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Insertion Reactions of Silacyclopropanes: Evidence for a Radical-Based Mechanism

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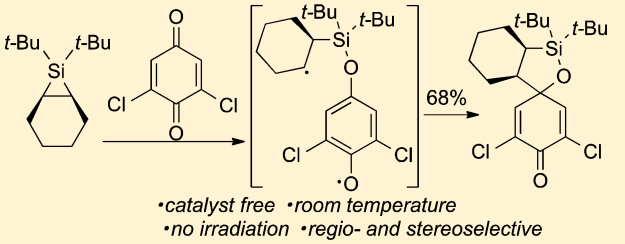
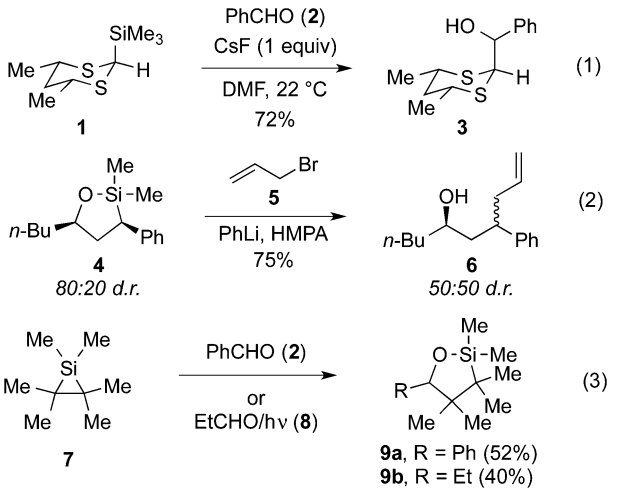
Supporting Information

ABSTRACT: Silacyclopropanes reacted rapidly and selectively with *p*-benzoquinones to provide oxasilacyclopentanes. Ring-expansion products were observed in the absence of a catalyst, elevated temperatures, or irradiation. As substitution was increased on the silacyclopropane ring, improved stereoselectivity was observed. In some cases, the regiochemistry was controlled depending on the extent of stabilization of the reactive intermediates involved. A radical clock experiment, along with stereochemical studies, confirmed that radical intermediates were involved in the ring-expansion reaction. The scope of this radical reaction was expanded to include dienones, aryl aldehydes, and electron-deficient enones in addition to benzoquinones. In the case of aryl aldehydes and electron-deficient enones, the radical reaction can be used to generate silylenes from silacyclopropanes.



INTRODUCTION

The reactions of organosilanes with carbon electrophiles are commonly used transformations in stereoselective synthesis.[1] Direct reactions of carbon−silicon bonds with carbon electrophiles[2] generally require activation, either by formation of ate complexes or by transmetalation (for example, eqs 1[3] and 2[4]).



By contrast, few uncatalyzed reactions[5] of carbon−silicon bonds with carbon electrophiles have been reported.[6] For example, radical intermediates were proposed in the reactions of three-membered-ring silanes with ketones because, in some cases, irradiation was required (eq 3)[7] and because disproportionation products were observed.[8] Although those experiments suggest the intermediacy of radical species, processes involving siliconate intermediates could also account for the results.[9]

Herein, we provide evidence that strained silanes undergo rapid, uncatalyzed reactions with carbonyl compounds at room temperature to provide oxasilacyclopentanes. These reactions can be highly selective, providing single diastereomers or regioisomers of ring-expanded products. Mechanistic studies, including determination of stereoselectivity and regioselectivity and experiments using radical clocks,[10] provide evidence that these reactions proceed via radical intermediates.

