to silyl enol ethers. The reaction of a silirane at high temperatures with an imine leads to reductive dimerization, presumably by way of intermediate-free silylene. The mechanism for the catalyzed insertion of benzaldehyde is discussed.

Introduction

Organic chemists have long recognized that the strain energy released upon cleavage of three-membered rings can be harnessed to achieve many otherwise unattainable goals.[1] For example, cyclopropanes have seen numerous applications in synthesis,[2] as have their counterparts the oxiranes[3] and aziridines.[4] In contrast, siliranes have not been recognized as useful reactive intermediates in organic synthesis. This situation is paradoxical, since the unique reactivity of silicon compounds has had a tremendous impact on organic chemistry.[5] Although seminal contributions to silirane chemistry have been reported by Seyferth,[6−11] Ando,[12] and others,[13−16] the use of these highly strained compounds[17] poses particular problems because of the difficulty in their synthesis, their high air sensitivity, and the lack of information regarding issues such as stereo- and regiochemistry of their ring-opening reactions.

We initiated our studies of silirane chemistry to discover new reactions of these compounds and to evaluate the stereo- and regiochemistry of their ring-opening reactions. Our early experiments were motivated by a report by Seyferth, who demonstrated that silirane **1** undergoes insertion of aldehydes to afford oxasilacyclopentanes **2** (eq 1).[10,18] Boudjouk and Chrusciel's efficient



(1)

synthesis of siliranes **3** from di-*tert*-butyldichlorosilane and alkenes[19] permits the synthesis of various substituted siliranes that can be used to elucidate the stereo- and regiochemistry of ring-opening reactions. We recently reported the dichotomous stereochemical courses of the thermal and catalyzed carbon−carbon bond-forming reactions of siliranes **3** with benzaldehyde.[20,21] The ability to oxidize carbon−silicon bonds, even those of sterically hindered silicon species,[22] led to the synthesis of 1,3-diols with three contiguous stereocenters.[20] Other reactions of siliranes have been developed in our laboratories, such as the thermal insertion of formamides[23] and palladium-catalyzed alkyne insertion and silylene transfer reactions.[24] Herein, we detail our investigations of the reactions of siliranes with aldehydes and related observations.

Results

Methanolysis. The first issue that needed to be addressed was the stereochemistry of silirane ring-

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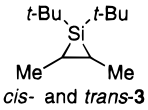
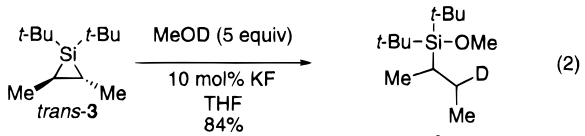


cis- and *trans*-**3**

opening reactions. The stereochemical course of silirane protonolysis[7,25] has not been determined, although the methanolysis of silirenes proceeds with retention of alkene configuration.[26,27] Jones demonstrated that the addition of MeOD to adducts of *trans*-2-butene or cyclohexene and photochemically generated dimethylsilylene gave stereospecific incorporation of a deuterium atom;[28] however, no direct evidence was given for the presence of silirane intermediates.

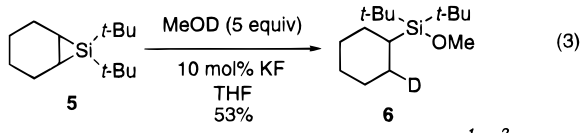
Deuterium-labeling experiments demonstrate that protonolysis of the Si−C bond of siliranes is a stereospecific process. Treatment of *trans*-**3** with MeOD in the presence of fluoride ions[25] provided silane **4** with the deuterium in only one of the diastereotopic positions of the methylene unit (eq 2), while deuteriomethanolysis of *cis*-**3**



(2)

one stereoisomer by ^{1}H, ^{2}H NMR

placed the deuterium atom at the other position as determined by ^{1}H and ^{2}H NMR spectroscopy.[28,29] Furthermore, ring opening of the bicyclic silirane **5** with MeOD incorporated a deuterium atom into a single position of **6**, according to ^{1}H and ^{2}H NMR spectroscopy (eq 3). Jones assigned cis stereochemistry to the dimeth-



(3)

one stereoisomer by ^{1}H, ^{2}H NMR

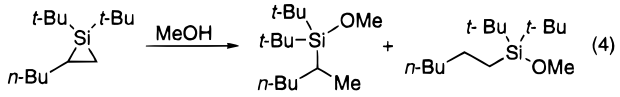
yl analogue of **6** on the basis of the chemical shift of the deuterium atom;[28] a similar chemical shift was observed for the deuterium atom of **6**, suggesting that the stereochemistry of **6** is cis. The similarities between the ^{1}H and ^{2}H NMR spectral data of Jones' dimethyl compounds[28] and the *tert*-butyl analogues described here suggest similar stereochemical outcomes.

The relative stereochemistry of the deuterated silanes **4** and **6** could not be determined unambiguously. The strategy for proof of relative stereochemistry rested on the oxidation of these silanes to the deuterated alcohols.[30] Extensive attempts failed to oxidize these silanes, even under our modified conditions.[22] Either starting materials were recovered or no products with the 2-butyl or cyclohexyl group were obtained. The volatility of the desired products could complicate isolation if only small amounts were formed. Even without unambiguous assignment of relative stereochemistry, these experiments do provide valuable data: they support Jones' argument that siliranes are reactive intermediates in photolytic experiments[28] and that silirane ring-opening reactions are stereospecific.

Table 1. Stereoselectivity of Insertion of PhCHO into Siliranes (eq 5)

silirane	conditions	**10a**	**10b**	**10c**	**10d**	yield (%)
trans-**3**	100 °C	75	7	8	10	50
cis-**3**	100 °C	48	6	32	14	26
trans-**3**	25% KO-*t*-Bu/18-crown-6	3	1	13	83	54
cis-**3**	10% KO-*t*-Bu/18-crown-6	69	30	<1	<1	73

The regioselectivity of methanolysis of unsymmetrical siliranes was found to depend upon the conditions employed (eq 4). The butylsilirane **7**, prepared from di-*tert*-butyldichlorosilane and 1-hexene in 85% yield, underwent fluoride-catalyzed methanolysis to cleave the less substituted C−Si bond. The regioselectivity was

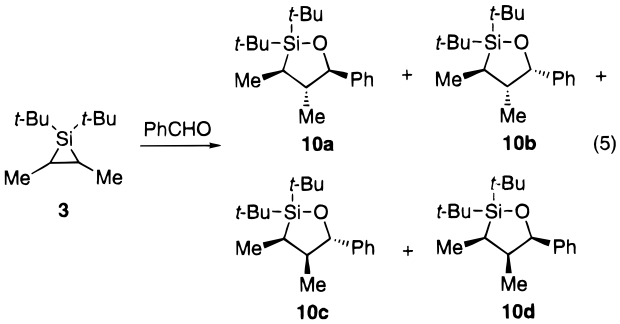


(4)

conditions	**8** : **9**
10 mol% KF	93 : 7
100 °C	17 : 83

reversed upon thermal methanolysis, which occurred preferentially at the more substituted carbon (eq 4). Fluoride-catalyzed ring cleavage does not always occur at the primary position: when benzaldehyde was employed as the electrophile, the ring opening occurred at the more substituted carbon (*vide infra*). Regioselective cleavage at the more hindered position by formamides has been explained by consideration of postulated pentacoordinate intermediates.[23]

Aldehyde Insertion. Since the insertion of methanol was found to proceed stereoselectively and regioselectively, the next step was to evaluate the formation of carbon−carbon bonds. Considering the methanolysis experiments, thermal aldehyde insertion was anticipated to proceed with some memory of the stereochemistry of the starting silirane. In fact, the reaction of *trans*-**3** with benzaldehyde at 100 °C occurred predominately with retention of configuration, affording a mixture of oxasilacyclopentanes **10a**−**d** with the major product **10a** possessing the anti−anti stereochemistry (eq 5, Table 1).



(5)

In contrast, insertion into *cis*-**3**[19] proceeded (albeit in low yield) with loss of stereochemistry, not with retention. Because the reactions of *cis*- and *trans*-**3** with benzaldehyde do not give the same distribution of products, the reactions do not involve precisely the same reactive intermediates. If these transformations proceed via

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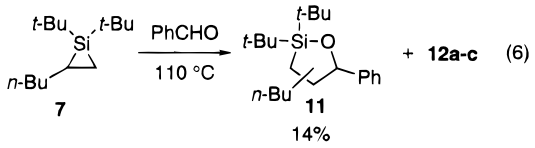
(29) Thermal deuteriomethanolysis proceeded with the same stereochemical outcome, albeit with extensive decomposition.

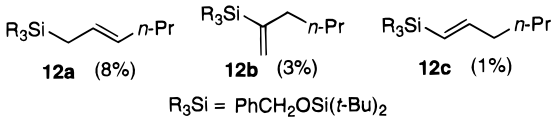
(30) For example, the 3-deuterio-2-butanols are known: Kabalka, G. W.; Bowman, N. S. *J. Org. Chem.* **1973**, *38*, 1607−1608.

diradical intermediates as was originally proposed for hexamethylsilirane (**1**) (eq 1),[10] the diradical must cyclize more rapidly than bond rotation or inversion of stereochemistry occurs.

