Stereospecific and Regioselective Reactions of Silacyclopropanes with Carbonyl Compounds Catalyzed by Copper Salts: Evidence for a Transmetalation Mechanism

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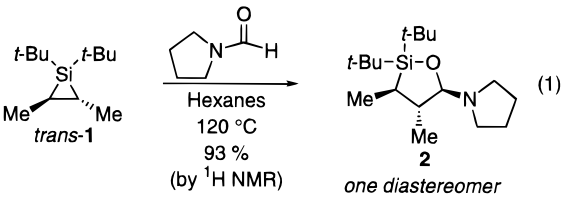
Abstract: Silacyclopropanes reacted with carbonyl compounds under mild conditions (10 mol % metal salt, ≤22 °C) in a stereospecific and highly stereo-, regio-, and chemoselective fashion. In most cases, CuI or $CuBr_2$ were the optimal catalysts although $ZnBr_2$ worked comparably well in a few examples. Insertion occurred with retention of configuration and, in the case of enals and formamides, with high diastereoselectivity at the newly formed stereogenic centers. For unsymmetrical substrates, insertion occurred at the more substituted carbon−silicon bond with complete regioselectivity. Competition experiments demonstrated that formamides reacted faster than enals, which reacted faster than enoates; saturated aldehydes did not undergo insertion. With a cis-disubstituted silacyclopropane, products of silylene transfer were observed. The stereochemistry, regiochemistry, and chemoselectivity of carbonyl insertion as well as the silylene transfer processes can be explained by a mechanism involving transmetalation of silicon to copper.

Introduction

Silacyclopropanes are reactive strained ring compounds that undergo a variety of carbon−carbon bond-forming reactions. The insertion reactions of substrates such as aldehydes[1] and alkynes[2] were first observed by Seyferth in his seminal studies with hexamethylsilirane. The generality of these transformations has been extended recently to include other silacyclopropanes such as *trans*-**1**,[3] allowing aldehydes,[4,5] formamides,[6] and isocyanides[7] to undergo insertion reactions (see for example, eq 1[6]). We demonstrated that the growing family of insertion



(1)

reactions of silacyclopropanes holds promise for synthetic organic chemistry because the insertion products can be oxidized[8−10] to afford oxygenated organic compounds.[4,5,11,12] The drawback to the insertion reactions of aldehydes[5] and amides[6] has been that they require strongly basic catalysts such as KO*t*-Bu or high temperatures (>100 °C), respectively. These conditions severely limit the generality of the reactions to non-enolizable aldehydes and thermally robust silacyclopropanes. Therefore, the development of mild conditions to effect reactions of silacyclopropanes would expand greatly the application of these compounds in organic synthesis.

In this paper, we describe the catalysis of insertion reactions by metal salts such as CuI. These conditions allow formamides as well as α,β-unsaturated aldehydes, ketones, and esters to insert into the carbon−silicon bond of silacyclopropanes at or below 22 °C. The insertions proceed stereospecifically, with high chemoselectivity, and with complete regioselectivity in the case of unsymmetrical silacyclopropanes. These reactions are likely to result from transmetalation of the carbon−silicon bond to form an intermediate organometallic species. This mechanism is consistent with observations of copper-catalyzed silylene transfer and the high reactivity of unsaturated aldehydes as compared to their saturated analogues.

Metal-Catalyzed Insertion Reactions

Because high temperatures limited the formamide insertion reaction to thermally robust silacyclopropanes[6] (eq 1), we searched for methods to catalyze the formamide insertion. We were previously unable to determine the stereospecificity of this insertion reaction with respect to silacyclopropane because *cis*-**1** decomposed at the temperatures required for insertion (eq 2).[13]

(1) Seyferth, D.; Duncan, D. P.; Shannon, M. L. *Organometallics* **1984**, *3*, 579−583 and references therein.
(2) Seyferth, D.; Duncan, D. P.; Shannon, M. L.; Goldman, E. W. *Organometallics* **1984**, *3*, 574−578.
(3) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1355−1356.
(4) Bodnar, P. M.; Palmer, W. S.; Shaw, J. T.; Smitrovich, J. H.; Sonnenberg, J. D.; Presley, A. L.; Woerpel, K. A. *J. Am. Chem. Soc.* **1995**, *117*, 10575−10576.
(5) Bodnar, P. M.; Palmer, W. S.; Ridgway, B. H.; Shaw, J. T.; Smitrovich, J. H.; Woerpel, K. A. *J. Org. Chem.* **1997**, *62*, 4737−4745.
(6) Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **1997**, *62*, 442−443.
(7) Kroke, E.; Willms, S.; Weidenbruch, M.; Saak, W.; Pohl, S.; Marsmann, H. *Tetrahedron Lett.* **1996**, *37*, 3675−3678.
(8) Smitrovich, J. H.; Woerpel, K. A. *J. Org. Chem.* **1996**, *61*, 6044−6046.
(9) Fleming, I. *Chemtracts: Org. Chem.* **1996**, *9*, 1−64.
(10) Jones, G. R.; Landais, Y. *Tetrahedron* **1996**, *52*, 7599−7662.
(11) Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **1997**, *62*, 6706−6707.
(12) Shaw, J. T.; Woerpel, K. A. *Tetrahedron* **1997**, *53*, 16597−16606.
(13) Control experiments indicate that *cis*-**1** is more thermally labile than *trans*-**1**.

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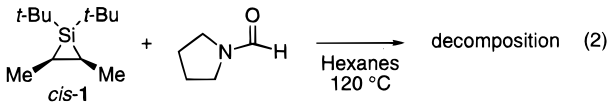
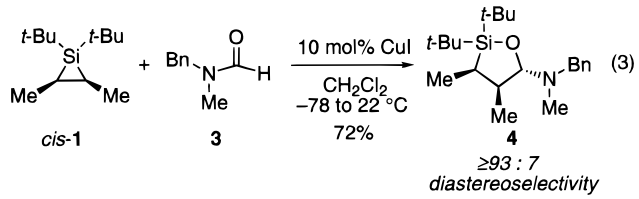
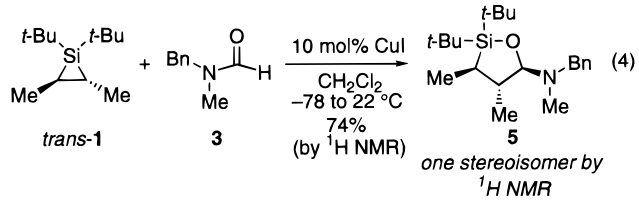


All manner of catalysts, either Brønsted or Lewis bases (for example, KO*t*-Bu, F^-) or acids (for example, camphorsulfonic acid, $SnCl_4$, $BF_3{\cdot}OEt_2$, $TiCl_4$), failed to provide more than trace quantities of insertion products for either *cis*-**1** or *trans*-**1**. In contrast, the use of 10 mol % of a metal salt catalyst lowered the temperatures required for insertion by more than 100 °C, thus allowing *cis*-**1** to participate in formamide insertion reactions. When a cold (−78 °C) solution of *cis*-**1** and CuI in CH_2Cl_2 was treated with *N*-benzyl-*N*-methyl formamide **3**,[14] insertion occurred upon warming to 22 °C over 3 h (eq 3). This

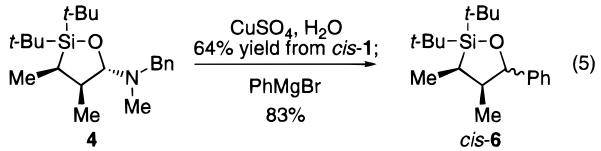


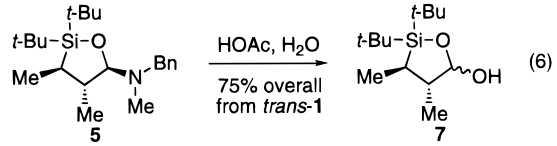
reaction provided predominately one stereoisomer of *N*,*O*-acetal **4** as determined using ^{1}H NMR spectroscopy.[15] Other metal salts such as $ZnBr_2$ and $InCl_3$ also proved to be effective catalysts, although some isomerization of the *cis*-dimethyl adduct **4** to the *trans*-dimethyl isomer **5** was observed. Control experiments indicated that halide ions (LiBr, KBr, and Bu_4NBr) were not responsible for the catalysis.

The copper-catalyzed insertion of formamide **3** into *trans*-**1** (eq 4) confirmed that these insertion reactions are stereospecific,



and carbon−carbon bond formation occurs with retention of configuration. The relative stereochemistries of the methyl-bearing stereocenters for *N*,*O*-acetals **4** and **5** were proven by correlation to materials of known stereochemistry (eqs 5 and 6).[5,12,16] The stereochemistries of the labile acetal stereocenters





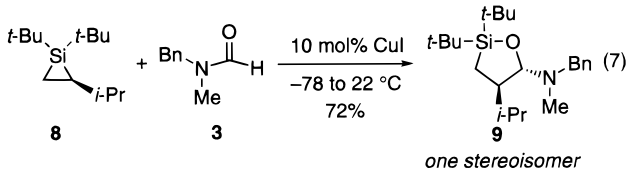
(14) This formamide was used to simplify spectral analyses.