RESULTS AND DISCUSSION

Stereochemical studies suggest that radical intermediates can be formed in reactions of silacyclopropanes with carbonyl compounds. In the presence of *p*-benzoquinone (**11**), *trans*-**10** and *cis*-**10** were consumed in less than 10 minutes at 22 °C to provide oxasilacyclopentanes **12a** and **12b** (eqs 4 and 5). That these reactions were rapid contrasts with earlier observations that elevated temperatures or catalysts were required to achieve carbon−carbon bond formation with other carbonyl compounds, such as aldehydes, esters, and amides.[11]

The loss of stereochemical integrity in these experiments suggests that carbon−carbon bond formation is not concerted. Instead, short-lived ring-opened intermediates such as radicals (e.g., **A**) or zwitterions (e.g., **B**) could intervene, leading to loss of configuration (Figure 1). Radicals are reasonable intermediates considering that benzoquinone can serve as a one-electron oxidant in reactions with organometallic compounds.[12] Furthermore, β-silyl radicals do not retain their stereochemical configuration.[13] By comparison, if intermediates such as **B** were involved, they would not necessarily lose their stereochemical

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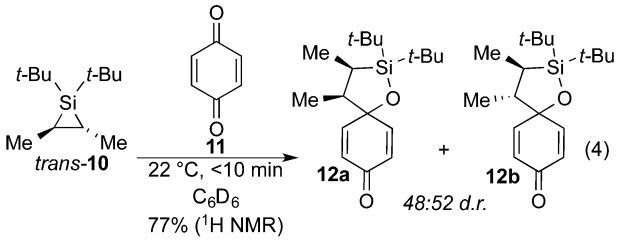


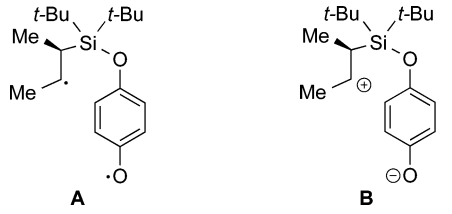
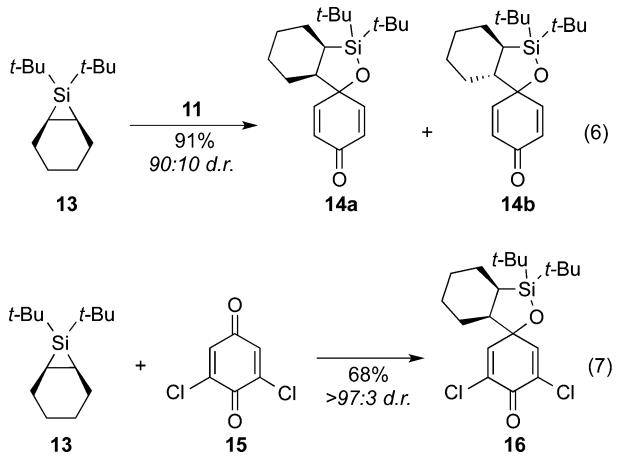


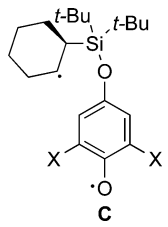
Figure 1. Radical (**A**) and zwitterionic (**B**) intermediates leading to oxasilacyclopropanes **12**.

configuration. Strong hyperconjugative stabilization by a carbon−silicon bond can restrict rotation of cationic intermediates,[14] leading to stereospecific processes.[15]

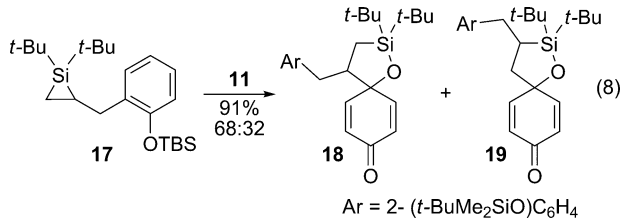
In the case of a silacyclopropane that was conformationally restricted, insertion reactions were stereoselective. The reaction of *p*-benzoquinone (**11**) with bicyclic silacyclopropane **13** occurred within minutes at 22 °C, forming products **14a** and **14b** with 90% retention of configuration (eq 6). Insertion of