The regiochemistry of the thermal insertion reaction was probed using unsymmetrical silirane **7** (eq 6). The



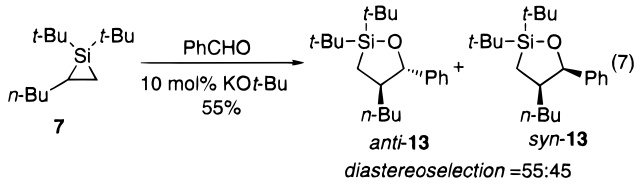
insertion occurred with poor regioselectively (71:29) and yield (14%) and was attended with extensive decomposition. Three side products, the alkoxysilanes **12a**−**c**, were also obtained in these reactions (8%, 3%, and 1%, respectively). The proposed mechanism for their formation involves coordination of the aldehyde to the silirane followed by hydrogen-atom transfer from a carbon that is β to the silicon atom. Related hydrogen-atom transfer reactions to ketones were observed by Seyferth upon irradiation of hexamethylsilirane (**1**) in the presence of cyclohexanone.[10]



Since siliranes are thermally sensitive,[19] it is not surprising that the elevated temperatures required for aldehyde insertion produce significant amounts of decomposition materials as well. For this reason, a catalyst would be desirable to effect this transformation. On the basis of observations of aldehyde insertions into silacyclobutanes,[31] nucleophilic catalysts were investigated. When a catalyst such as *t*-BuOK/18-crown-6 (10−25 mol %) was added to a solution of *trans*-**3** and benzaldehyde in THF at 22 °C,[31] insertion ensued with >95% *inversion* of stereochemistry (54% yield, eq 5, Table 1). Under similar conditions, *cis*-**3** also underwent nearly complete inversion (73% yield), affording the anti-anti isomer **10a** as the dominant product. The preponderance of inversion of stereochemistry contrasts with the stereochemical outcome of the thermal reactions.[32]

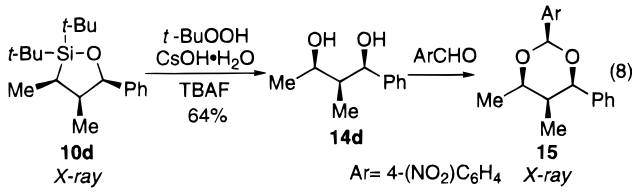
A wide variety of nucleophilic catalysts effect the insertion of benzaldehyde, including halide, azide, and aryloxide ions as well as DMF, HMPA, PPh_3, and DMAP. In all cases, the stereochemical outcome was similar to that observed for *t*-BuOK (within 5−10% for each isomer), but the yields were dramatically inferior (<20%). The necessity of a strong base seriously limits the generality of the insertion reaction, rendering only nonenolizable aldehydes as suitable substrates (*vide infra*).

The milder conditions for the catalyzed insertion proved amenable to the insertion of benzaldehyde into the unsymmetrical silirane **7** (eq 7). The catalyzed insertion of benzaldehyde proceeded with high regioselection (85:15) for cleavage of the ring at the more sterically hindered center, providing oxasilacyclopentanes **13** as a mixture of diastereomers. The regioselection of this insertion is opposite to the outcome of fluoride-



catalyzed methanolysis, which cleaved the less substituted bond. This difference is not due to the use of fluoride: insertion catalyzed by fluoride ion occurred with similar regioselectivity and stereoselectivity, albeit in low yield.

Stereochemistry and Oxidation of Silanes. Critical to the results presented above are the stereochemical assignments of the oxasilacyclopentane products. Definitive proof for the structure of oxasilacyclopentane **10d** was obtained by X-ray crystallography.[20] Since C−Si bonds can be oxidized to C−O bonds with retention of configuration,[33−35] oxidation of the oxasilacyclopentanes **10a**−**c** provided 1,3-diols, whose stereochemistry could be proven unambiguously. Exposure of oxasilacyclopentane **10d** to previously reported oxidation conditions[33] resulted in recovered starting material.[34] Under our recently reported conditions (*t*-BuOOH, $CsOH{\cdot}H_2O$, TBAF in DMF at 75 °C),[22] however, the corresponding 1,3-diol **14d** was obtained as a single isomer in 64% yield (eq 8). The fact that the reaction proceeded with retention of configuration was confirmed by conversion of **14d** to the *p*-nitrobenzylidene acetal **15** and analysis by X-ray crystallography.[20]



The stereochemical proof of the remaining oxasilacyclopentanes **10a**−**c** was accomplished by oxidation to the corresponding diols **14a**−**c**. For each isomeric diol, the relative stereochemistry between the hydroxyl groups was confirmed by analysis of the derived acetonides by ^{13}C NMR spectroscopy.[36,37] Two-dimensional heteronuclear correlation experiments were necessary to assign the resonances of the acetonide methyl groups. To determine the configuration of the remaining stereocenter, reference materials were prepared by stereoselective aldol reactions (both syn[38] and anti[39]) between propiophenone and acetaldehyde (Scheme 1). As in other aldol reactions,[40] acetaldehyde showed diminished stereoselectivity compared to other aldehydes. The aldol adducts were then reduced stereoselectively by methods that are known to proceed with the illustrated stereochemical course.[41−43]

(31) These conditions were inspired by insertions of aldehydes into silacyclobutanes: Takeyama, Y.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 6059−6062.

(32) Control experiments indicate that the products are formed kinetically and that no isomerization of the silirane occurred during either the thermal or catalyzed insertions.

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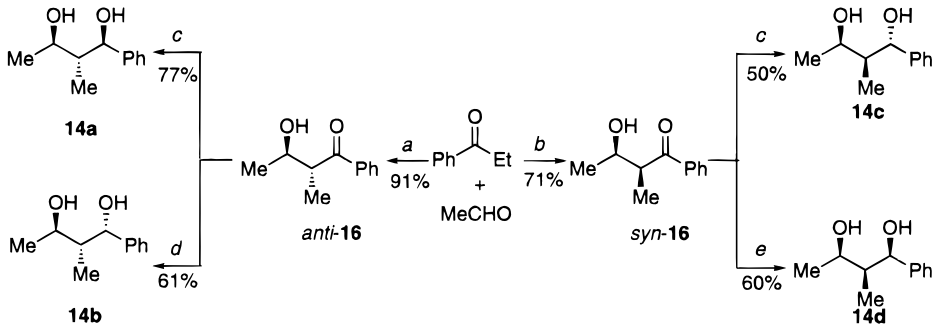
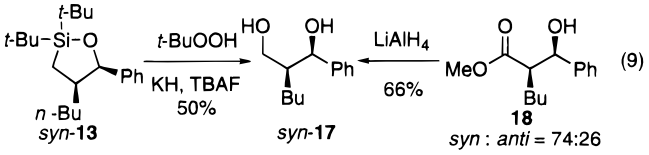
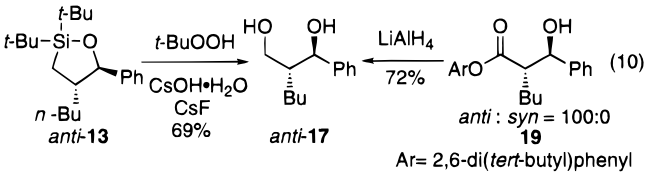
Scheme 1[a]



[a] $(C_6H_{11})_2BCl$, Et_3N, 81% ds. [b] $PhBCl_2$, $EtN(i\text{-}Pr)_2$, 94% ds. [c] TBSCl; $LiAlH_4$, 70% ds (**14b**), 80% ds (**14c**). [d] $Me_4N(AcO)_3BH$, >95% ds. [e] $EtB(OMe)_2$, $NaBH_4$, >95% ds.

The structures of the products obtained from the reactions of unsymmetrical silirane **7** were determined using a similar strategy. The regioselectivity of aldehyde insertion was evident by ^1H NMR spectroscopy. The stereochemistry was determined (and the regioselectivity confirmed) by oxidation of the diastereomeric oxasilacyclopentanes **13** to the diols **17** and by comparison to reference compounds (eqs 9 and 10). The latter were prepared by reduction of the esters **18** and **19**, obtained by stereoselective syn[44] and anti[45] ester enolate aldol reactions.

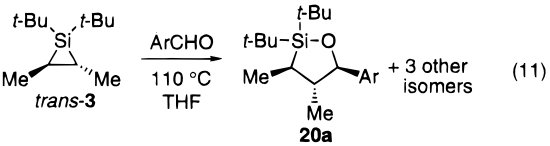




Ar= 2,6-di(*tert*-butyl)phenyl

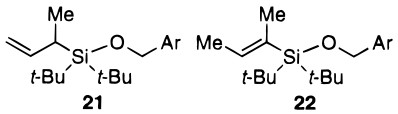
Other Aryl Aldehydes: Electronic Effects upon Insertion. If the assumption is made that the insertion reactions involve the silirane as nucleophile and aldehyde as electrophile, it is logical that electron-poor aldehydes should be better substrates for insertion than electron-rich ones. This straightforward analysis does not apply to other carbonyl compounds, however: formamides, notoriously poor electrophiles, undergo thermal insertion reactions whereas alkyl aldehydes do not.[23] To provide insight into the relationship between the aldehyde and formamide insertions, we examined the reactions of substituted aryl aldehydes with silirane *trans*-**3** under the thermal and catalyzed reaction conditions.