(15) The minor amount (≤7%) of *N*,*O*-acetal **5** detected by ^{1}H NMR spectroscopy is most likely due to the presence of *trans*-2-butene as an impurity in commercially available *cis*-2-butene, from which silacyclopropane *cis*-**1** was made. The typical purity of *cis*-**1** is ≥95%.

(16) The stereochemistry of these products was proven rigorously. The details are provided as Supporting Information.

were assigned using nuclear Overhauser effect (NOE) spectroscopic methods.

The copper-catalyzed insertion of formamides into unsymmetrical silacyclopropanes proceeded with complete regioselectivity. Insertion into isopropyl-substituted silacyclopropane **8**[17] occurred at the more substituted carbon−silicon bond to afford a single stereoisomer of *N*,*O*-acetal **9** (eq 7) as determined



using GC−MS.[18] This regiochemical preference is similar to that observed for the thermal formamide insertion.[6]

The mild conditions employed for formamide insertion (10 mol % copper salt, ≤22 °C) can be applied to reactions with a variety of carbonyl compounds (eq 8, Table 1).[18] In all cases,

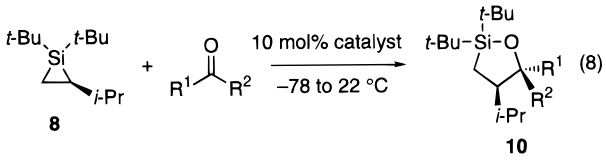


Table 1. Copper-Catalyzed Addition of Silacyclopropane **8** to Carbonyl Compounds (Eq 8)

entry	R^1	R^2	catalyst	product	yield (%)[a]	diastereoselectivity[b]
1	Ph	H	$CuBr_2$	**10a**	82[c]	91 : 9
2		H	$CuBr_2$	**10b**	74	98 : 2
3		H	$CuBr_2$	**10c**	75	>99 : 1
4	–CH=CH(CH$_2$)$_3$–		CuI	**10d**	63	65 : 35
5		Me	$CuBr_2$	**10e**	78	62 : 38[d]
6	*n*-Pr	H	CuI	–	no reaction[e]	–

[a] Yield of purified materials. [b] As determined on the basis of GC analysis unless otherwise indicated. [c] In addition, 7% of **11** was isolated. [d] As determined using ^{1}H NMR spectroscopy. [e] No reaction was observed after heating at 85 °C for 3 days in a sealed NMR tube. $CuBr_2$ also did not catalyze the reaction.

insertion occurred at the more substituted carbon−silicon bond with complete regioselectivity. Only net 1,2-addition was observed with unsaturated carbonyl compounds. The salt $CuBr_2$, which was most likely reduced to CuBr under the reaction conditions,[19,20] proved to be the optimal catalyst in many cases. Even 1 mol % of $CuBr_2$ provided high yields of insertion products. Addition to benzaldehyde (entry 1) was accompanied by the formation of hydride transfer product **11** (7%), a process

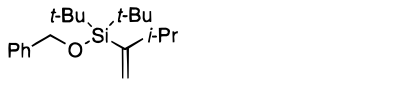
(17) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 1097−1099.

(18) The stereochemistries of insertion products derived from **8** were determined by analysis of NOE data. A summary of these data is provided as Supporting Information.

(19) Bleaching of the characteristic blue-green color of copper(II) salts was observed upon addition of the silacyclopropane. The reduction of palladium(II) salts with silacyclopropanes was demonstrated: Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57−62.

(20) The reduction of copper(II) to copper(I) by pentafluorosiliconates was reported: Yoshida, J.-i.; Tamao, K.; Kakui, T.; Kurita, A.; Murata, M.; Yamada, K.; Kumada, M. *Organometallics* **1982**, *1*, 369−380.

that was also observed under thermal conditions.[5] Reactions with unsaturated aldehydes occurred with high diastereoselectivity at the newly formed stereogenic centers (entries 2 and 3).[21] Using our previously reported conditions with enolizable aldehydes such as crotonaldehyde, only silylenol ethers were observed.[5] Enones also provided 1,2-addition products (entries 4 and 5); attempts to encourage 1,4-addition to cyclohexenone by addition of Me_3SiCl[22] or $Sc(OTf)_3$[23] led to the isolation of significant amounts of enolized product **12** (eq 9).[24] In contrast



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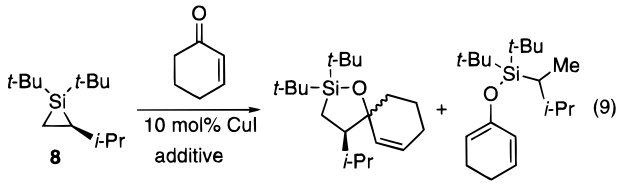
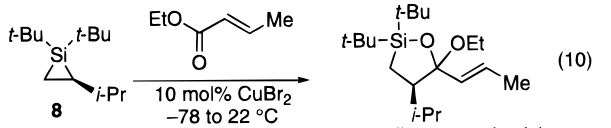


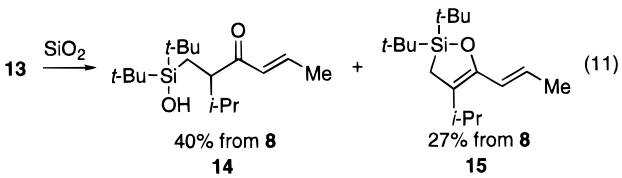
additive	**10d** : **12**
Me_3SiCl	61 : 39
$Sc(OTf)_3$	7 : 93 (41% yield)

to the reactions with α,β-unsaturated aldehydes, no reaction was observed with alkyl aldehydes, even at elevated temperatures (entry 6).

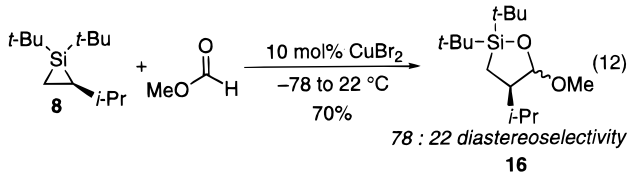
Esters also inserted into the carbon−silicon bond of silacyclopropanes to provide ketal adducts. Treatment of silacyclopropane **8** with ethyl crotonate in the presence of catalytic quantities of $CuBr_2$ led to the formation of a mixture of diastereomeric ketals **13** (eq 10). Although the structure of **13**



was assigned using ^1H and ^{13}C NMR spectroscopies, its acid lability precluded complete characterization. Attempts to purify **13** by chromatography over silica gel led to the isolation of hydrolysis product **14** and elimination product **15** (eq 11).



Treatment of silacyclopropane **8** with methyl formate afforded acetal **16** as a mixture of diastereomers (eq 12). We previously demonstrated the utility of such acetals in synthesis.[11,12]



Not only did a wide range of carbonyl compounds (namely, formamides, enals, enones, and esters) participate in insertion reactions, but silacyclopropanes differentiated between the different carbonyl compounds with high chemoselectivity. Competition experiments were conducted in which silacyclopropane **8** was mixed with an excess of two carbonyl compounds in the presence of copper salts; the relative amounts of insertion products were measured using ^1H NMR spectroscopy. The order of reactivity was found to be formamide **3** > crotonaldehyde > ethyl crotonate. These reactions were completely chemoselective: in each pairwise experiment, only one insertion product was observed.

The regio- and stereoselectivity observed for the insertion of crotonaldehyde into silacyclopropane **8** was observed with other monosubstituted substrates. Silacyclopropanes **17** with *n*-butyl and *tert*-butyl substituents reacted with complete regioselectivity at the more substituted carbon−silicon bond (eq 13, Table

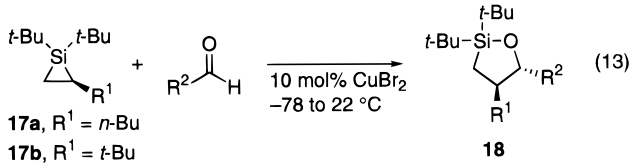
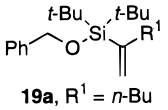


Table 2. Stereoselectivity of the Addition of Silacyclopropanes **17** to Carbonyl Compounds (Eq 13)

entry	R^1	R^2	product	yield (%)[a]	diastereoselectivity[b]
1	*n*-Bu	Ph	**18a**	61[c]	90:10
2	*n*-Bu	CHC═CHMe	**18b**	54	95:5
3	*t*-Bu	Ph	**18c**	59[d]	89:11
4	*t*-Bu	CHC═CHMe	**18d**	56	99:1

[a] Yield of purified materials. [b] As determined on the basis of GC analysis. [c] Accompanied by ≤5% of **19a**. [d] In addition, 26% of **19b** was isolated.

2).[25] Hydride transfer products **19a**[5] (≤5%) and **19b** (26%) were the only significant side-products observed in the reactions with benzaldehyde.



Silylene Transfer Reactions and Evidence for a Transmetalation Mechanism

The metal salt catalyzed insertion of carbonyl compounds into silacyclopropanes represents a significant improvement over the thermal and nucleophile-catalyzed conditions previously reported.[5,6] The dramatic rate acceleration provided by the catalyst as well as the stereospecificity, high stereo- and regioselectivity, and high chemoselectivity suggest that this transformation will find use in organic synthesis. The mechanism for catalysis is not easily elucidated, however. Whatever explanation is chosen to rationalize these results, it must ad-

(21) Use of 10 mol % CuI with crotonaldehyde led to a 64% yield of **10b** as an 87:13 mixture of diastereomers; $ZnBr_2$ afforded a 62% yield of an 87:13 mixture. An 87:13 mixture was observed for CuI-catalyzed insertion of tiglic aldehyde. These mixtures permitted comparison of NOE data between the major and minor diastereomers.