2,6-dichlorobenzoquinone (**15**) also occurred rapidly, providing a single diastereomer and regioisomer of oxasilacyclopentane **16**, in which the configuration of the starting silacyclopropane was retained (eq 7). These stereochemical outcomes are consistent with reactions via radical intermediates. Coupling of the nucleophilic secondary alkyl radical component of diradical **C** should occur faster with the more electron-deficient ketyl radical (**C**, X = Cl) because of better matches of SOMO energies.[16] The slower reaction of an unsubstituted ketyl radical (**C**, X = H) would allow for some loss of stereochemical configuration. The observation that smaller quantities of products resulting from loss of stereochemistry (i.e., **14b**) were formed compared to the reactions of monocyclic silacyclopropanes (eqs 4 and 5) could be because the trans isomer is more strained,[17] leading to little driving force for isomerization.[18]



Depending upon the extent of substitution, insertions of silacyclopropanes can be regioselective.[11] Monosubstituted silacyclopropane **17** reacted with *p*-benzoquinone (**11**) at 22 °C to give two regioisomeric products, **18** and **19** (eq 8).



The fact that significant quantities of regioisomer **19** are formed provides strong support that the reactions proceed via radical intermediates (**D**) and not zwitterionic intermediates (**E**, Figure 2). Had **E** been an intermediate, the cationic center

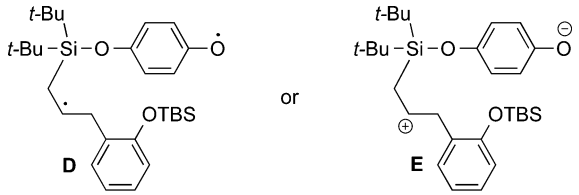


Figure 2. Radical (**D**) and zwitterionic (**E**) intermediates leading to oxasilacyclopropane **18**.

would experience considerably more stabilization (10 kcal·mol^{-1}) as a secondary β-silyl carbocation than it would as the primary β-silyl carbocation.[19] As a result, if an ionic mechanism were operating, formation of regioisomer **19** should have been strongly disfavored.[20] By contrast, the difference in stabilities between primary and secondary β-silyl radicals is much smaller ($\leq$2 kcal·mol^{-1}), so reaction through a primary, β-silyl radical is not as strongly disfavored as it would be for reactions proceeding via a primary carbocation.[19]

In the case of a more substituted silacyclopropane ring, high regioselectivity was observed. Geminally substituted silacyclopropane **20** provided a single isomer of product, although the reaction was not clean (eq 9). The lower yield in this reaction may be the result of developing steric interactions between the tertiary radical and the quinone radical (intermediate **F**) that decelerates this bond formation.

Vinylsilacyclopropanes also underwent regioselective carbon−carbon bond formation. The reaction of vinylsilacyclopropane **22** with *p*-benzoquinone (**11**) provided insertion

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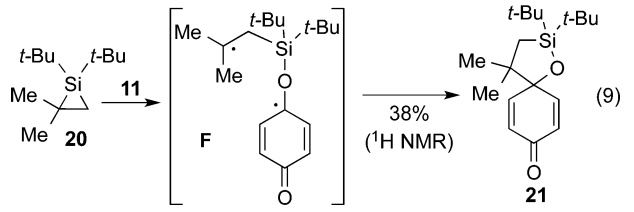
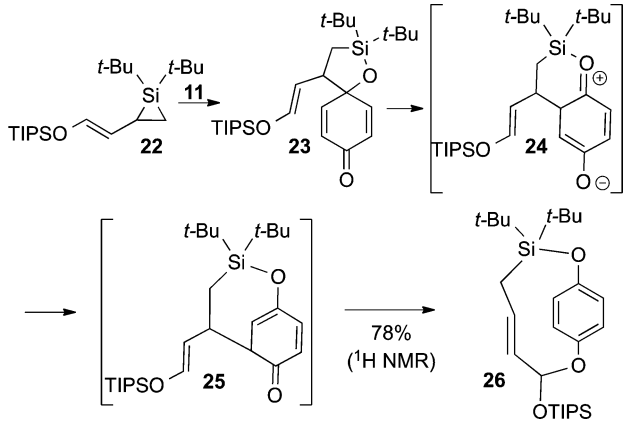


product **23** as a single regioisomer (Scheme 1). The formation of one regioisomer suggests that the adjacent double bond and