Heating *trans*-**3** with *p*-anisaldehyde or *p*-(trifluoromethyl)benzaldehyde at 110 °C afforded mixtures of insertion products **20** along with hydride transfer products **21** and **22**, favoring insertion over hydride transfer by a ratio of 65:35 by GC/MS in both cases (eq 11). The stereoselectivities observed for the oxasilacyclopentanes

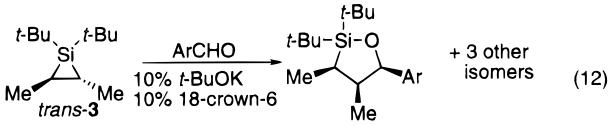


Ar = 4-$MeOC_6H_4$ **20a** : other isomers = 62 : 14 : 14 : 10 (29% yield)
Ar = 4-$(CF_3)C_6H_4$ **20a** : other isomers = 61 : 14 : 14 : 11 (31% yield)

20 (62:14:14:10 for R = OMe, 61:14:14:11 for R = CF_3) are similar to those obtained for benzaldehyde (Table 1).[46] Competition experiments between the different aldehydes establish a reactivity order of *p*-$CF_3C_6H_4CHO$ > C_6H_5CHO > *p*-$CH_3OC_6H_4CHO$.



The catalyzed reactions of substituted benzaldehydes proceed in significantly higher yield than the thermal reactions, and no hydride-transfer side products were obtained. The stereochemistries of the major products (**20d**) were proven unambiguously by methods analogous to those for **10d**.[47] As was observed for benzaldehyde, the catalyzed processes occurred with predominately inversion of stereochemistry. As was observed for the thermal insertions, the order of reactivity was *p*-$CF_3C_6H_4CHO$ > C_6H_5CHO > *p*-$CH_3OC_6H_4CHO$ (eq 12). Therefore, for both the thermal and catalyzed insertions, more electrophilic aldehydes undergo insertions faster.

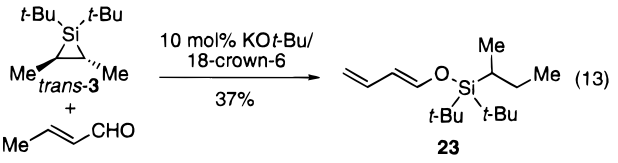


Ar = 4-$MeOC_6H_4$ **20d** : other isomers = 63 : 22 : 10 : 5 (55% yield)
Ar = 4-$(CF_3)C_6H_4$ **20d** : other isomers = 70 : 21 : 8 : 1 (71% yield)

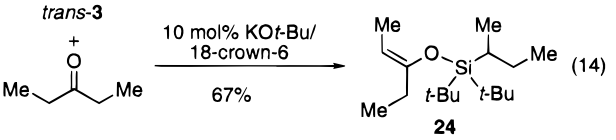
Enolizable Aldehydes and Ketones. Because strongly basic catalysts proved optimal for the insertion of benzaldehyde, it was expected that problems would be encountered upon attempted insertion of enolizable substrates. In accord with this prediction, treatment of silirane *trans*-**3** with crotonaldehyde and catalytic amounts of alkoxide (eq 13) provided the unstable dienol ether **23** in 37% yield as a single alkene isomer (by ^1H NMR

(41) TBSCl/$LiAlH_4$: Bloch, R.; Gilbert, L.; Girard, C. *Tetrahedron Lett.* **1988**, *29*, 1021−1024.
(42) $Me_4N(AcO)_3BH$: Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560−3578.
(43) $EtB(OMe)_2$/$NaBH_4$: Chen, K.; Goetz, E. H.; Prasad, K.; Repic, O.; Shapiro, M. J. *Tetrahedron Lett.* **1987**, *28*, 155−158.
(44) Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, *21*, 3975−3978.
(45) Heathcock, C. H.; Pirrung, M. C.; Montgomery, S. H.; Lampe, J. *Tetrahedron* **1981**, *37*, 4087−4095.

(46) The stereochemistries of the major isomers are assigned on the basis of the comparable selectivity and the striking similarities of the ^1H NMR spectra of the major isomers **20a** of the two substituted systems compared to that of **10a**. Because the reactions were low-yielding, no further attempts were made to prove the stereochemistry.
(47) The details are provided as Supporting Information.

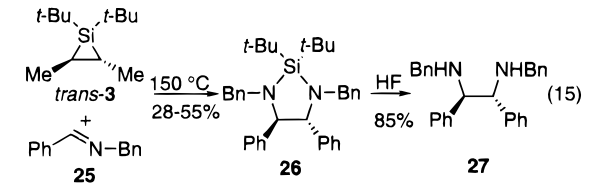


spectroscopy).[10] Similar products were observed with fluoride and chloride catalysis, although the yields were lower. Attempts to effect insertion under thermal conditions failed: heating siliranes with enolizable aldehydes such as crotonaldehyde and isobutyraldehyde led to decomposition and no insertion. When the catalyzed insertion was attempted with 3-pentanone (eq 14), the



silyl enol ether **24** was isolated as the *Z* stereoisomer (>95:5 by ^{1}H NMR spectroscopy). Isomerization occurred in $CDCl_3$ solution, resulting in a 1:1 mixture of (*E*)- and (*Z*)-alkenes, which allowed the stereochemical assignment of the kinetic enol ether **24** from spectroscopic data.[48] This result may be rationalized as attack of the thermodynamically preferred (*Z*)-enolate[49] to the silirane followed by protonation of the ring, in analogy to the methanolysis reactions (eq 2).

Reaction with Imines. Since aldehyde insertion lacked generality, the insertion of imines was investigated. Reactions of several imines such as $PhCHNCH_2Ph$ (**25**) with siliranes **3** and various catalysts failed to provide any identifiable products. Thermal conditions, however, led to a new product: heating the silirane *trans*-**3** and imine **25** to 150 °C (eq 15) afforded the silylene-protected diamine **26** (28−55% yield) in 90% diastereoselectivity (as determined by ^{1}H NMR spectroscopy). The stereochemistry of this product was tenta-

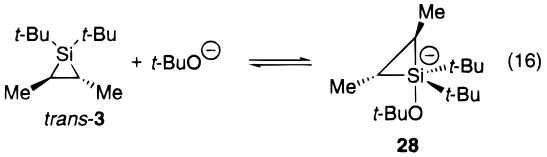


tively assigned as trans because ^{1}H and ^{13}C NMR spectroscopy indicated that the two *tert*-butyl groups were equivalent. To confirm this stereochemical assignment, the silyl group was removed with HF to afford the known 1,2-diamine **27**.[50−52] The mechanism for the formation of this product most likely involves the liberation of di-*tert*-butylsilylene[8,19] followed by reductive coupling of the imines.[53] A similar stereoselective reductive coupling of aldehydes by an isolable silylene was recently reported.[54,55]

Discussion

Although the mechanism of aldehyde insertion has not been elucidated in any detail, the stereochemical data presented here allows a working mechanism to be generated. The mechanistic picture for the thermal reaction is more difficult to evaluate because of the lack of stereochemical fidelity and low yields; the formation of products may occur by several different mechanisms operating simultaneously. The catalyzed insertion of aldehydes is a cleaner reaction and consequently lends itself more favorably to analysis.[21]

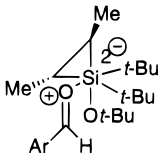
Because the insertion is catalyzed by Lewis bases, we favor a mechanism that involves the silirane as a Lewis acid. Gas phase experiments[56] demonstrate that the ring strain of silacyclobutanes renders the silicon atom electrophilic, because strain is released upon coordination of a fifth group to silicon.[56−58] Similar (and possibly enhanced) Lewis acidity would be expected for siliranes because they are even more strained.[17] We believe that an interaction occurs between the nucleophilic catalyst and the silirane as shown in eq 16 to provide pentacoordinate intermediate **28**.[59] No interaction has been



observed between the silirane *trans*-**3** and carbonyl compounds such as crotonaldehyde[60] and DMF by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy from −80 to 25 °C. Because of the severe steric constraints imposed by the two *tert*-butyl groups and the incoming *tert*-butoxide catalyst, formation of the pentacoordinate siliconate **28** is more likely than that of a hexacoordinate siliconate.