(22) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6015−6018.

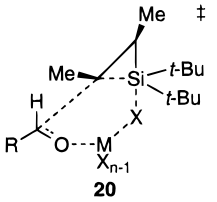
(23) Lipshutz, B. H.; Sclafani, J. A.; Takanami, T. *J. Am. Chem. Soc.* **1998**, *120*, 4021−4022.

(24) The connectivity of this structure was determined using COSY experiments.

(25) The stereochemistry of **18a** was determined unambiguously (ref 5). The stereochemistries of **18b**−**d** were assigned by analogy.

dress the relative reactivity of carbonyl compounds (formamide > enal > enoate) and the lack of reactivity of saturated aldehydes.

An initial analysis of the metal salt catalyzed insertion might suggest that the salt acts as a Lewis acid to activate the carbonyl compound toward nucleophilic attack by the silacyclopropane. A six-membered transition state such as **20** could be considered in which the metal complex brings both nucleophile and electrophile together, reminiscent of catalyzed nucleophilic additions to carbonyl groups.[26] If this were the case, carbonyl



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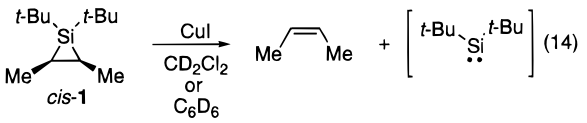
compounds, which are relatively hard Lewis bases, would be expected to interact most favorably with hard Lewis acids. Contrary to this expectation, the softer Lewis acids CuI and $ZnBr_2$ proved to be superior catalysts.[27] Furthermore, this mechanism does not explain why crotonaldehyde reacted rapidly, whereas its saturated analogue, butanal, resisted insertion even at elevated temperatures.

To resolve these issues and to determine the role of the metal salt, we monitored control experiments using NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra (CD_2Cl_2) of formamide **3** were not affected by the presence of CuI, indicating that the amide and metal salt do not interact.[28] Separate control experiments, however, demonstrated an interaction between silacyclopropanes and CuI. Using C_6D_6 as solvent, *cis*-**1** liberated *cis*-2-butene stereospecifically in the presence of CuI (eq 14),



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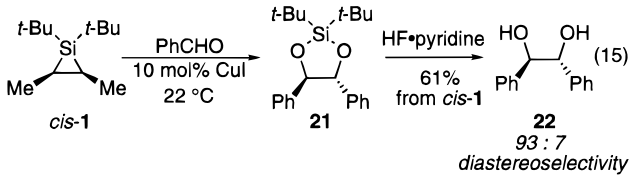
and *trans*-**1** generated *trans*-2-butene.[29] Butene was liberated more rapidly from *cis*-**1** than *trans*-**1**,[30] and monosubstituted silacyclopropane **8** liberated alkene only upon heating. Presumably, the silicon atom was produced as a silylene or silylenoid species (vide infra). These results clearly suggest a direct reaction between the copper salt and the silacyclopropane that cannot be accounted for by a mechanism involving CuI strictly as a Lewis acid.

The extrusion of a silylene species from silacyclopropane *cis*-**1** by copper salts was confirmed in preparative experiments with substrates other than formamide **3**. Treatment of *cis*-**1** with PhCHO and 10 mol % of CuI (or CuI·2LiI) at 22 °C provided dioxasilolane **21**[31] as predominately one stereoisomer (eq 15).[32]



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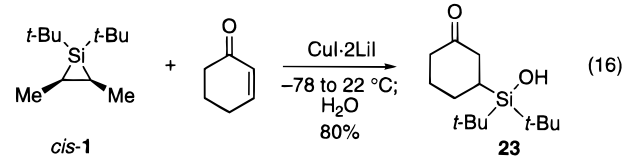
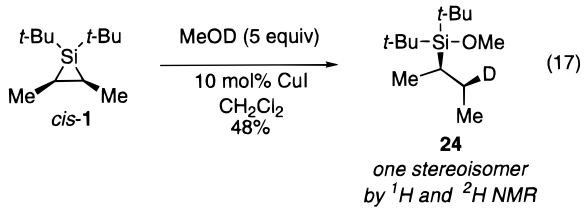
The stereochemistry of **21** was assigned by desilylation to afford *trans*-hydrobenzoin (**22**) as a 93:7 mixture of diastereomers as determined on the basis of ^{1}H NMR spectroscopic analysis.[33] Product **21** results from trapping of in situ-derived silylene by reductive dimerization of benzaldehyde.[34] Enones also trapped the liberated silylene (eq 16). The β-silylcyclohexanone **23**



(16)

presumably arises from silylene trapping followed by hydrolysis. The observation of silylene-derived products **21** and **23** is not easily rationalized by consideration of Lewis acid−base adducts between the metal salt and the carbonyl compound. These experiments have implications beyond the mechanism for insertion: they suggest that copper-mediated silylene transfer may be conducted under mild conditions. To date, silylene transfer has required either temperatures above 22 °C or photolytic conditions,[3,35] although metal-mediated processes have been reported.[17,30,36−38]

Deuterium incorporation experiments were conducted to intercept any intermediates resulting from a reaction between the silacyclopropane and the metal salt. Treatment of silacyclopropane *cis*-**1** with MeOD and 10 mol % of CuI provided the volatile deuterated silane **24** as a single stereoisomer (eq 17). The reaction of *trans*-**1** under similar conditions led to a



(17)

single stereoisomer that was distinct from **24**.[39] The stereochem-

(26) For a review that includes the use of metal complexes to catalyze carbonyl additions, see: Evans, D. A. *Science* **1988**, *240*, 420−426.

(27) Maitlis observed that weak Lewis acids catalyzed rearrangement reactions of cyclopropane-containing strained ring compounds: Kaiser, K. L.; Childs, R. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1971**, *93*, 1270−1272.

(28) Copper(II) salts lower the barrier to inversion of amides by preferential coordination to the amide nitrogen: Cox, C.; Ferraris, D.; Murthy, N. N. *J. Am. Chem. Soc.* **1996**, *118*, 5332−5333.

(29) Butene was also observed using CD_2Cl_2 as solvent. The stereochemistry of the butene could not be unambiguously determined, however, because the ^{1}H NMR signals of *cis*- and *trans*-2-butene are not well resolved in this solvent.

(30) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824−4827.

(31) This compound was identified on the basis of its spectral properties. The rapid hydrolysis of this dioxasilolane was reported by Corey: Corey, E. J.; Hopkins, P. B. *Tetrahedron Lett.* **1982**, *23*, 4871−4874.

(32) When this transformation was performed starting at −78 °C and the reaction solution was warmed to 22 °C, dioxasilolane **21** was accompanied by 13% of *cis*-**6** as a 63:37 ratio of diastereomers.

(33) Clerici, A.; Porta, O. *J. Org. Chem.* **1985**, *50*, 76−81.

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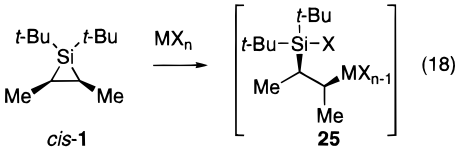
(39) No deuteriomethanolysis was observed at 22 °C in the absence of copper salts.

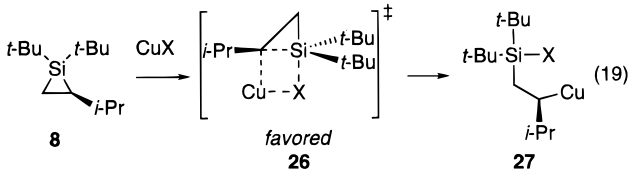
istries of the methanolysis products were assigned tentatively by analogy to transformations of silacyclopropanes that proceed with retention of configuration (eqs 3, 4, and 14). We observed similar stereospecific methanolysis using fluoride catalysis,[5] where silane **24** was also formed exclusively from *cis*-**1**.

Consideration of the insertion, silylene transfer, and methanolysis experiments together suggests a mechanism involving transmetalation of the silacyclopropane to form an organometallic reagent (eq 18). Retention of configuration at the migrating

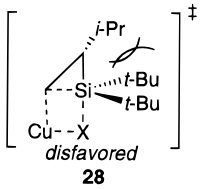


carbon atom of the silacyclopropane is consistent with transmetalations of alkyl groups from main group organometallic compounds to metals.[40] Aryl, alkenyl, and alkynyl carbon−silicon bonds have been demonstrated to undergo transmetalation to form carbon−copper bonds.[41−44] In addition, transmetalation of silacyclobutenes with copper salts was recently postulated.[45] Cyclopropanes are known to experience ring-opening reactions similar to those in eq 18 with mercury(II),[46] zinc(II),[47] and electrophilic platinum(II)[48] salts.[49] Reaction of the organometallic intermediate **25** with carbonyl compounds would lead to the observed insertion products (for example, eq 3).