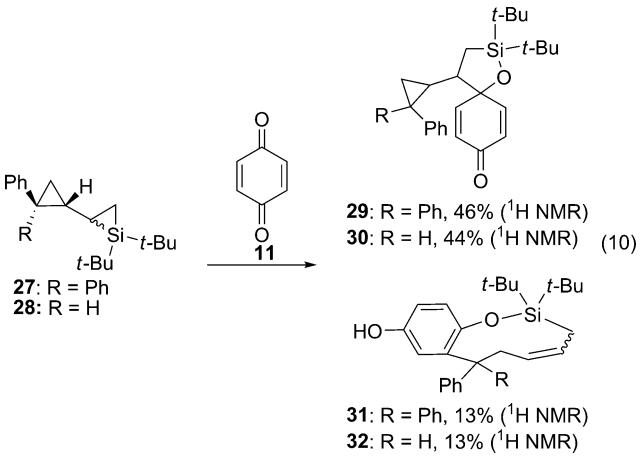
Scheme 1. Formation of Oxasilacyclopropane 23 and Paracyclophane 26 from Vinylsilacyclopropane 22



silyloxy group stabilize the radical intermediate.[21] The oxasilacyclopentane **23** could not be isolated in pure form, however. Within 12 h, it rearranged to paracyclophane **26**.

The hydroquinone derivative **26** could arise from a series of rearrangements. Oxasilacyclopentane **23** could undergo a [1,2]-alkyl shift to provide ring-expanded intermediate **24**. This intermediate is poised to undergo a subsequent rearrangement to provide enone **25**. This enone can then undergo a retro-Claisen rearrangement to provide hydroquinone derivative **26**.[22]

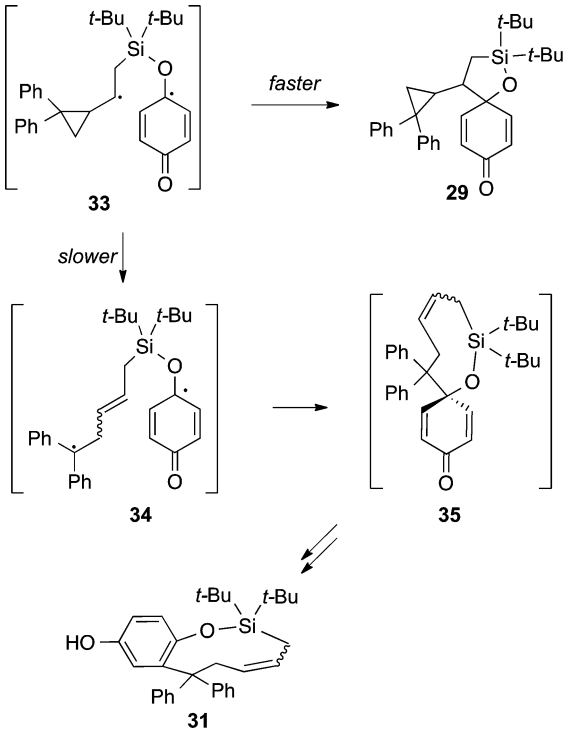
Experiments with silacyclopropanes **27** and **28** bearing radical clocks[23] provided additional evidence that radical intermediates were involved in reactions with strained silanes.[24] When these silacyclopropanes were subjected to the reaction conditions, mixtures of products were obtained (eq 10). Due to



difficulties associated with purification, not all products could be unambiguously identified. The major products could be assigned as **29** and **30**, however, and they were formed without opening of the cyclopropane ring. Two minor ring-opened products, **31** and **32**, were also formed.