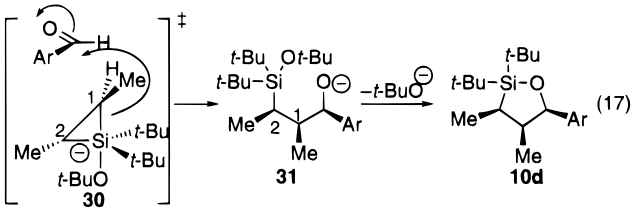
The next step in the mechanism is the formation of a new carbon−carbon bond, setting two stereogenic centers in the process. The nucleophilicity of the carbon atoms of the ring is enhanced in the ate complex **28** compared to the neutral silirane,[59] so this intermediate is the one that would attack the electrophilic carbonyl group of the aldehyde. Competition experiments demonstrated that electron-deficient aldehydes react faster than electron-rich ones, suggesting that the silirane behaves as a nucleophile in (or before) the rate-determining step. The insertion could proceed by prior coordination of the aldehyde or direct nucleophilic attack on free aldehyde. The prior-coordination manifold would require a six-coordinate intermediate such as **29**, which would suffer from significant steric destabilization. Alternatively, back-side S_E2 attack[61] upon free aldehyde (as shown for

(48) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066−1081.
(49) Fataftah, Z.; Kopka, I. E.; Rathke, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3959−3960.
(50) Mangeney, P.; Tejero, T.; Alexakis, A.; Grosjean, F.; Normant, J. *Synthesis* **1988**, 255−257.
(51) Enholm, E. J.; Forbes, D. C.; Holub, D. P. *Synth. Commun.* **1990**, *20*, 981−987.
(52) Further confirmation of the stereochemistry of **27** was obtained by reductive amination of the corresponding primary diamine with benzaldehyde.
(53) For reactions of silylenes with imines, see: (a) Weidenbruch, M.; Piel, H.; Peters, K.; von Schnering, H. G. *Organometallics* **1993**, *12*, 2881−2882. (b) Belzner, J.; Ihmels, H.; Pauletto, L.; Noltemeyer, M. *J. Org. Chem.* **1996**, *61*, 3315−3319.
(54) Jutzi, P.; Eikenberg, D.; Bunte, E.-A.; Möhrke, A.; Neumann, B.; Stammler, H.-G. *Organometallics* **1996**, *15*, 1930−1934.
(55) Belzner, J.; Ihmels, H.; Pauletto, L.; Noltemeyer, M. *J. Org. Chem.* **1996**, *61*, 3315−3319.
(56) Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480−481.
(57) Myers, A. G.; Kephart, S. E.; Chen, H. *J. Am. Chem. Soc.* **1992**, *114*, 7922−7923.
(58) Denmark, S. E.; Griedel, B. D.; Coe, D. M. *J. Org. Chem.* **1993**, *58*, 988−990.
(59) For a review covering penta- and hexacoordinate silicon compounds, see: Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448.
(60) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801−808.



29

30, eq 17) with inversion of configuration at the migrating carbon (C-1) would explain the observed stereochemistry at this stereocenter. The oxygen-bearing stereocenter, although set with only modest selectivity (2−6:1), is controlled by the distal stereocenter (C-2), not the proximal one (C-1, eq 17). The major products obtained



(17)

from both *cis*- and *trans*-**3** bear a 1,3-syn relationship (Table 1), indicating that the staggered transition states leading to the major products minimize interaction between the aryl moiety and the methyl group on C-2, as shown for **30**.[21] The final step involves cyclization of the alkoxide **31**, providing the observed product **10d** and regenerating the nucleophilic catalyst, or **31** could itself act as the catalyst in these reactions. The latter situation would explain why the stereoselectivity of insertion is roughly independent of catalyst employed.

Conclusion

In conclusion, siliranes undergo stereoselective and regioselective insertions of benzaldehyde to provide oxasilacyclopentane products. Whereas the thermal reaction (>100 °C) leads to extensive decomposition and sideproducts, the catalyzed variant (*t*-BuOK, <25 °C) proceeds more cleanly and with a high degree of inversion. Treatment with enolizable aldehydes leads to clean silyl enol ether formation. The working mechanism for the catalyzed insertion process entails addition of the catalyst to form a pentacoordinate siliconate intermediate followed by back-side electrophilic attack on the C−Si bond.

Experimental Section

General. General experimental details are provided as Supporting Information. Microanalyses were performed by Atlantic Microlab, Atlanta, GA. Analytical gas−liquid chromatography (GLC) was performed on a Hewlett-Packard 5890 Level 4 chromatograph, equipped with a split-mode capillary injection system and a flame ionization detector. Fused silica capillary columns (30 × 0.32 mm) wall-coated with DB-1 or DB-1701 (J&W Scientific) were used with helium as the carrier gas. All reactions were carried out under an atmosphere of nitrogen in glassware which had been flame-dried under a stream of nitrogen. Siliranes were stored and handled in an Innovative Technologies nitrogen atmosphere drybox. Solvents were dried and distilled prior to use.

(3-Deuterio-*sec*-butyl)di-*tert*-butylmethoxysilane (4). Boudjouk's procedure was employed, starting with *trans*-**3**, except that MeOD was employed in place of MeOH:[25] ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.58 (s, 3H), 1.20 (m, 1H), 1.13 (d, J = 7.0, 3H), 1.05 (s, 9H), 1.04 (s, 9H), 1.02 (m, 1H), 0.97 (d, J = 7.2, 3H); ^{2}H NMR (77 MHz, $CHCl_3$) δ 1.83; ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.2, 29.1, 29.0, 25.1 (t, $^1J_{CD}$ = 19.4), 22.2, 22.0, 20.4, 14.6, 14.0; HRMS (CI) m/z calcd for $C_{13}H_{30}DOSi$ $(M + H)^+$ 232.2208, found 232.2207.

(3-Deuterio-*sec*-butyl)di-*tert*-butylmethoxysilane (4′). Boudjouk's procedure was employed, starting with *cis*-**3**, except that MeOD was employed in place of MeOH:[25] ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.58 (s, 3H), 1.80 (m, 1H), 1.13 (d, J = 6.9, 3H), 1.05 (s, 9H), 1.04 (s, 9H), 1.02 (m, 1H), 0.97 (d, J = 7.3, 3H); ^{2}H NMR (77 MHz, $CHCl_3$) δ 1.17; ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.2, 29.1, 29.0, 25.0 (t, $^1J_{CD}$ = 19.7), 22.2, 22.0, 20.4, 14.5, 14.0.

(2-Deuteriocyclohexyl)di-*tert*-butylmethoxysilane (6). Boudjouk's procedure was employed, starting with **5**, except that MeOD was employed in place of MeOH:[25] ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.59 (s, 3H), 1.90 (m, 2H), 1.74 (m, 3H), 1.42 (m, 1H), 1.18 (m, 4H), 1.05 (s, 18H); ^{2}H NMR (77 MHz, $CHCl_3$) δ 1.42.

1,1-Di-*tert*-butyl-2-(1-butyl)silirane (7). To a cooled (−78 °C) slurry of lithium powder (obtained by washing a 30% lithium dispersion with 3 × 10 mL of hexanes to give 0.77 g, 111 mmol) in 10 mL of THF were added 1-hexene (10.0 mL, 175 mmol) and di-*tert*-butyldichlorosilane (3.8 mL, 18 mmol). The reaction mixture was stirred at 25 °C for 12 h. The supernatant was decanted, and the residual solids were washed with 2 × 10 mL of hexanes. The combined solutions were concentrated *in vacuo* to give an impure oil. Purification by bulb-to-bulb distillation afforded the product as a clear liquid (3.47 g, 86%): bp 72−73 °C (0.05 Torr); IR (thin film) 2958, 1470, 1364 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.63 (m, 1H), 1.56 (m, 1H), 1.43 (m, 1H), 1.33 (m, 3H), 1.13 (s, 9H), 1.04 (s, 9H), 0.90 (t, J = 7.1, 3H), 0.75 (m, 1H), 0.66 (dd, J = 12.1, 10.4, 1H), 0.05 (dd, J = 10.1, 8.8, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.7, 31.8, 30.7, 29.8, 22.6, 18.9, 18.1, 14.3, 13.9, 3.2; HRMS (CI) m/z calcd for $C_{14}H_{30}SiNH_4^+$ $(M + NH_4)^+$ 244.2462, found 244.2458.

Di-*tert*-butyl(2-hexyl)methoxysilane (8). To a 25 °C solution of **7** (0.33 g, 1.5 mmol) in 3 mL of THF were added KF (8 mg, 0.15 mmol) and MeOH (0.30 mL, 7.4 mmol).[25] The reaction mixture was stirred at 25 °C for 7 h and then concentrated *in vacuo*. Purification by flash chromatography (0:100−2:98 EtOAc:hexanes) afforded a clear oil (0.25 g, 65%) as a 93:7 ratio of **8** and **9** (as determined by ^{1}H NMR spectroscopy): IR (thin film) 2934, 1470, 1386, 1190, 1105 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 3.44 (s, 3H), 1.83 (m, 1H), 1.55 (m, 1H), 1.30 (m, 4H), 1.165 (m, 1H), 1.160 (d, J = 2.6, 3H), 1.13 (s, 18H), 0.93 (t, J = 7.3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.2, 32.2, 31.6, 29.2, 29.1, 22.8, 22.2, 22.1, 18.2, 15.1, 14.2; HRMS (CI) m/z calcd for $C_{15}H_{35}OSi$ $(M + H)^+$ 259.2458, found 259.2469. Anal. Calcd for $C_{15}H_{34}OSi$: C, 69.69; H, 13.26. Found: C, 69.43; H, 13.09.