The transmetalation mechanism is also compatible with the regioselectivity observed for unsymmetrical silacyclopropanes. Transmetalation at the more substituted carbon atom of **8** via the four-centered transition state[40,50] **26** (eq 19) would generate

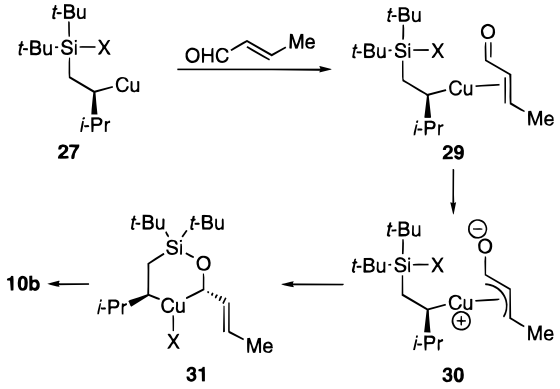


organocopper intermediate **27**. The alternative transition structure **28** would suffer from an unfavorable steric interaction between the *tert*-butyl groups and the isopropyl group.



The transmetalation mechanism explains the lack of reactivity of saturated aldehydes and the higher reactivity of enals versus enoates. Silyl halides, which would be produced in situ under the copper-catalyzed conditions, are known to accelerate the conjugate addition of organocuprates to α,β-unsaturated carbonyl compounds.[22,51−53] Chlorosilane-promoted conjugate addition reactions have also been reported for isoelectronic nickel(0) complexes.[54,55] The silyl halide generated upon transmetalation of silacyclopropane **8** with a copper salt could play a similar role. Coordination of the enal to transmetalation product **27** followed by oxidative addition would form the oxy-π-allyl complex **30** (Scheme 1). Oxidative addition would occur faster for an enal than for an enoate, and would not be possible for a saturated aldehyde. Silylation of the oxy-π-allyl unit by the silyl halide would generate the six-membered ring σ-copper(III) adduct **31**. Reductive elimination from this intermediate would provide the 1,2-addition product **10b**. Conversely, a net 1,4-addition to the α,β-unsaturated carbonyl compound would require formation of an eight-membered ring intermediate, which should be disfavored.

Scheme 1



The anomalous reactivity of formamides using copper catalysts can also be accounted for by in situ formation of a silyl halide upon transmetalation. In the presence of silyl chlorides, organometallic reagents such as organozinc species react with formamides to form silylated *N*,*O*-acetals.[56] Transmetalation of a silacyclopropane would generate both the organometallic species and the silyl halide required for this reaction. The silyl halide moiety of **27** would activate the amide toward nucleophilic attack by formation of an intermediate such as **32** (eq 20). Carbon−carbon bond formation at the activated carbonyl

(40) For some examples of the stereochemistry of transmetalation reactions, see: (a) Silicon to palladium: Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990**, *112*, 7793−7794. (b) Tin to copper: Falck, J. R.; Bhatt, R. K.; Ye, J. *J. Am. Chem. Soc.* **1995**, *117*, 5973−5982. (c) Boron to palladium: Ridgway, B. H.; Woerpel, K. A. *J. Org. Chem.* **1998**, *63*, 458−460. Matos, K.; Soderquist, J. A. *J. Org. Chem.* **1998**, *63*, 461−470.

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(49) For additional examples, see: Ryu, I.; Matsumoto, K.; Kameyama, Y.; Ando, M.; Kusumoto, N.; Ogawa, A.; Kambe, N.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1993**, *115*, 12330−12339 and references therein.

(50) For a recent discussion of transmetalation from tin to palladium, see: Casado, A. L.; Espinet, P. *J. Am. Chem. Soc.* **1998**, *120*, 8978−8985.

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(55) Other oxaphilic reagents, such as organozinc reagents, promote similar reactions: Montgomery, J.; Oblinger, E.; Savchenko, A. V. *J. Am. Chem. Soc.* **1997**, *119*, 4911−4920.

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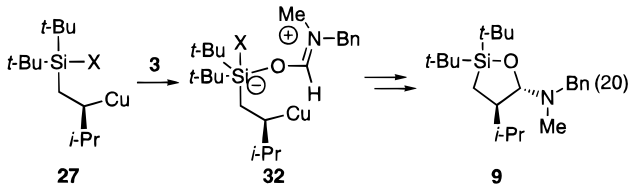
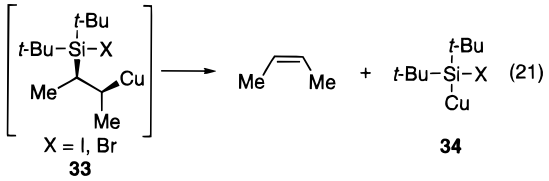
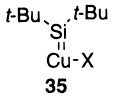


group would provide silylated *N*,*O*-acetal **9**. Whereas silylation of a nucleophilic amide carbonyl is precedented,[56,57] silylation of the less nucleophilic carbonyl group of an α,*β*-unsaturated aldehyde ester is unlikely.[58] As a result, the formamide displays heightened reactivity relative to an α,*β*-unsaturated aldehyde or ester.

In the absence of a highly reactive substrate such as formamide **3**, the *β*-silyl organometallic reagent **33** derived from *cis*-**1** would undergo a *β*-silyl elimination reaction (eq 21).[59−61]



This operation would liberate butene stereospecifically to generate a metal-bound silylene species. The precise structure of this intermediate can only be surmised, but we postulate that it is silylenoid **34**. This structure is similar to the lithium silylenoid species invoked for silylene transfer[3] or the zinc reagents postulated for carbene transfer.[62,63] Alternatively, a copper(III) silylene structure **35** could describe the copper



species. This species might react as a metal-bound silylenoid or it might liberate free *t*-Bu_2Si.[64] The silylene or silylenoid intermediate can be trapped, as demonstrated by reactions with benzaldehyde (eq 15) or cyclohexenone (eq 16).

Conclusions

We have demonstrated that silacyclopropanes reacted with carbonyl compounds under mild conditions (10 mol % metal salt, ≤22 °C) in a stereospecific and highly stereo-, regio-, and chemoselective fashion. In most cases, CuI or $CuBr_2$ were the optimal catalysts although $ZnBr_2$ worked comparably well in a few examples. Insertion occurred with retention of configuration, and in the case of enals and formamides, with high diastereoselectivity at the newly formed stereogenic centers. For unsymmetrical substrates, insertion occurred at the more substituted carbon−silicon bond with complete regioselectivity. Competition experiments demonstrated that formamides reacted faster than enals, which reacted faster than enoates; saturated aldehydes did not undergo insertion. With a cis-disubstituted silacyclopropane, products of silylene transfer were observed. The stereochemistry, regiochemistry, and chemoselectivity of carbonyl insertion as well as the silylene transfer processes can be explained by a mechanism involving transmetalation of silicon to copper.

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 split-mode capillary injection system and a flame ionization detector. Fused silica capillary columns (30 × 0.32 mm) wall-coated with DB-1 (J & W Scientific) were used with helium as the carrier gas. All reactions were carried out under a stream of nitrogen in glassware that had been flame-dried. Silacyclopropanes were stored and handled in an Innovative Technologies nitrogen atmosphere drybox. Solvents were dried and distilled prior to use.

1-Oxa-3,4-dimethyl-5-(1-*N*-benzyl-*N*-methylamino)-2,2-di-*tert*-butyl-silacyclopentane (4). To a cooled (−78 °C) solution of silacyclopropane *cis*-**1** (≥95:5 cis/trans, as determined on the basis of ^{1}H NMR spectroscopy) (0.200 g, 1.01 mmol), in 8 mL of CH_2Cl_2 were added CuI (0.019 g, 0.10 mmol) and *N*-benzyl-*N*-methyl formamide **3** (0.452 g, 3.03 mmol). The mixture was allowed to warm to 22 °C and stirred for 3 h, and then 10 mL of Et_3N/MeOH (2:1) was added. The mixture was concentrated in vacuo. The resultant yellow oil was extracted with 3 × 5 mL of hexanes/Et_3N (95:5), and the combined layers were washed with 3 × 10 mL of sodium potassium tartrate (saturated aqueous), 2 × 10 mL of H_2O, dried (Na_2SO_4), and concentrated in vacuo to afford product **4** (0.25 g, 72%) as a colorless oil consisting of a >93:7 (**4**:**5**) mixture of diastereomers as determined by analysis of ^{1}H NMR spectral data. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.31 (m, 5H), 4.25 (d, *J* = 9.9, 1H), 3.86 (d, *J* = 13.9, 1H), 3.71 (d, *J* = 13.9, 1H), 2.28 (s, 3H), 2.18 (m, 1H), 1.41 (m, 1H), 1.07 (s, 9H), 1.05 (d, *J* = 6.8, 3H), 1.03 (s, 9H), 0.95 (d, *J* = 6.8, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 140.5, 128.7, 128.0, 126.5, 97.5, 57.9, 37.8, 34.9, 28.6, 28.1, 22.0, 20.7, 18.9, 12.5, 11.2. IR (thin film): 3064, 2957, 1472, 1363, 1069, 912 cm^{-1}. High-resolution mass spectrometry (HRMS) (chemical ionization (CI)/isobutane): *m/z* calcd for $C_{21}H_{37}NOSi$ (M^+), 347.2664; found, 347.2648.