A mechanism involving radical intermediates is consistent with the results described in eq 10. This mechanism is illustrated for silacyclopropane **27** (Scheme 2). Formation of

Scheme 2. Mechanism for the Insertion of Carbonyl Compounds into the Carbon−Silicon Bond of Silacyclopropanes



diradical **33** occurs,[25] likely after coordination of the carbonyl oxygen atom to the Lewis acidic silicon atom.[26] Homolytic cleavage of the activated carbon−silicon bond provides diradical **33**. Cleavage of the more substituted carbon−silicon bond due to stabilization of the alkyl component of radical **33** also explains the trends in regioselectivity observed for other silacyclopropanes. Radical recombination of **33** would form the major product **29**.[27]

Although this radical recombination[28] should be rapid, opening of the cyclopropane ring is competitive.[23] Cyclopropylcarbinyl radical rearrangement leads to diradical **34**. Recombination of this diradical would form enone **35**, which can undergo a dienone-phenol rearrangement[29] to provide phenol **31**. A single stereoisomer of **31** was formed, but, due to the small quantities of product formed and difficulties associated with purification, the geometry of the carbon−carbon double bond could not be unambiguously determined.[30]

The formation of minor quantities of phenols **31** and **32** provides insight into the lifetime of diradical **33**. The rate of cyclopropylcarbinyl radical rearrangement of phenyl-substituted cyclopropanes is about 10^{11} s^{-1}.[23] The ring closure of diradical intermediate **33** to form the oxasilacyclopentane **29** therefore must proceed at a competitive rate.[31] In the case of a monocyclic silacyclopropane, persistence of this radical would lead to loss of stereochemistry (eqs 4 and 5) considering the rapid pyramidal inversion of alkyl radicals.[18]

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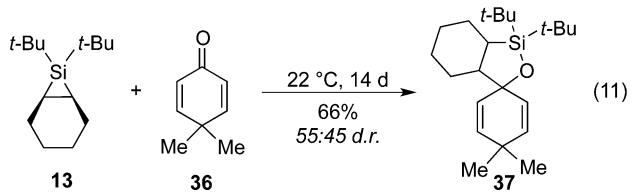
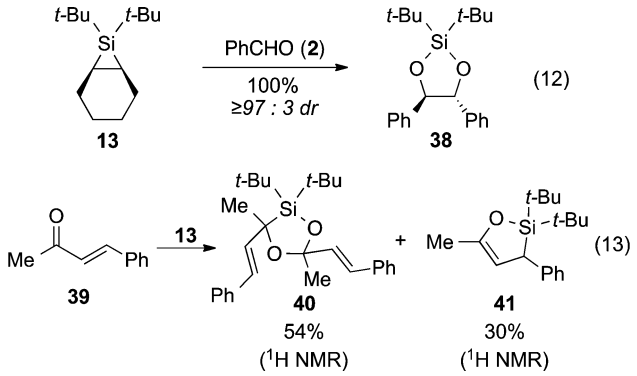
The uncatalyzed reactions of carbon−silicon bonds were not restricted to quinones. When dienone **36** was added to silacyclopropane **13**, ring-expanded products **37** were observed (eq 11). The rate of this ring expansion was slow, requiring 2



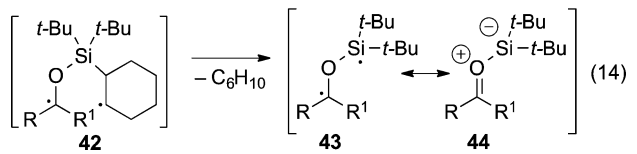
weeks to proceed to completion compared to less than 10 minutes in the case of benzoquinone (eq 6). This difference in relative rate is consistent with the fact that divinyl ketones are much less prone to single-electron reduction than benzoquinones, presumably because the radical intermediate is not as delocalized.[32] Furthermore, the corresponding enone, 4,4-dimethylcyclohexenone, did not react under these conditions, indicating that the stabilization by a single double bond is not sufficient to stabilize a radical intermediate that would be formed.