Di-*tert*-butyl(1-hexyl)methoxysilane (9). Silirane **7** (0.64 g, 2.8 mmol) and methanol (2.0 mL, 49 mmol) were added to a clean flame-dried bomb, which was then cooled to −78 °C and evacuated. The bomb was sealed under vacuum, and the reaction mixture was heated in a 95 °C oil bath for 32 h. The mixture was cooled, and ^{1}H NMR spectroscopy of the unpurified mixture indicated an 87:13 ratio of **9**:**8**. Purification by flash chromatography (hexanes) afforded the product as a clear oil (0.22 g, 30%): IR (thin film) 2931, 1470, 1189, 1107 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 3.45 (s, 3H), 1.57 (m, 2H), 1.32 (m, 6H), 1.10 (s, 18H), 0.92 (t, J = 6.5, 3H), 0.77 (m, 2H); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.58 (s, 3H), 1.48 (m, 1H), 1.30 (m, 1H), 1.00 (m, 6H), 1.00 (s, 18H), 0.89 (t, J = 6.9, 3H), 0.73 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.6, 34.1, 31.5, 28.3, 24.5, 22.7, 21.4, 14.1, 10.6; HRMS (CI) m/z calcd for $C_{15}H_{35}OSi$ $(M + H)^+$ 259.2458, found 259.2458. Anal. Calcd for $C_{15}H_{34}OSi$: C, 69.69; H, 13.26. Found: C, 69.47; H, 13.24.

3,4-Dimethyl-5-phenyl-2,2-di-*tert*-butyl-1-oxa-2-silacyclopentane (10a−d) from *cis*-3: Representative Procedure for Catalyzed Insertion. To a cooled (−78 °C) solution of *cis*-**3** (425 mg, 2.14 mmol) in 3 mL of THF was added benzaldehyde (0.435 mL, 4.30 mmol) followed by potassium *tert*-butoxide (24 mg, 0.21 mmol) and 18-crown-6 (58 mg, 0.22

(61) Electrophilic attack of pentacoordinate silanes with electrophiles can occur with either retention or inversion of configuration: Tamao, K.; Yoshida, J.-i.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics* **1982**, *1*, 355−368.

mmol). The reaction mixture was stirred for 30 min at −78 °C and then 12 h at 22 °C. To the mixture was added 2 mL of MeOH, and the mixture was concentrated *in vacuo*. GC of the unpurified product showed a mixture of four diastereomers (**10a-d**) in the ratio of 69.2:29.6:0.3:0.8. Purification by flash chromatography (5:95 CH_2Cl_2:hexanes) yielded the products as a clear oil (477 mg, 73%). The diastereomeric oxasilacyclopentanes were separated by careful flash chromatography.

3,4-Dimethyl-5-phenyl-2,2-di-*tert*-butyl-1-oxa-2-silacyclopentane (10a−d) from *trans*-3: Representative Procedure for Thermal Insertion. To a solution of *trans*-**3** (68 mg, 0.34 mmol) in 5 mL of THF was added benzaldehyde (70.0 μL, 0.69 mmol). The reaction mixture was brought to reflux for 16 h. To the reaction mixture was added 2 mL of MeOH, and the mixture was concentrated *in vacuo*. GC of the unpurified product showed a mixture of four diastereomers (**10a**−**d**) in the ratio of 77.1:6.1:8.3:8.5. Purification by flash chromatography (5:95 CH_2Cl_2:hexanes) yielded a diastereomeric mixture of products as a clear oil (52 mg, 50%).

Oxasilacyclopentane 10a: IR (thin film) 3117, 1492, 1472, 1386, 1363, 1063 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38−7.25 (m, 5H), 4.24 (d, J = 10.0, 1H), 1.62 (m, 1H), 1.25 (d, J = 7.4, 3H), 1.19 (s, 9H), 1.09 (s, 9H), 1.05 (m, 1H), 0.88 (d, J = 6.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 128.2, 127.4, 126.6, 86.7, 49.4, 28.2, 27.9, 26.0, 21.5, 21.4, 15.2, 12.7; HRMS (EI) m/z calcd for $C_{15}H_{23}OSi$ $(M - C_4H_9)^+$ 247.1517, found 247.1522. Anal. Calcd for $C_{19}H_{32}OSi$: C, 74.93; H, 10.59. Found: C, 74.69; H, 10.68.

Oxasilacyclopentane 10b: IR (thin film) 3117, 1473, 1387, 1363, 1072 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29−7.20 (m, 5H), 5.26 (d, J = 8.8, 1H), 2.40 (m, 1H), 1.26 (d, J = 7.4, 3H), 1.17 (s, 9H), 1.15 (s, 9H), 1.15 (m, 1H), 0.61 (d, J = 7.1, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.8, 127.7, 127.5, 126.9, 83.4, 44.0, 29.1, 28.6, 24.2, 22.6, 20.6, 17.5, 14.2; HRMS (EI) m/z calcd for $C_{15}H_{23}OSi$ $(M - C_4H_9)^+$ 247.1517, found 247.1517. Anal. Calcd for $C_{19}H_{32}OSi$: C, 74.93; H, 10.59. Found: C, 74.86; H, 10.64.

Oxasilacyclopentane 10c: IR (thin film) 2962, 1471, 1387, 1363, 1004 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21−7.40 (m, 5H), 4.38 (d, J = 10.5, 1H), 2.04 (m, 1H), 1.54 (m, 1H), 1.19 (d, J = 8.1, 3H), 1.15 (s, 9H), 1.14 (s, 9H), 0.78 (d, J = 6.8, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 128.2, 127.4, 126.6, 84.5, 45.4, 28.7, 28.4, 22.1, 20.8, 20.6, 12.3, 11.0; HRMS (EI) m/z calcd for $C_{15}H_{23}OSi$ $(M - C_4H_9)^+$ 247.1517, found 247.1513. Anal. Calcd for $C_{19}H_{32}SiO$: C, 74.93; H, 10.59. Found: C, 74.93; H, 10.56.

Oxasilacyclopentane 10d: mp 63−64 °C; IR (KBr) 2942, 1476, 1388, 1364, 1102, 1056, 1019 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.17−7.34 (m, 5H), 5.09 (d, J = 5.0, 1H), 4.43 (d-quintet, J = 5.0, 7.5, 1H), 1.89 (q, J = 7.9, 1H), 1.22, (d, J = 7.8, 3H), 1.17 (s, 9H), 1.10 (s, 9H), 0.48 (d, J = 7.5, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.7, 127.9, 126.3, 125.6, 81.9, 42.7, 29.1, 28.4, 22.8, 22.3, 20.7, 12.2, 10.8. Anal. Calcd for $C_{19}H_{32}SiO$: C, 74.93; H, 10.59. Found: C, 74.68; H, 10.50.

1-(Benzyloxy)-1-(2-hexenyl)di-*tert*-butylsilane (12a): IR (thin film) 3026, 1470, 1384, 1110 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35−7.21 (m, 5H), 5.55 (m, 1H), 5.35 (m, 1H), 4.91 (s, 2H), 1.93 (q, J = 7.1, 2H), 1.78 (d, J = 7.0, 2H), 1.32 (q, J = 7.4, 2H), 1.06 (s, 18H), 0.86 (t, J = 7.3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 129.9, 128.1, 126.7, 126.4, 125.8, 66.1, 35.0, 28.2, 22.8, 21.7, 16.8, 13.8; HRMS (CI) m/z calcd for $C_{21}H_{35}OSi$ $(M - H)^+$ 331.2457, found 331.2465. Anal. Calcd for $C_{21}H_{36}OSi$: C, 75.84; H, 10.91. Found: C, 75.91; H, 10.84.

1-(Benzyloxy)-2-(1-hexenyl)di-*tert*-butylsilane (12b): IR (thin film) 3061, 1470, 1382, 1114 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39−7.33 (m, 4H), 7.24 (m, 1H), 5.76 (s, 1H), 5.48 (s, 1H), 4.98 (s, 2H), 2.18 (t, J = 7.9, 2H), 1.48 (m, 2H), 1.30 (m, 2H), 1.09 (s, 18H), 0.88 (t, J = 7.3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 141.6, 128.1, 126.7, 126.4, 125.6, 66.0, 35.8, 30.7, 28.6, 22.8, 21.2, 14.0; HRMS (CI) m/z calcd for $C_{21}H_{35}OSi$ $(M - H)^+$ 331.2457, found 331.2449. Anal. Calcd for $C_{21}H_{36}OSi$: C, 75.84; H, 10.91. Found: C, 75.93; H, 10.98.

1-(Benzyloxy)-1-(1-hexenyl)di-*tert*-butylsilane (12c): IR (thin film) 3065, 1615, 1469, 1382, 1110 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38−7.32 (m, 4H), 7.25 (m, 1H), 6.22 (dt, J = 18.7, 6.4, 1H), 5.57 (d, J = 19.1, 1H), 4.91 (s, 2H), 2.16 (q, J = 6.8, 2H), 1.35 (m, 4H), 1.04 (s, 18H), 0.90 (t, J = 7.2, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.0, 141.8, 128.1, 126.6, 125.7, 122.0, 66.0, 36.9, 30.9, 28.1, 22.2, 20.8, 13.9; HRMS (CI) m/z calcd for $C_{17}H_{27}OSi$ $(M - C_4H_9)^+$ 275.1831, found 275.1836. Anal. Calcd for $C_{21}H_{36}OSi$: C, 75.84; H, 10.91. Found: C, 75.62; H, 10.84.