1-Oxa-3,4-dimethyl-5-(1-*N*-benzyl-*N*-methylamino)-2,2-di-*tert*-butyl-silacyclopentane (5). The procedure used for the synthesis of **4** was employed using silacyclopropane *trans*-**1** (0.202 g, 1.02 mmol), CuI (0.020 g, 0.10 mmol), and *N*-benzyl-*N*-methyl formamide **3** (0.492 g, 3.30 mmol). After extraction, product **5** was isolated as a colorless oil along with small amounts of formamide **3** (a 74% yield could be estimated from ^{1}H NMR spectroscopy). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.27 (m, 5H), 4.07 (d, *J* = 9.6, 1H), 3.87 (d, *J* = 13.8, 1H), 3.71 (d, *J* = 13.8, 1H), 2.29 (s, 3H), 1.76 (m, 1H), 1.20 (d, *J* = 7.5, 3H), 1.08 (s, 9H), 1.00 (s, 9H), 0.99 (3H), 0.93 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 140.4, 128.6, 128.1, 126.6, 99.4, 58.1, 42.5, 35.4, 28.1, 28.0, 24.4, 21.5, 21.2, 15.7, 13.1. IR (thin film): 3064, 1471, 1364, 1069, 912 cm^{-1}. HRMS (CI/isobutane): *m/z* calcd for $C_{21}H_{37}NOSi$ (M^+), 347.2664; found, 347.2647.

4-Isopropyl-5-(*N*-benzyl-*N*-methylamino)-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (9). The procedure used for the synthesis of **4** was employed using silacyclopropane **8**[17] (0.150 g, 0.706 mmol), CuI (0.015 g, 0.079 mmol), and *N*-benzyl-*N*-methyl formamide **3** (0.334 g, 2.24 mmol). After extraction, product **9** was isolated as a colorless oil (0.176 g, 69%). Only one diastereomer of product was obtained on the basis of GC−MS analysis. ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.32 (m, 5H), 4.31 (d, *J* = 10.0, 1 H), 3.85 (d, *J* = 13.7, 1H), 3.72 (d, *J* = 13.7, 1H), 2.13 (s, 3H), 1.96 (m, 2H), 1.03 (s, 9H), 0.98 (s, 9H), 0.93 (d, *J* = 6.9, 3H), 0.71 (d, *J* = 6.7, 3H), 0.67 (dd, *J* = 14.7, 7.8, 1H), 0.52 (dd, *J* = 14.7, 12.5, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 140.4, 128.8, 128.0,

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126.6, 96.2, 58.4, 45.4, 34.9, 27.9, 27.7, 27.6, 22.2, 20.9, 20.3, 16.1, 4.5. IR (thin film): 2958, 2857, 1471, 1365, 1011 cm^{-1}. HRMS (GC−MS, electron ionization (EI)): *m/z* calcd for $C_{22}H_{39}NOSi$ (M^+), 361.2801; found, 361.2803.

4-Isopropyl-5-phenyl-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (10a). Representative Procedure for Copper-Catalyzed Insertion. To a cooled (−78 °C) solution of silacyclopropane **8** (0.200 g, 0.937 mmol) in 8 mL of CH_2Cl_2 were added $CuBr_2$ (0.023 g, 0.102 mmol) and benzaldehyde (0.300 mL, 2.82 mmol). The mixture was allowed to warm to 22 °C and was stirred for 12 h, and then 5 mL of MeOH was added. The mixture was treated with 10 mL of sodium potassium tartrate (saturated aqueous), and the aqueous layer was extracted with 3 × 10 mL of CH_2Cl_2. The combined organic layers were washed with 10 mL of brine, dried (Na_2SO_4), and concentrated in vacuo. After extraction, GC analysis of the unpurified product showed a pair of diastereomers in a ratio of 91:9 as well as product **11**. Purification by flash chromatography (0:100−10:90 CH_2Cl_2/hexanes) yielded **11** (0.020 g, 7%) and a mixture of diastereomers **10a** as colorless oil. The mixture of diastereomers solidified over several days (0.246 g, 82%). Combustion analysis and IR data were obtained for **10a** as a mixture of diastereomers. IR (thin film): 3030, 1471, 1386, 1068, 1019 cm^{-1}. Anal. Calcd for $C_{20}H_{34}OSi$: C, 73.95; H, 11.76. Found: C, 73.89; H, 11.72. The resonances for each diastereomer were identifiable in the spectra.

10a. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (m, 5H), 4.52 (d, J = 10.7, 1 H), 1.84 (m, 1H), 1.58 (m, 1H), 1.14 (s, 9H), 1.07 (s, 9H), 0.89 (d, J = 6.7, 3H), 0.81 (d, J = 6.8, 3H), 0.78 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 128.2, 127.4, 126.6, 83.3, 53.3, 27.8, 27.7, 26.5, 22.5, 21.1, 20.3, 15.5, 5.3. HRMS (GC−MS, EI): *m/z* calcd for $C_{20}H_{33}OSi$ $(M - H)^+$, 317.2301; found, 317.2302.

Minor cis Isomer of 10a. ^{1}H NMR (500 MHz, $CDCl_3$, distinctive peaks): δ 7.29 (m, 5H), 5.18 (d, J = 8.3, 1H), 2.29 (m, 1H), 1.53 (m, 1H), 1.09 (s, 9H), 1.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.6, 129.3, 127.6, 127.2, 83.5, 51.2, 31.4, 28.7, 28.4, 22.3, 21.7, 21.2, 20.0, 11.2. HRMS (GC−MS, EI): *m/z* calcd for $C_{20}H_{33}OSi$ $(M - H)^+$, 317.2301; found, 317.2299.

1-(Benzyloxy)-1-[2-(3-methyl-1-butenyl)]di-*tert*-butylsilane (11). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (m, 4H), 7.25 (m, 1H), 5.82 (dd, J = 1.7, 0.9, 1H), 5.49 (d, J = 2.0, 1H), 5.02 (s, 1H), 2.59 (m, 1H), 1.09 (s, 18H), 1.06 (d, J = 6.8, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 141.6, 128.2, 126.7, 125.6, 124.4, 66.2, 31.3, 28.7, 23.5, 21.4. HRMS (EI): *m/z* calcd for $C_{20}H_{34}OSi$ $(M - C_4H_9)^+$, 261.1675; found, 261.1670.

4-Isopropyl-5-(1-propenyl)-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (10b). The representative procedure for copper-catalyzed insertion was followed using silacyclopropane **8** (0.070 g, 0.35 mmol), $CuBr_2$ (0.008 g, 0.035 mmol), and crotonaldehyde (0.100 mL, 1.21 mmol). After extraction, GC analysis of the unpurified product showed a pair of diastereomers (**10b**) in a ratio of 98:2. The resulting oil was purified by flash chromatography (5:95−15:85 CH_2Cl_2/hexanes) to yield the major diastereomer and an enriched sample of the minor diastereomer (0.074 g, 74% combined).[21] Combustion analysis and IR data were obtained for the mixture of diastereomers. IR (thin film): 2958, 1471, 1365, 1068, 1000. Anal. Calcd for $C_{17}H_{34}OSi$: C, 72.27; H, 12.13. Found: C, 72.00; H, 12.11.

10b. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.66 (m, 1H), 5.40 (dd, J = 15.2, 7.8, 1H), 3.93 (dd, J = 10.2, 8.0, 1H), 1.75 (m, 1H), 1.71 (d, J = 6.5, 3H), 1.61 (m, 1H), 1.02 (s, 18H), 0.91 (d, J = 6.9, 3H), 0.79 (d, J = 6.8, 3H), 0.69 (dd, J = 14.7, 7.9, 1H), 0.61 (dd, J = 14.6, 12.5, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.8, 127.7, 82.6, 50.4, 27.8, 27.6, 27.3, 22.6, 20.8, 19.9, 17.8, 15.8, 5.0. HRMS (GC−MS, EI): *m/z* calcd for $C_{17}H_{34}OSi$ (M^+), 282.2379; found, 282.2376.

Minor cis Isomer of 10b. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.68 (m, 1H), 5.46 (m, 1H), 4.53 (dd, J = 9.9, 7.2, 1H), 1.83 (m, 1H), 1.69 (dd, J = 6.5, 1.6, 3H), 1.60 (m, 1H), 1.32 (m, 1H), 1.04 (s, 9H), 1.02 (s, 9H), 0.95 (d, J = 6.7, 3H), 0.83 (d, J = 6.4, 3H), 0.47 (t, J = 14.1, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 130.0, 128.7, 82.3, 49.6, 31.0, 29.7, 28.6, 28.1, 22.4, 21.1, 19.6, 17.8, 10.0. HRMS (GC−MS, EI): *m/z* calcd for $C_{17}H_{34}OSi$ (M^+), 282.2379; found, 282.2381.

4-Isopropyl-5-(1-methyl-1-propene)-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (10c). The representative procedure for copper-catalyzed insertion was followed using silacyclopropane **8** (0.118 g, 0.555 mmol), $CuBr_2$ (0.009 g, 0.040 mmol), and 2-methyl-2-butenal (0.180 mL, 2.14 mmol). After extraction, GC analysis of the unpurified product showed a pair of diastereomers (**10c**) in a ratio of 99:1. The resulting oil was purified by flash chromatography (5:95−12:88 CH_2Cl_2/hexanes) to yield the product as a clear oil (0.123 g, 75%) as an inseparable mixture of diastereomers. The resonances for each isomer were identifiable in the spectra.[21] Combustion analysis and IR data were obtained for the mixture of diastereomers. IR (thin film): 2960, 1472, 1365, 1068, 982 cm^{-1}. Anal. Calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.24. Found: C, 72.82; H, 12.26.