Although aliphatic aldehydes did not react with the carbon−silicon bond of silacyclopropanes, aryl aldehydes and phenyl-substituted enones did.[11a] When benzaldehyde was added to cyclohexene silacyclopropane (**13**), aldehyde dimer **38** was formed within 4 h (eq 12).[11b] This dimer is the product of



silylene transfer from silacyclopropane **13**. In the absence of other reaction partners, the silylene intermediate is transferred to another molecule of benzaldehyde, providing dimer **38**. The reaction of enone **39** and bicyclic silacyclopropane **13** formed both ketone dimer **40** and oxasilacyclopentene **41** (eq 13). In the case of enone **39**, dimerization could be slow considering the steric hindrance at the carbonyl carbon atom, so 6π-electrocyclization[33] becomes competitive, providing **41** in addition to the dimer.

These results are consistent with the proposal that radical intermediates are involved. β-Silyl radical intermediates **42** could undergo fragmentation reactions, leading to silylene transfer products (eq 14). Coordination of the silicon atom of



silacyclopropane **13** followed by homolytic bond cleavage provides diradical **42**. Elimination of cyclohexene affords new diradical **43**. This species (shown as its resonance form silacarbonyl ylide **44**) can undergo either electrocyclization or dimerization, the net products of silylene transfer reactions.[34]

CONCLUSIONS

In conclusion, the reactions of carbonyl compounds with the carbon−silicon bond of a silane can occur through a single-electron transfer mechanism. This conclusion was supported by experiments using substrates bearing radical clocks, which showed that radical recombination is rapid, in addition to stereochemical studies. Benzoquinones, electron-deficient enones, and aryl aldehydes all react with silacyclopropanes at room temperature in the absence of catalysts. In some cases, the reactions of silacyclopropanes with benzoquinones were regio- or stereoselective. The uncatalyzed reactions of aryl aldehydes and electron-deficient enones provided the products of net silylene transfer, indicating that the radical fragmentation can also provide silylene intermediates.

EXPERIMENTAL SECTION

General Procedures. General experimental procedures are provided as Supporting Information.

Oxasilacyclopentanes 12a and 12b (from *cis*-10). To a solution of silacyclopropane *cis*-**10** (0.055 g, 0.19 mmol of silacyclopropane **10**, contaminated with 0.070 mmol of cyclohexene silacyclopropane **13** from the preparation of **10**) in C_6D_6 (0.50 mL) in a J. Young NMR tube were added 1,4-benzoquinone **11** (0.023 g, 0.21 mmol) in C_6D_6 (0.50 mL) and mesitylene (0.0020 mL, 0.014 mmol, internal standard). Oxasilacyclopentanes **12a** and **12b** were formed in 68% yield (as a 57:43 mixture of diastereomers), and oxasilacyclopentane **14** (derived from silacyclopropane **13**) was formed in 43% yield based on comparison of the standard peak (δ 2.17) and the enone protons. Purification by flash chromatography (3:97 EtOAc/hexanes, with silica gel that was pretreated with a Et_3N solution, 1:99 Et_3N/hexanes) provided oxasilacyclopentanes **12a** and **12b** as a colorless oil in a 80:20 mixture with oxasilacyclopentane **14**: ^{1}H NMR (600 MHz, C_6D_6) δ 6.53 (dd, J = 10.3, 3.1, 1H, HC═C), 6.41−6.40 (m, 0.7H, HC═C), 6.31 (dd, J = 10.0, 3.0, 0.7H, HC═C), 6.25 (dd, J = 10.1, 3.0, 1H, HC═C), 6.15−6.09 (m, 3.4H, HC═C), 2.05−2.00 (m, 1H, HC−CSi), 1.62−1.56 (m, 0.7H, HC−CSi), 1.16−1.14 (m, 1H, HC−Si), 1.05 (s, 9H, *t*-Bu), 1.00 (s, 6.5H, *t*-Bu), 0.96 (s, 6.5H, *t*-Bu), 0.94 (appar s, 11.4H, *t*-Bu and CH_3), 0.86 (d, J = 8.2, 3H, CH_3), 0.76−0.70 (m, 0.7H, CH−Si), 0.53 (d, J = 7.3, 3H, CH_3), 0.50 (d, J = 6.8, 2.1H, CH_3); ^{13}C NMR (150 MHz, C_6D_6) δ 185.49 (C), 185.45 (C), 152.9 (CH), 152.0 (CH), 149.1 (CH), 148.3 (CH), 81.2 (C), 79.7 (C), 48.3 (CH), 45.1 (CH), 29.5 (CH_3), 29.1 (CH_3), 28.9 (CH_3), 28.8 (CH_3), 24.7 (CH), 22.0 (C), 21.8 (C), 21.2 (C), 20.8 (C), 20.5 (CH), 14.2 (CH_3), 13.2 (CH_3), 13.1 (CH_3), 11.6 (CH_3); IR (ATR) 1672, 1631, 1041, 831 cm^{-1}; HRMS (TOF MS ES+) *m*/*z* calcd for $C_{18}H_{31}O_2Si$ $(M + H)^+$ 307.2089, found 307.2085.