4-(1-Butyl)-5-phenyl-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (13). To a cooled (−78 °C) solution of silirane **7** (0.17 g, 0.76 mmol) in 2 mL of THF were added benzaldehyde (0.24 mL, 2.3 mmol), potassium *tert*-butoxide (8.0 mg, 0.07 mmol), and 18-crown-6 (0.02 g, 0.08 mmol). The mixture was stirred at 25 °C for 16 h, and then 0.5 mL of MeOH was added. The mixture was concentrated *in vacuo* and purified by flash chromatography (3:97 EtOAc:hexanes) to afford the product as a clear oil (0.14 g, 55%) as a mixture of four isomers (two pairs of diastereomers *anti*-**13**/*syn*-**13** and two others in the ratio 38:47:9:6, respectively, determined by GC analysis).

***anti*-13:** IR (thin film) 3031, 1470, 1364, 1004 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39−7.21 (m, 5H), 4.29 (d, J = 10.2, 1H), 1.78 (m, 1H), 1.36 (m, 2H), 1.19 (dd, J = 14.8, 7.2, 1H), 1.14 (s, 9H), 1.09 (m, 4H), 1.07 (s, 9H), 0.81 (t, J = 7.1, 3H), 0.53 (dd, J = 14.8, 11.9, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 128.2, 127.4, 126.8, 86.5, 47.8, 33.0, 30.0, 27.8, 27.7, 22.7, 20.8, 20.2, 14.1, 13.3; HRMS (EI) m/z calcd for $C_{21}H_{36}OSi$ (M^+) 332.2537, found 332.2527. Anal. Calcd for $C_{21}H_{36}OSi$: C, 75.84; H, 10.91. Found: C, 75.78; H, 11.00.

***syn*-13:** IR (thin film) 3025, 1471, 1364, 1021 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32−7.26 (m, 4H), 7.20 (m, 1H), 5.17 (d, J = 6.3, 1H), 2.40 (m, 1H), 1.21 (m, 1H), 1.13 (s, 9H), 1.08 (s, 9H), 1.07 (m, 2H), 0.93 (m, 4H), 0.82 (dd, J = 15.5, 2.8, 1H), 0.74 (t, J = 7.3, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 127.8, 126.5, 126.2 , 83.3, 42.0, 30.4, 30.2, 28.6, 28.1, 22.4, 21.7, 19.7, 14.0, 10.7; HRMS (EI) m/z calcd for $C_{17}H_{27}OSi$ $(M - C_4H_9)^+$ 275.1832, found 275.1830. Anal. Calcd for $C_{21}H_{36}OSi$: C, 75.84; H, 10.91. Found: C, 75.66; H, 10.84.

Oxidation of Oxasilacyclopentanes: General Procedure. To a cooled (0 °C) slurry of KH (0.066 g, 1.65 mmol, 30% dispersion washed with 3 × 1 mL of hexanes prior to use) in 1.9 mL of DMF was added *tert*-butyl hydroperoxide (0.193 g, 90%, 1.93 mmol) dropwise by syringe. After the solution was warmed to 25 °C, a solution of **10a** (0.042 g, 0.140 mmol) in 1 mL of DMF was added dropwise by syringe followed by TBAF (0.180 g, 0.690 mmol, hydrate, lyophilized from benzene). The reaction mixture was heated at 70 °C for 8 h. After the solution was cooled to 25 °C, $Na_2S_2O_3$ (0.60 g) was added. After 0.5 h, the solvent was removed *in vacuo*. The resultant oily solid was partitioned between 5 mL of 0.5 M $Na_2S_2O_3$ and 10 mL of Et_2O. The layers were separated, and the aqueous layer was extracted with 3 × 5 mL of Et_2O. The combined organic layers were washed with 3 × 1 mL of H_2O and 2.5 mL of brine, dried ($MgSO_4$),and concentrated *in vacuo* to afford a yellow oil. The oil was purified by flash chromatography (15:85 EtOAc:hexanes) to yield the product as a white solid (17 mg, 68%). All physical and spectroscopic data were identical to those of the reference compound.

(1*R,2*R**,3*R**)-1-Phenyl-2-methyl-1,3-butanediol (14a).** A solution of *anti*-**16** (0.305 g, 1.71 mmol) in 10 mL of DMF was treated with *tert*-butyldimethylsilyl chloride (0.39 g, 2.57 mmol) and imidazole (0.23 g, 3.4 mmol) for 12 h. The reaction mixture was diluted with 20 mL of ether, washed with 4 × 5 mL of water, reduced to an oil, and redissolved in CH_2Cl_2. The resultant solution was filtered through a cotton plug and reduced *in vacuo* to yield a clear oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (m, J = 6.3, 2H), 7.59−7.43 (m, 3H), 4.11 (m, 1H), 3.48 (m, 1H), 1.21 (d, J = 7.0, 3H), 1.08 (d, J = 7.0, 3H), 0.68 (s, 9H), 0.01 (s, 3H), −0.16 (s, 3H). The major alcohol isomer underwent quantitative conversion to the silyl ether. The silylated intermediate was dissolved in 10 mL of ether and cooled to −78 °C before being treated with lithium aluminum hydride (100 mg, 2.57 mmol).[41] The reaction mixture was slowly warmed to 22 °C over a period of 2 h before being treated with water (4 drops), KOH (4 drops, 4 N, aqueous), and water (12 drops). The resultant white precipitate was filtered, and the ether solution was stirred with HCl (3 N, aqueous) to cleave the silyl ether. The organic layer was recovered and the aqueous layer extracted twice with ether. Reduction *in vacuo* and purification by flash chromatography (40:60 EtOAc:hexanes) yielded the desired product as the

major isomer (0.237 g, 77%, mixture of isomers, 70% **14a**): IR (KBr) 3383, 3033, 1454, 1376, 1314, 1230, 1128, 1089 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38−7.28 (m, 5H), 4.52 (d, J = 7.4, 1H), 3.90 (m, 1H) 3.71 (bs, 1H), 3.46 (bs, 1H), 1.83 (m, 1H), 1.24 (d, J = 6.0, 3H), 0.54 (d, J = 7.2, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 128.5, 128.0, 127.1, 81.2, 73.3, 46.4, 21.8, 13.5; HRMS (FAB) m/z calcd $(M + H)^+$ 181.1228, found 181.1225. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H 8.95. Found: C, 73.17; H, 8.92.

(1*S,2*R**,3*R**)-1-Phenyl-2-methyl-1,3-butanediol (14b).** To a mixture of acetic acid (2 mL) and acetonitrile (2 mL, freshly distilled) was added tetramethylammonium triacetoxyborohydride (0.875 g, 3.33 mmol). The solution was stirred at 25 °C for 1.5 h. The mixture was cooled to −40 °C before a solution of *anti*-**16** (0.075 g, 0.42 mmol) in acetonitrile (0.5 mL) was added. The solution was stirred and for 18 h at −40 °C.[42] The mixture was treated with 5 mL of sodium potassium tartrate solution (saturated aqueous), warmed to 22 °C, and partitioned between H_2O (10 mL) and CH_2Cl_2 (10 mL). The organic layer was recovered, and the aqueous layer was extracted with 2 × 10 mL of CH_2Cl_2. The combined organic layers were filtered through a cotton plug and reduced *in vacuo* to a clear oil. Flash chromatography yielded the product as a white solid (0.037 g, 61% based on 81:19 mixture of *anti*-**16**:*syn*-**16**): mp 110−111 °C; IR (KBr) 3406, 3301, 2968, 1459, 1348, 1205, 1125, 1096 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26−7.36 (m, 5H), 5.12 (d, J = 1.8, 1H), 3.83 (quintet, J = 6.3, 1H) 3.15 (bs, 1H), 2.56 (bs, 1H), 1.84 (m, 1H), 1.31 (d, J = 6.2, 3H), 0.82 (d, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 128.0, 127.0, 126.1, 75.0, 70.9, 45.5, 21.9, 11.5; HRMS (CI) m/z calcd for $C_{11}H_{20}NO_2$ $(M + NH_4)^+$ 198.1494, found 198.1499. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H 8.95. Found: C, 73.03 ; H, 8.86.

(1*S,2*S**,3*R**)-1-Phenyl-2-methyl-1,3-butanediol (14c).** The procedure described for **14a** was employed to provide **14c**: IR (thin film) 3342, 2972, 2894, 1455, 1380, 1305, 1202, 1105, 1072, 1021, 926, 891, 757, 702 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26−7.36 (m, 5H), 4.71 (d, J = 6.6, 1H), 4.04 (m, 1H) 3.14 (bs, 1H), 2.75 (bs, 1H), 1.95 (m, 1H), 1.22 (d, J = 6.6, 3H), 0.83 (d, J = 7.2, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 128.4, 127.6, 126.4, 78.1, 69.2, 44.5, 19.4, 12.1; HRMS (EI) m/z calcd for $C_{11}H_{16}O_2$ (M^+) 180.1150, found 180.1156. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.23; H, 9.03.