10c. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.49 (m, 1H), 3.95 (d, J = 10.8, 1H), 1.83 (m, 1H), 1.66 (d, J = 6.2, 3H + m, 1H) 1.65 (s, 3H), 1.08 (s, 9H), 1.06 (s, 9H), 0.93 (d, J = 6.9, 3H), 0.81 (d, J = 6.7, 3H), 0.73 (dd, J = 14.6, 7.4, 1H), 0.65 (dd, J = 14.6, 12.5, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.1, 123.4, 87.6, 46.6, 27.8, 27.7, 27.2, 22.4, 21.0, 20.1, 15.5, 13.3, 10.1, 4.9. HRMS (GC−MS, EI): *m/z* calcd for $C_{18}H_{36}OSi$ (M^+), 296.2535; found, 296.2544.

Minor cis Isomer of 10c. ^{1}H NMR (500 MHz, $CDCl_3$, not all signals were sufficiently resolved): δ 5.53 (m, 1H), 4.60 (d, J = 8.4, 1H), 1.67 (s, 3H), 1.61 (d, J = 6.7, 3H), 1.51 (m, 1H), 1.09 (s, 9H), 1.07 (s, 9H), 0.97 (d, J = 6.6, 3H), 0.88 (d, J = 6.3, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.1, 124.0, 86.9, 49.4, 30.7, 28.9, 28.4, 22.8, 22.7, 21.4, 20.2, 14.9, 13.1, 11.4. HRMS (GC−MS, EI): *m/z* calcd for $C_{18}H_{36}OSi$ (M^+), 296.2535; found, 296.2535.

Oxasilacyclopentane 10d. The representative procedure for copper-catalyzed insertion was followed using silacyclopropane **8** (0.228 g, 1.07 mmol), CuI (0.019 g, 0.10 mmol), and 2-cyclohexene-1-one (0.350 mL, 3.64 mmol). After extraction, GC analysis of the unpurified product showed a pair of diastereomers (**10d**) in a ratio of 65:35. The resulting oil was purified by flash chromatography (5:95−10:90 CH_2Cl_2/hexanes) to yield each diastereomer of product as a clear oil (0.197 g, 60% combined). Combustion analysis and IR data were obtained for products **10d** as a mixture of diastereomers. IR (thin film): 3036, 1473, 1384, 1082, 958 cm^{-1}. Anal. Calcd for $C_{19}H_{36}OSi$: C, 75.40; H, 10.76. Found: C, 75.49; H, 10.79.

10d. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.72 (m, 1H), 5.64 (d, J = 10.1, 1H), 2.03 (m, 1H), 1.89 (m, 2H), 1.79 (m, 1H), 1.69 (m, 1H), 1.56 (m, 3H), 1.01 (s, 9H), 1.00 (s, 9H), 0.98 (m, 1H), 0.93 (d, J = 6.3, 3H), 0.90 (d, J = 6.5, 3H), 0.61 (dd, J = 14.9, 12.7, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 130.3, 127.9, 79.9, 54.3, 38.2, 31.0, 29.7, 28.4, 28.1, 25.2, 23.8, 22.0, 19.7, 19.7, 10.0. HRMS (CI/isobutane): *m/z* calcd for $C_{19}H_{36}OSi$ (M^+), 308.2535; found, 308.2528.

Minor Isomer of 10d. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.74 (m, 1H), 5.58 (dd, J = 11.0, 1.0, 1 H), 2.11 (m, 1H), 1.93 (m, 1H), 1.86 (m, 1H), 1.70 (m, 1H), 1.64 (m, 1H), 1.60 (m, 2H), 1.52 (m, 2H), 1.03 (s, 9H + m, 1H), 1.02 (s, 9H), 0.96 (d, J = 6.5, 3H), 0.87 (d, J = 6.5, 3H), 0.57 (t, J = 14.1, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.2, 128.8, 79.7, 55.6, 31.3, 30.2, 28.7, 28.5, 25.5, 22.9, 22.7, 20.5, 19.7, 18.2, 11.1. HRMS (CI/isobutane): *m/z* calcd for $C_{19}H_{36}OSi$ (M^+), 308.2535; found, 308.2526.

4-Isopropyl-5-methyl-5-(2-methyl-1-propenyl)-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (10e). The representative procedure for copper-catalyzed insertion was followed using silacyclopropane **8** (0.124 g, 0.584 mmol), $CuBr_2$ (0.010 g, 0.044 mmol), and mesityl oxide (0.200 mL, 1.75 mmol). After extraction, analysis of the unpurified product by ^{1}H NMR spectroscopy showed a pair of diastereomers (**10e**) in a ratio of 62:38. The resulting oil was purified by flash chromatography (95.5:0.5 hexanes/Et_3N) to yield the products as a clear oil (0.142 g, 78% combined). Analytical data were obtained for products **10e** as a mixture of diastereomers. IR (thin film): 2931, 2857, 1474, 1370, 1105 cm^{-1}. Anal. Calcd for $C_{19}H_{38}OSi$: C, 73.47; H, 12.33. Found: C, 73.29; H, 12.25.

10e. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.34 (dd, J = 1.5, 1.0, 1H), 1.86 (d, J = 1.5, 3H), 1.74 (m, 1H), 1.68 (d, J = 1.0, 3H), 1.60 (m, 1H), 1.25 (s, 3H), 1.03 (s, 9H), 0.98 (s, 9H), 0.95 (d, J = 6.5, 6H), 0.83 (m, 1H), 0.48 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 132.8, 131.5, 83.2, 55.6, 30.8, 28.6, 28.1, 27.9, 24.4, 23.7, 21.9, 20.6, 19.7, 19.1, 8.9. HRMS (CI/isobutane): *m/z* calcd for $C_{19}H_{38}OSi$ (M^+), 310.2692; found, 310.2696.

Minor Isomer of 10e. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.39 (dd, J = 1.5, 1.0, 1H), 1.87 (d, J = 1.0, 3H), 1.66 (d, J = 1.0, 3H), 1.63 (m, 1H), 1.53 (s, 3H), 1.52 (m, 1H), 1.01 (s, 9H), 0.99 (d, J = 6.5, 3H), 0.95 (s, 9H), 0.94 (d, J = 7.5, 3H), 0.93 (m, 1H), 0.49 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.3, 127.4, 82.9, 57.7, 31.7, 31.4, 28.4, 28.3, 27.5, 23.5, 22.8, 20.4, 19.8, 19.7, 11.7. HRMS (CI/isobutane): *m/z* calcd for $C_{19}H_{38}OSi$ (M^+), 310.2692; found, 310.2696.

Di-*tert*-butyl-(3-methyl-2-butyl)−(1,3-cyclohexadien-2-oxy)silane (12). To a cooled (−78 °C) solution of silacyclopropane **8** (0.053 g, 0.25 mmol) in 2 mL of CH_2Cl_2 were added CuI (0.005 g, 0.03 mmol), $Sc(OTf)_3$ (0.013 g, 0.026 mmol), and 2-cyclohexene-1-one (0.080 mL, 0.83 mmol). The mixture was allowed to warm to 22 °C and was stirred for 9 h, and then 5 mL of H_2O was added. The aqueous layer was extracted with 2 × 10 mL of CH_2Cl_2. The combined organic layers were washed with 10 mL of brine, dried (Na_2SO_4), and concentrated in vacuo. The resulting oil was purified by flash chromatography (5:95−10:90 CH_2Cl_2/hexanes) to yield the product as a clear oil (0.032 g, 41%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.92 (m, 2H), 5.57 (m, 1H), 2.12 (m, 3H), 2.03 (m, 1H), 1.51 (m, 1H), 1.03 (d, J = 6.4, 3H), 1.02 (s, 9H), 0.94 (s, 9H), 0.94 (d, J = 6.5, 3H), 0.77 (d, J = 6.7, 3H), 0.74 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.1, 128.2, 125.4, 121.4, 48.9, 34.0, 27.8, 27.4, 22.5, 22.2, 21.2, 21.0, 20.7, 20.5, 10.6. IR (thin film): 2959, 1471, 1386, 1101, 785 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{15}H_{25}OSi$ ($M - C_4H_9 - 2H)^+$, 249.1675; found, 249.1672.