Oxasilacyclopentanes 12a and 12b (from *trans*-10). To a solution of silacyclopropane *trans*-**10** (0.050 g, 0.14 mmol of silacyclopropane **10**, contaminated with 0.11 mmol of cyclohexene silacyclopropane **13** from the preparation of **10**) in C_6D_6 (0.50 mL) in a J. Young NMR tube were added 1,4-benzoquinone **11** (0.027 g, 0.26 mmol) in C_6D_6 (0.50 mL) and mesitylene (0.0020 mL, 0.014 mmol, internal standard). Oxasilacyclopentanes **12a** and **12b** were formed in 77% yield (as a 48:52 mixture of diastereomers), and oxasilacyclopentane **14** (derived from silacyclopropane **13**) was formed in 67% yield based on comparison of the standard peak (δ 2.17) and the enone protons. The spectroscopic data for oxasilacyclopentanes **12a** and **12b** agree with those reported (from silacyclopropane *cis*-**10**, above).

Oxasilacyclopentanes 14a and 14b. To a solution of 1,4-benzoquinone **11** (0.051 g, 0.47 mmol) in C_6H_6 (2 mL) was added cyclohexene silacyclopropane **13** (0.15 g, 0.67 mmol) as a solution in C_6H_6 (0.5 mL). After 10 min, the reaction mixture was concentrated *in*

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vacuo. Purification by flash chromatography (5:95 EtOAc/hexanes) provided oxasilacyclopentanes **14a** and **14b** as a colorless oil (90:10 mixture of diastereomers, 0.144 g, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (dd, J = 10.3, 3.0, 1H, HC═C), 6.76 (dd, J = 10.1, 2.9, 0.1H, HC═C), 6.72 (dd, J = 10.0, 3.0, 0.1H, HC═C), 6.62 (dd, J = 10.0, 3.1, 1H, HC═C), 6.15 (dd, J = 10.0, 2.0, 1.1H, HC═C), 6.11 (dd, J = 10.3, 1.9, 1.1H, HC═C), 2.34−2.32 (m, 1H, HC−CSi), 2.06−2.02 (m, 0.1H, HC−CSi), 1.92−1.82 (m, 1.1H, CH_2), 1.72−1.70 (m, 1.1H, CH_2), 1.59−1.55 (m, 2.2H, CH_2), 1.49−1.40 (m, 2.2H, CH_2), 1.30−1.26 (m, 1.1H, CH_2), 1.22−1.17 (m, 1.1H, CH_2), 1.13 (appar s, 10H, *t*-Bu and HC−Si), 1.08 (s, 1.0H, *t*-Bu and HC-Si), 1.07 (s, 0.9 H, *t*-Bu), 1.03 (s, 9H, *t*-Bu); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.1 (C), 186.0 (C), 153.4 (CH), 152.1 (CH), 150.9 (CH), 148.7 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.1 (CH), 81.0 (C), 78.4 (C), 51.3 (CH), 44.4 (CH), 29.9 (CH), 29.3 (CH_3), 28.7 (CH_3), 28.6 (CH_2), 28.4 (CH_3), 28.0 (CH_3), 27.9 (CH_2), 27.7 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 25.9 (CH_2), 24.3 (CH), 23.4 (CH_2), 22.8 (CH_2), 21.7 (C), 21.5 (C), 21.0 (C), 20.4 (C); ^{29}Si (99 MHz, $CDCl_3$) δ 34.3, 28.2; IR (ATR) 1673, 1631, 1039, 822 cm^{-1}; HRMS (TOF MS ES+) m/z calcd for $C_{20}H_{33}O_2Si$ $(M + H)^+$ 333.2244, found 333.2243.[35]