(1*R,2*S**,3*R**)-1-Phenyl-2-methyl-1,3-butanediol (14d).** To a stirred solution of *syn*-**16** (199 mg, 1.12 mmol) in 20% MeOH/THF (11 mL total, cooled to −78 °C) was added diethylmethoxyborane (0.612 mL, 1.23 mmol). After 20 min, sodium borohydride (0.047 g, 1.2 mmol) was added and the mixture was stirred at −78 °C for 3 h.[43] The reaction was quenched with HOAc (1 mL), warmed to 25 °C, diluted in 20 mL of ether, and washed with 4 × 10 mL of $NaHCO_3$ (saturated aqueous). The ether layer was reduced *in vacuo* and the resultant material was dissolved in CH_2Cl_2 before being filtered through a cotton plug. Reduction *in vacuo* and purification by flash chromatography (12:88 EtOAc:hexanes) yielded the product as a clear oil (0.012 g, 60%, >95% isomeric purity by GC and ^1H NMR): IR (thin film) 3355, 2975, 1453, 1380, 1199, 1072 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36−7.24 (m, 5H), 5.04 (d, J = 1.7, 1H), 3.83 (quintet, J = 6.3, 1H), 3.15 (bs, 1H), 2.56 (bs, 1H), 1.84 (m, 1H), 1.31 (d, J = 6.2, 3H), 0.82 (d, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 128.0, 127.0, 126.1, 75.0, 70.9, 45.5, 21.9, 11.5; HRMS (CI) m/z calcd for $C_{11}H_{17}O_2$ $(M + H)^+$ 181.1228, found 181.1225. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.09; H, 9.04.

***p*-Nitrobenzylidene Acetal 15.** To a solution of diol **14d** (0.028 g, 0.16 mol) in 1.6 mL of benzene was added *p*-nitrobenzaldehyde (0.026 g, 0.171 mmol) followed by 4 Å molecular sieves. The mixture was heated to reflux for 12 h before being cooled, filtered, and reduced *in vacuo*. Purification by flash chromatography (4:96−5:95 EtOAc:hexanes) yielded the product as a colorless crystalline solid. Crystals suitable for X-ray crystallography[20] were obtained by slow crystallization from 10−20% CH_2Cl_2 in hexanes: mp 125−127 °C; IR (KBr) 2978, 1609, 1529, 1396, 1350, 1158, 1066 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 8.1, 2H), 7.79 (d, J = 8.8, 2H), 7.39−7.26 (m, 5H), 5.82 (s, 1H), 5.12 (d, J = 1.8, 1H), 4.33 (qd, J = 6.2, 2.1, 1H), 1.85 (m, 1H), 1.33 (d, J = 6.6, 3H), 0.77 (d, J = 7, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 148.6, 145.9, 140.7, 128.5, 127.8, 127.4, 125.6, 123.7, 100.3, 82.5, 77.3, 38.5, 18.9, 5.8; HRMS (CI) m/z calcd for $C_{18}H_{20}NO_4$ $(M + H)^+$ 314.1392, found 314.1407. Anal. Calcd for $C_{18}H_{19}O_4N$: C, 69.00; H, 6.11. Found: C, 68.96; H, 6.17.

(1*R,2*S**)-1-Phenyl-2-(1-butyl)-1,3-propanediol (*syn*-17).** To a cooled (−78 °C) solution of **18** (0.34 g, 1.4 mmol) in 4 mL of THF was added $LiAlH_4$ (85 mg, 2.2 mmol), and the mixture was stirred for 12 h at 25 °C. The reaction was then quenched with 5 mL of sodium potassium tartrate solution (saturated aqueous), then 20 mL of water was added, the organic layer was separated, and the aqueous layer was washed with ether (2 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl (20 mL), dried over Na_2SO_4, and concentrated *in vacuo* to give an impure yellow liquid. Purification by flash chromatography (40:60 EtOAc:hexanes) afforded a clear viscous oil (0.27 g, 92%): IR (thin film) 3355, 3063, 1454, 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35−7.33 (m, 4H), 7.28 (m, 1H), 5.00 (t, J = 3.5, 1H), 3.72 (t, J = 4.6, 2H), 3.00 (d, J = 3.7, 1H), 2.41 (t, J = 4.6, 1H), 1.93 (m, 1H), 1.24 (m, 6H), 0.83 (t, J = 7.2, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 128.2, 127.3, 126.2, 77.2, 64.1, 46.1, 29.6, 24.6, 22.8, 13.9; HRMS (CI) m/z calcd for $C_{13}H_{20}O_2$ (M^+) 208.1464, found 208.1468. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.76; H, 9.67.

(1*R,2*R**)-1-Phenyl-2-(1-butyl)-1,3-propanediol (*anti*-17).** This compound was prepared in a manner similar to that of *syn*-**17**: mp 39.0−40.0 °C; IR (thin film) 3337, 3030, 1454, 1026 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36−7.24 (m, 5H), 4.61 (dd, J = 7.0, 2.6, 1H), 3.91 (d, J = 3.3, 1H), 3.73 (m, 1H), 3.59 (m, 2H), 1.75 (m, 1H), 1.19 (m, 6H), 0.80 (t, J = 6.9, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 128.2, 127.4, 126.4, 79.0, 64.5, 46.1, 29.1, 27.7, 22.7, 13.8; HRMS (CI) m/z calcd for $C_{13}H_{21}O_2$ $(M + H)^+$ 209.1542, found 209.1542. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.73; H, 9.65.

Catalyzed Insertion of Anisaldehyde: 2,2-Di-*tert*-butyl-3,4-dimethyl-5-(4-methoxyphenyl)-1-oxa-2-silacyclopentane (20d, Ar = 4-MeOC$_6$H$_4$). Anisaldehyde (530 mg, 3.9 mmol) was added to *trans*-**3** (515 mg, 2.60 mmol) and 18-crown-6 (79 mg, 0.30 mmol) in 10 mL of THF at −78 °C. Potassium *tert*-butoxide (67 mg, 0.60 mmol) was added. The reaction mixture was stirred for 12 h at 22 °C. The reaction mixture was reduced *in vacuo*, yielding a turbid orange-brown oil. GC-MS of the unpurified product gave a diastereomeric distribution of oxasilacyclopentanes as 5:10:22:63. Purification by flash chromatography (3:97 EtOAc:hexane) gave the major product[47] (**20d**, Ar = 4-$MeOC_6H_4$) as a white solid and a mixture of the three other isomers as an oil (**20d**, Ar = 4-$MeOC_6H_4$, 201 mg; mixture, 275 mg, 55% combined). **20d**, Ar = 4-$MeOC_6H_4$: mp 97−98 °C; IR (KBr) 2857, 1612, 1513 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, J = 8.8, 2H), 6.86 (d, J = 8.7, 2H), 5.05 (d, J = 4.8, 1H), 3.79 (s, 3H), 2.38 (tq, J = 7.6, 5.1, 1H), 1.88 (q, J = 7.9, 1H), 1.21 (d, J = 7.6, 3H), 1.17 (s, 9H), 1.10 (s, 9H), 0.48 (d, J = 7.6, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.1, 134.9, 126.6, 113.3, 81.6, 55.2, 42.8, 29.1, 28.4, 22.8, 22.3, 20.7, 12.3, 10.8; HRMS (CI) m/z calcd for $C_{20}H_{34}O_2Si$ (M^+) 334.2328, found 334.2320. Anal. Calcd for $C_{20}H_{34}O_2Si$: C, 71.80; H, 10.24. Found: C, 71.65; H, 10.17.

Catalyzed Insertion of 4-(Trifluoromethyl)benzaldehyde. 4-(Trifluoromethyl)benzaldehyde (820 mg, 4.71 mmol) was added to *trans*-**3** (623 mg, 3.14 mmol) and 18-crown-6 (82 mg, 0.31 mmol) in 12.5 mL of THF at −78 °C. To the mixture was added potassium *tert*-butoxide (89 mg, 0.79 mmol). The reaction mixture was stirred for 12 h at 22 °C. The reaction mixture was reduced *in vacuo*, yielding a turbid, colorless oil. GC of the unpurified product gave a diastereomeric distribution of 1:8:21:70. Purification by flash chromatography (0:100−5:95 CH_2Cl_2:hexane) gave the major product[47] as a white solid and a mixture of the three other isomers as an oil (**20d**, Ar = 4-$(CF_3)C_6H_4$, 554 mg; minor isomers, 272 mg, 71% combined). **20d**, Ar = 4-$(CF_3)C_6H_4$: mp 55−57 °C; IR (thin film) 2969, 1619, 1475, 1126 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.1, 2H), 7.42 (d, J = 8.0, 2H), 5.12 (d, J = 4.9, 1H), 2.49 (m, 1H), 1.92 (quintet, J = 7.8, 1H), 1.22 (d, J = 7.7, 3H), 1.17 (s, 9H), 1.10 (s, 9H), 0.46 (d, J = 7.5, 3H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 147.1, 128.7 (q, $^2J_{CF}$ = 33), 125.9, 124.4 (q, $^1J_{CF}$ = 271), 124.9, 81.4, 42.6, 29.0, 28.3, 22.9, 22.3, 20.7, 12.1, 10.7. Anal. Calcd for $C_{20}H_{30}F_3OSi$: C, 64.48; H, 8.39. Found: C, 64.44; H, 8.41.