Reaction of Silacyclopropane 8 with Ethyl Crotonate (Eqs 10, 11). To a cooled (−78 °C) solution of silacyclopropane **8** (0.148 g, 0.697 mmol) in 6 mL of CH_2Cl_2 were added $CuBr_2$ (0.016 g, 0.070 mmol) and *trans*-ethyl crotonate (0.150 mL, 2.20 mmol). The mixture was allowed to warm to 22 °C and was stirred for 12 h, and then 5 mL of H_2O was added. The mixture was treated with 10 mL of sodium potassium tartrate (saturated aqueous), and the aqueous layer was extracted with 3 × 10 mL of CH_2Cl_2. The combined organic layers were washed with 10 mL of brine, dried (Na_2SO_4), and concentrated in vacuo. The unpurified product **13** was characterized on the basis of ^{1}H NMR and ^{13}C NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$, distinctive peaks for mixture of two isomers): δ 5.92 (m, 2H), 5.62 (d, J = 15, 1H), 5.40 (d, J = 15, 1H), 3.47 (m, 4H), 1.06 (s, 9H), 1.04 (s, 18H), 1.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, distinctive peaks for mixture of two isomers): δ 133.5, 130.1, 127.1, 126.0, 107.9, 107.0, 57.1, 56.6, 55.4, 55.0, 28.5, 28.2, 28.1, 27.8. Purification by flash chromatography (2:98−10:90 ethyl acetate/hexanes) yielded products **14** (0.084 g, 40%) and **15** (0.053 g, 27%), each as a clear oil.

1-(Di-*tert*-butyl-hydroxysilyl)-2-isopropyl-hex-4-ene-3-one (14). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.88 (m, 1H), 6.26 (dd, J = 15.5, 1.5, 1H), 2.81 (m, 1H), 2.03 (m, 1H), 1.88 (dd, J = 6.5, 1.5, 3H), 1.83 (bs, 1H), 1.03 (m, 1H), 0.98 (s, 9H), 0.97 (s, 9H), 0.96 (d, J = 6.5, 3H), 0.79 (d, J = 6.5, 3H), 0.65 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.4, 142.4, 130.6, 52.6, 31.5, 27.8, 27.5, 21.1, 20.9, 20.3, 18.2, 17.8, 5.6. IR (thin film): 3489, 2959, 2858, 1682, 1471 cm^{-1}. HRMS (CI/isobutane): *m/z* calcd for $C_{17}H_{33}O_2Si$ ($M - H)^+$, 297.2250; found, 297.2252. Anal. Calcd for $C_{17}H_{34}O_2Si$: C, 68.39; H, 11.48. Found: C, 68.46; H, 11.44.

4-Isopropyl-5-(1-propenyl)-2-di-*tert*-butyl-1-oxa-2-silacyclopent-4-ene (15). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.19 (d, J = 15, 1H), 6.08 (m, 1H), 2.81 (m, 1H), 1.08 (dd, J = 7.0, 1.0, 3H), 1.05 (m, 2H), 1.00 (s, 18H), 0.98 (d, J = 6.8, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.6, 124.8, 121.5, 119.1, 27.3, 26.9, 21.4, 20.3, 18.1, 7.4. IR (thin film): 2960, 2931, 2858, 1471, 1387 cm^{-1}. HRMS (CI/isobutane): *m/z* calcd for $C_{17}H_{32}OSi$ (M^+), 280.2222; found, 280.2221.

4-Isopropyl-5-methoxy-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (16). The representative procedure for copper-catalyzed insertion was followed using silacyclopropane **8** (0.299 g, 1.41 mmol), $CuBr_2$ (0.026 g, 0.12 mmol), and methyl formate (0.280 mL, 4.53 mmol). After extraction, GC analysis of the unpurified product showed a pair of diastereomers (**16**) in a ratio of 78:22. The resulting oil was purified by flash chromatography (1:99−2:98 ethyl acetate/hexanes) to yield the product as a clear oil (0.269 g, 70%) as an inseparable pair of diastereomers. The resonances for each isomer were identifiable in the ^{1}H NMR spectrum. Combustion analysis, IR, ^{13}C NMR, and mass spectrometry data were obtained for **16** as a mixture of diastereomers. IR (thin film): 2958, 1472, 1365, 1203, 1111, 1017 cm^{-1}. ^{13}C NMR ($CDCl_3$, 125 MHz): 108.1, 104.9, 55.6, 54.9, 51.7, 50.6, 31.1, 30.5, 28.1, 27.8, 27.6, 27.4, 22.1, 21.6, 21.1, 20.3, 20.3, 19.8, 19.4, 18.9, 8.6, 7.0. HRMS (CI/isobutane): *m/z* calcd for $C_{15}H_{32}O_2Si$ ($M - H)^+$, 271.2093; found, 271.2097. Anal. Calcd for $C_{15}H_{32}O_2Si$: C, 66.11; H, 11.84. Found: C, 66.21; H, 11.73.

Major Isomer of 16. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.63 (d, J = 6.9, 1H), 3.43 (s, 3H), 1.70 (m, 2H), 1.03 (s, 9H), 1.00 (s, 9H), 0.93 (d, J = 6.6, 3H), 0.89 (d, J = 6.5, 3H), 0.83 (dd, J = 15.0, 8.6, 1H), 0.51 (dd, J = 15.0, 11.5, 1H).

Minor Isomer of 16. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.92 (d, J = 4.3, 1H), 3.36 (s, 3H), 1.56 (m, 2H), 1.04, (s, 9H), 1.01 (s, 9H), 0.94 (d, J = 6.5, 3H), 0.91 (d, J = 6.3, 3H), 0.84 (dd, J = 14.3, 7.3, 1H), 0.52 (dd, J = 14.4, 12.4, 1H).

4-(1-Butyl)-5-phenyl-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (18a). The representative procedure for copper-catalyzed insertion was followed using silacyclopropane **17a**[5] (0.060 g, 0.265 mmol), $CuBr_2$ (0.023 g, 0.010 mmol), and benzaldehyde (0.100 mL, 0.984 mmol). After extraction, GC analysis of the unpurified product showed a pair of diastereomers (**18a**) in a ratio of 90:10 (**18a**) as well as product **19a**. Purification by flash chromatography (0:100−2:98 ethyl acetate/hexanes) yielded a diastereomeric mixture of products **18a** as a colorless oil (0.054 g, 61%). The structures and stereochemistries of **18a** and **19a** were previously reported.[5]

4-(1-Butyl)-5-(1-propenyl)-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (18b). The representative procedure for copper-catalyzed insertion was followed using silacyclopropane **17a** (0.147 g, 0.650 mmol), $CuBr_2$ (0.014 g, 0.062 mmol), and crotonaldehyde (0.175 mL, 2.11 mmol). After extraction, GC analysis of the unpurified product showed a pair of diastereomers (**18b**) in a ratio of 95:5. Purification by flash chromatography (5:95−20:80 CH_2Cl_2/hexanes) yielded a diastereomeric mixture of products **18b** as a colorless oil (0.103 g, 56%). Combustion analysis and IR data were obtained for **18b** as a mixture of diastereomers. IR (thin film): 2959, 1471, 1364, 1001, 963 cm^{-1}. Anal. Calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.24. Found: C, 72.76; H, 12.14.

18b. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.66 (m, 1H), 5.41 (m, 1H), 3.72 (t, J = 8.8, 1 H), 1.71 (d, J = 6.4, 3H), 1.46 (m, 3H), 1.29 (m, 3H), 1.01 (s, 18H + m, 2H), 0.90 (t, J = 6.9, 3H), 0.39 (dd, J = 14.6, 11.9, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.4, 127.6, 85.5, 44.9, 33.7, 30.2, 27.7, 27.6, 22.8, 20.5, 19.8, 17.8, 14.7, 12.8. HRMS (GC−MS, EI): *m/z* calcd for $C_{18}H_{36}OSi$ (M^+), 296.2535; found, 296.2532.

Minor cis Isomer of 18b. ^{1}H NMR (500 MHz, $CDCl_3$, distinctive peaks): δ 4.19 (m, 1H). HRMS (GC−MS, EI): *m/z* calcd for $C_{18}H_{36}OSi$ (M^+), 296.2535; found, 296.2538.

4-*tert*-Butyl-5-phenyl-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (18c). The representative procedure for copper-catalyzed insertion was followed using silacyclopropane **17b** (0.186 g, 0.822 mmol), $CuBr_2$ (0.023 g, 0.010 mmol), and benzaldehyde (0.280 mL, 2.74 mmol). After extraction, GC analysis of the unpurified product showed a pair of diastereomers (**18c**) in a ratio of 89:11 as well as product **19b**. Purification by flash chromatography (0:100−15:85 CH_2Cl_2/hexanes) yielded product **19b** as a colorless oil (0.070 g, 26%) and a diastereomeric mixture of products **18c** as a colorless oil (0.162 g, 59%). Combustion analysis and IR data were obtained for **18c** as a mixture of diastereomers. IR (thin film): 3030, 1472, 1365, 998 cm^{-1}. Anal. Calcd for $C_{21}H_{36}OSi$: C, 75.84; H, 10.91. Found: C, 75.73; H, 10.93.

18c. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (d, J = 7.9, 2H), 7.29 (t, J = 7.5, 2H), 7.23 (m, 1H), 4.58 (d, J = 10.4, 1H), 2.06 (m, 1H), 1.12 (s, 9H), 1.07 (s, 9H), 0.99 (dd, J = 14.7, 7.3, 1H), 0.86 (dd, J = 14.6, 12.4, 1H), 0.71 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.2, 128.4, 127.75, 127.68, 83.3, 55.8, 32.8, 28.7, 27.82, 27.80, 21.1, 20.2, 10.0. HRMS (EI): *m/z* calcd for $C_{20}H_{33}OSi$ ($M - CH_3)^+$, 317.2301; found, 317.2297.