Thermal Insertion of Anisaldehyde (eq 11). To a bomb were added *trans*-**3** (135 mg, 0.680 mmol) and THF (1 mL). The solution was cooled to −78 °C, and anisaldehyde (102 mg, 0.750 mmol) was added. The solution was degassed (freeze, pump, thaw ×2) and then heated at 110 °C for 24 h. The reaction mixture was reduced *in vacuo*, and then purified by flash chromatography (30:70 CH_2Cl_2:hexane), yielding the four oxasilacyclopentane isomers (66 mg, 29%) and two isomeric silanes **21** and **22** (61 mg, 27%). GC-MS of the unpurified product gave a mixture (62:14:14:10) of oxasilacyclopentanes **20**. GC-MS indicated a diastereomeric mixture (82:18) of alkenes (**21**:**22**, Ar = 4-$MeOC_6H_4$). Because of the difficulty in isolating pure stereoisomers of oxasilacyclopentanes, the stereochemistry of the products was assigned by analogy to the benzaldehyde experiments.[46]

4,4-Di-*tert*-butyl-6-(4-methoxyphenyl)-3-methyl-4-sila-5-oxa-1-hexene (21, Ar = 4-$MeOC_6H_4$): IR (thin film) 3075, 1614, 1513, 1247, 1096 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 9.6, 2H), 6.88 (d, J = 9.6, 2H), 6.21 (m, 1H), 4.91 (m, 4H), 3.79 (s, 3H), 2.27 (m, 1H), 1.29 (d, J = 6.4, 3H), 1.10 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 142.0, 133.7, 127.0, 113.6, 110.9, 65.5, 55.2, 28.9, 28.6, 26.0, 22.7, 21.0, 14.4; HRMS (CI) m/z calcd for $C_{20}H_{33}O_2Si$ $(M - H)^+$ 333.2249, found 333.2243. Anal. Calcd for $C_{20}H_{34}O_2Si$: C, 71.80; H, 10.24. Found: C, 71.65; H, 10.15.

Thermal Insertion of 4-(Trifluoromethyl)benzaldehyde. A similar procedure was used as described above. Because of the difficulty in isolating pure stereoisomers of oxasilacyclopentanes, the stereochemistry of the products was assigned by analogy to the benzaldehyde experiments.[46] The side product **21**, Ar = 4-$(CF_3)C_6H_4$, was isolated from the reaction mixture: ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0, 2H), 7.48 (m, 2H), 6.17 (ddd, J = 17.3, 10.4, 6.9, 1H), 5.03 (s, 2H), 4.95 (m, 2H), 2.28 (m, 1H), 1.29 (d, J = 7.6, 3H), 1.11 (s, 9H), 1.08 (s, 9H); HRMS (CI) m/z calcd for $C_{20}H_{31}OSiF_2$ $(M - F)^+$ 353.2112, found 353.2108.

Di-*tert*-butyl-*sec*-butyl-1,3-(butadienyloxy)silane (23). To a solution of *trans*-**3** (200 mg, 1.0 mmol), 18-crown-6 (66 mg, 0.25 mmol), and 2 mL of THF was added crotonaldehyde (90.0 μL, 1.1 mmol) followed by potassium *tert*-butoxide (11 mg, 0.1 mmol) at −78 °C. The solution was stirred at −78 °C for 3 h, allowed to warm to 22 °C, and stirred for 17 h. The reaction mixture was concentrated *in vacuo* and then partitioned between CH_2Cl_2 (30 mL) and water (10 mL). The aqueous layer was washed with 2 × 50 mL of CH_2Cl_2. The combined organic layers were filtered through Na_2SO_4/glass wool and reduced *in vacuo* to yield a brown, turbid oil. Purification by flash chromatography (hexane) yielded a clear, colorless oil (100 mg, 37%, >95:5 *E*:*Z* by ^1H NMR spectroscopy): IR (thin film) 2965, 1645, 1195, 1012 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.69 (d, J = 11.6, 1H), 6.25 (td, J = 16.9, 10.7, 1H), 5.74 (t, J = 11.4, 1H), 4.98 (m, J = 16.7, 1H), 4.80 (dd, J = 10.3, 1.1, 1H), 1.84 (m, 1H), 1.27 (m, 1H), 1.15 (d, J = 7.3, 3H), 1.073 (s, 9H), 1.071 (s, 9H), 1.11 (m, 1H), 0.98 (t, J = 8.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 133.6, 113.6, 111.3, 28.8, 28.7, 25.4, 22.1, 22.0, 20.9, 14.4, 14.0; HRMS (CI) m/z calcd for $C_{16}H_{32}OSi$ (M^+) 268.2222, found 268.2227.

Di-*tert*-butyl-*sec*-butyl-3-ethyl-2-(propenyloxy)silane (24). To a cooled (−78 °C), stirring solution of *trans*-**3** (120 mg, 0.60 mmol), 18-crown-6 (40.0 mg, 0.15 mmol), and 1.2 mL of THF was added 3-pentanone (96 μL, 0.90 mmol) followed by potassium *tert*-butoxide (7 mg, 0.06 mmol). The solution was stirred for 18 h at 22 °C and then reduced *in vacuo*. The resulting turbid oil was purified by flash chromatography (hexane), yielding a clear, colorless oil (115 mg, 67%, >95:5 *Z*:*E* by ^1H NMR spectroscopy): IR (thin film) 2968, 1674, 1194, 1069 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 4.41 (m, 1H), 2.1 (m, 2H), 1.96 (m, 1H), 1.71 (d, J = 6.7, 3H), 1.23 (m, 1H), 1.18 (d, J = 7.6, 3H), 1.16 (s, 9H), 1.14 (s, 9H), 1.08 (m, 1H), 0.98 (td, J = 7.5, 0.9, 3H), 0.95 (t, J = 7.2, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 153.4, 98.9, 29.5, 29.4, 29.3, 26.0, 24.2, 22.8, 22.4, 14.9, 14.2, 12.0, 11.3; HRMS (FAB) m/z calcd for $C_{17}H_{37}OSi$ $(M + H)^+$ 285.2613, found 285.2611. Anal. Calcd for $C_{17}H_{36}OSi$: C, 71.76; H, 12.75. Found: C, 71.88; H, 12.85.

2,5-Dibenzyl-3,4-diphenyl-2,5-diaza-1,1-di-*tert*-butyl-1-silacyclopentane (26). To a bomb were added *trans*-**3** (200 mg, 1.0 mmol) and *N*-benzylphenylimine **25**[62] (430 mg, 2.2 mmol). The reaction mixture was degassed (freeze, pump, thaw ×2) and heated to 150 °C for 20 h, yielding a yellow oil. The reaction mixture was purified by flash chromatography (5:95 CH_2Cl_2:hexane), yielding a yellow oil (150 mg, 28%, anti:syn >10:1 by ^1H NMR spectroscopy): IR (thin film) 3062, 1602, 1069 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.0 (m, 10H), 6.98 (m, 6H), 6.89 (m, 4H), 4.23 (s, 2H), 4.19 (d, J = 15.5, 2H), 4.11 (d, J = 15.5, 2H), 1.37 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.5, 140.4, 129.1, 128.2, 127.4, 127.2, 126.5, 125.5, 74.2, 51.3, 29.4, 24.2; HRMS (CI) m/z calcd for $C_{36}H_{45}N_2Si$ $(M + H)^+$ 533.3352, found 533.3332. Anal. Calcd for $C_{36}H_{44}N_2Si$: C, 81.15; H, 8.32; N, 5.26. Found: C, 81.16; H, 8.36; N, 5.19.

***N,N′*-Dibenzyl-1,2-diphenylethylenediamine (27).** To a stirring solution of **26** (76 mg, 0.14 mmol) in 3 mL of THF was added excess HF (2 mL, 48% aqueous solution). The solution was stirred at 22 °C for 4 h, followed by dropwise addition of 1 M NaOH (aq) until pH > 7 was achieved. The reaction mixture was partitioned between CH_2Cl_2 (50 mL) and NaOH (1 M aqueous, 50 mL). After separation, the aqueous layer was washed 3 × 50 mL of CH_2Cl_2. The organic fractions were combined, filtered through Na_2SO_4/glass wool, and reduced *in vacuo*, yielding a turbid oil. Purification by flash chromatography (5:1:94 EtOAc:Et_3N:hexane) yielded a clear oil (32 mg, 58%). The product was identical to a reference sample and comparison to literature data:[50,51] ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 4H), 7.21 (m, 5H), 7.11 (m, 6H), 7.04 (m, 5H), 3.70 (s, 2H), 3.65 (d, J = 13.1, 2H), 3.48 (d, J = 13.5, 2H), 2.40 (bs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 140.6, 128.3, 128.2, 128.1, 127.9, 126.9, 126.7, 68.4, 51.3.

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Supporting Information Available: A listing of full spectral and experimental details for stereochemical proof (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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