Minor cis Isomer of 18c. ^{1}H NMR (500 MHz, $CDCl_3$, distinctive peaks): δ 5.14 (d, J = 8.3, 1H), 2.64 (m, 1H), 1.11 (s, 9H), 0.73 (s, 9H). HRMS (EI): *m/z* calcd for $C_{20}H_{33}OSi$ ($M - CH_3)^+$, 317.2301; found, 317.2294.

1-(Benzyloxy)-1-[2-(3,3-dimethyl-1-butenyl)]di-*tert*-butylsilane (19b). IR (thin film): 3066, 1474, 1386, 1360, 1108 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (dd, J = 7.5, 0.5, 2H), 7.33 (t, J = 7.6, 2H), 7.24 (t, J = 7.3, 1H), 5.75 (d, J = 0.9, 1H), 5.30 (d, J = 1.0, 1H), 5.11 (s, 2H), 1.13 (s, 9H), 1.10 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ

157.7, 141.0, 128.2, 126.9, 126.6, 122.4, 67.2, 37.7, 30.5, 29.4, 22.4. HRMS (CI/isobutane): *m/z* calcd for $C_{21}H_{35}OSi$ $(M - H)^+$, 331.2457; found, 331.2450.

4-*tert*-Butyl-5-(1-propenyl)-2-di-*tert*-butyl-1-oxa-2-silacyclopentane (18d). The representative procedure for copper-catalyzed insertion was followed using silacyclopropane **17b** (0.205 g, 0.906 mmol), $CuBr_2$ (0.023 g, 0.010 mmol), and crotonaldehyde (0.240 mL, 2.90 mmol). After extraction, GC analysis of the unpurified product showed a pair of diastereomers (**18d**) in a ratio of 99:1. Purification by flash chromatography (5:95−15:85 CH_2Cl_2/hexanes) yielded a diastereomeric mixture of products **18d** as a colorless oil (0.154 g, 56%). Combustion analysis and IR data were obtained for **18d** as a mixture of diastereomers. IR (thin film): 2954, 1472, 1364, 990 cm^{-1}. Anal. Calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.24. Found: C, 73.02; H, 12.26.

18d. ^1H NMR (500 MHz, $CDCl_3$): δ 5.65 (m, 1H), 5.48 (m, 1H), 4.10 (t, $J = 9.0$, 1 H), 1.69 (dd, $J = 6.4$, 1.4, 3H), 1.64 (m, 1H), 1.02 (s, 18H), 0.91 (s, 9H), 0.84 (dd, $J = 14.9$, 8.0, 1H), 0.72 (dd, $J = 14.8$, 12.2, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.5, 127.2, 81.9, 54.5, 33.0, 28.8, 27.8, 27.6, 20.7, 19.9, 17.9, 9.4. HRMS (EI): *m/z* calcd for $C_{18}H_{36}OSi$ (M^+), 296.2535; found, 296.2536.

Minor cis Isomer of 18d. ^1H NMR (500 MHz, $CDCl_3$, distinctive peaks): δ 4.49 (m, 1H), 1.72 (d, $J = 6.5$, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, distinctive peaks): δ 135.9, 125.0, 74.8, 54.6, 30.6, 29.7, 28.6, 13.5. HRMS (EI): *m/z* calcd for $C_{18}H_{36}OSi$ (M^+), 296.2535; found, 296.2538.

Hydrobenzoin (22). To a solution of silacyclopropane *cis*-**1** (90:10 cis/trans, as determined by ^1H NMR spectroscopy) (0.204 g, 1.03 mmol) and 8 mL of CH_2Cl_2 were added $CuBr_2$ (0.024 g, 0.106 mmol) and benzaldehyde (0.350 mL, 3.44 mmol) at 22 °C. The reaction mixture was stirred for 5 h, and then 2 mL of MeOH was added. The mixture was treated with 10 mL of sodium potassium tartrate solution (saturated aqueous), and the aqueous layer was extracted with 2 × 10 mL of CH_2Cl_2. The combined organic layers were washed with 10 mL of brine, dried (Na_2SO_4), and concentrated in vacuo to afford a yellow oil. Unpurified **21** was characterized on the basis of ^1H NMR spectroscopy and mass spectrometry. ^1H NMR (500 MHz, $CDCl_3$): δ 7.17 (m, 4H), 7.28 (m, 6H), 4.78 (s, 2H), 1.25 (s, 18H). HRMS (EI): *m/z* calcd for $C_{18}H_{21}SiO_2$ $(M - C_4H_9)^+$, 297.1331; found, 297.1309. For further characterization, the silylene ketal was deprotected: A solution of unpurified **21** in 8 mL of THF at 22 °C was treated with excess HF (2 mL, 70% solution in pyridine). After 50 min, excess pyridine was added and the reaction was partitioned between 10 mL of $NaHCO_3$ (saturated aqueous) and 10 mL of CH_2Cl_2. The organic layer was washed with 10 mL of $NaHCO_3$, 10 mL of H_2O, 2 × 10 mL of $CuSO_4$ (aqueous), 10 mL of brine, dried (Na_2SO_4), and concentrated in vacuo to afford pale yellow crystals. Analysis of the unpurified product using ^1H NMR spectroscopy showed the formation of hydrobenzoin (**22**) as a 92:8 (trans/cis) mixture of stereoisomers. The solid was purified by flash chromatography (10:90−50:50 ethyl acetate/hexanes) to afford hydrobenzoin (**22**) as a white crystalline solid (0.134 g, 61% from silacyclopropane *cis*-**1**). The spectral data match reported values for the trans isomer of **22**.[33]

3-(Di-*tert*-butylhydroxysilyl)cyclohexane-1-one (23). To a cooled (−78 °C) solution of silacyclopropane *cis*-**1** (90:10 cis/trans, as determined on the basis of ^1H NMR spectroscopy) (0.152 g, 0.767 mmol) in 1.5 mL of CH_2Cl_2 were added 1.5 mL of CuI·2LiI (0.5 M solution in tetrahydrofuran (THF)) and 2-cyclohexene-1-one (0.250 mL, 2.50 mmol). The mixture was allowed to warm to 22 °C and was stirred for 5 h. The reaction mixture was treated with 5 mL of NH_4Cl/NH_4OH (9:1, saturated aqueous) and stirred for 1 h. The aqueous layer was extracted with 2 × 10 mL of CH_2Cl_2. The combined organic layers were washed with 10 mL of brine, dried (Na_2SO_4), and concentrated in vacuo to afford a white solid. The solid was purified by flash chromatography (5:95−10:90 ethyl acetate/hexanes) to yield the product as a white crystalline solid (0.158 g, 80%). The structure of product **23** was assigned on the basis of two-dimensional $^1H,^1H$ and $^1H,^{13}C$ correlated NMR experiments: mp 108−110 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 2.57 (m, 1H), 2.45 (t, $J = 14.1$, 1H), 2.43 (m, 1H), 2.30 (m, 1H), 2.19 (m, 1H), 2.07 (m, 1H), 1.79 (bs, 1H), 1.78 (qd, $J = 12.9$, 3.0, 1H), 1.68 (m, 1H), 1.46 (m, 1H), 1.07 (s, 9H), 1.06 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 212.3, 43.8, 42.1, 30.2, 28.4, 28.3, 27.6, 27.3, 21.6, 21.5. IR (KBr): 3541, 2933, 1698, 1471, 1239, 1079 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{14}H_{28}O_2Si$ (M^+), 256.1858; found, 256.1857. Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.57; H, 11.00. Found: C, 65.62; H, 11.04.

(3-Deuterio-*sec*-butyl)di-*tert*-butylmethoxysilane (24). To a cooled (−78 °C) solution of silacyclopropane *cis*-**1** (99:1 cis/trans, as determined on the basis of ^1H NMR spectroscopy) (0.057 g, 0.29 mmol) in 2 mL of CH_2Cl_2 were added CuI (0.007 g, 0.04 mmol) and MeOD (0.120 mL, 2.95 mmol). After the mixture was allowed to warm to 22 °C and was stirred for 7 h, 10 mL of H_2O was added. The aqueous layer was extracted with 3 × 10 mL of CH_2Cl_2. The combined organic layers were washed with 10 mL of brine, dried (Na_2SO_4), and concentrated in vacuo to obtain a colorless oil. The oil was purified by filtering through a plug of silica gel (ethyl acetate) to yield the product as a colorless oil (0.032 g, 48%). ^1H NMR (500 MHz, $CDCl_3$): δ 3.58 (s, 3H), 1.81 (m, 1H), 1.13 (d, $J = 7.4$, 3H), 1.05 (s, 9H), 1.04 (s, 9H), 1.02 (m, 1H), 0.97 (d, $J = 7.3$, 3H). ^2H NMR (77 MHz, $CHCl_3$): δ 1.25. ^{13}C NMR (125 MHz, $CDCl_3$): δ 52.2, 29.1, 29.0, 25.0 (t, $^1J_{CD} = 19.2$), 22.2, 22.0, 20.4, 14.5, 13.9. HRMS (CI/isobutane): *m/z* calcd for $C_{13}H_{30}DOSi$ $(M + H)^+$, 232.2208; found, 232.2204.

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Supporting Information Available: Descriptions of stereochemistry proofs; ^1H and ^{13}C NMR spectra for **4**, **5**, **9**, **11**−**13**, **15**, and **19b**; and GC traces of **10a**−**c** and **18a**−**d** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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