Oxasilacyclopentane 16. To a solution of 2,6-dichlorobenzoquinone **15** (0.087 g, 0.49 mmol) in C_6H_6 (2 mL) was added cyclohexene silacyclopropane **13** (0.149 g, 0.66 mmol) as a solution in C_6H_6 (0.50 mL). After 10 min, the reaction mixture was concentrated *in vacuo*. Purification by flash chromatography (3:97 EtOAc/hexanes, with silica gel that was pretreated with a Et_3N solution, 1:99 Et_3N/hexanes) provided oxasilacyclopentane **16** as a white solid (single isomer, 0.135 g, 69%): mp = 46−47 °C; ^{1}H NMR (600 MHz, C_6D_6) δ 7.11 (d, J = 2.8, 1H, HC═C), 6.63 (d, J = 2.8, 1H, HC═C), 1.99 (t, J = 7.3, 1H, HC−CSi), 1.47−1.41 (m, 2H, CH_2), 1.25−1.14 (m, 4H, HC−Si and CH_2), 1.05−1.02 (m, 1H, CH_2), 0.99 (s, 9H, *t*-Bu), 0.94−0.93 (m, 1H, CH_2), 0.83 (s, 9H, *t*-Bu), 0.80−0.76 (m, 1H, CH_2); ^{13}C NMR (150 MHz, C_6D_6) δ 173.0 (C), 149.4 (CH), 147.2 (CH), 131.7 (C), 130.5 (C), 83.7 (C), 45.8 (CH), 29.5 (CH_3), 28.6 (CH_3), 26.6 (CH_2), 26.2 (CH_2), 24.2 (CH), 23.9 (CH_2), 23.2 (CH_2), 21.7 (C), 21.1 (C); IR (ATR) 2933, 2859, 1691 cm^{-1}; HRMS (TOF MS ES+) m/z calcd for $C_{20}H_{31}Cl_2O_2Si$ $(M + H)^+$ 401.1465, found 401.1462. Anal. Calcd for $C_{20}H_{30}Cl_2O_2Si$: C, 59.84; H, 7.53. Found: C, 59.57; H, 7.67.

Oxasilacyclopentanes 18 and 19. To a solution of silacyclopropane **17** (0.073 g, 0.19 mmol, from silylene transfer step) in C_6D_6 (0.8 mL) in a J. Young NMR tube were added a solution of 1,4-benzoquinone **11** (0.40 mL, 0.54 mM in C_6D_6, 0.22 mmol) and mesitylene (0.0020 mL, 0.014 mmol, internal standard). After 10 min, the reaction mixture was analyzed by ^{1}H NMR spectroscopy, and all of the starting material had been consumed. The reaction mixture was concentrated *in vacuo*. Purification by flash chromatography (3:97 EtOAc/hexanes) provided oxasilacyclopentanes **18** and **19** as a colorless oil (62:38 mixture of regioisomers, 0.087 g, 87%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13−7.11 (m, 0.6H, Ar−H), 7.09−7.05 (m, 1.6H, Ar−H), 7.03−7.01 (m, 1H, Ar−H), 6.95−6.84 (m, 3.8H, Ar−H and HC═C), 6.81−6.76 (m, 2.6H, HC═C), 6.23 (dd, J = 10.3, 1.8, 1H, HC═C), 6.20 (dd, J = 10.0, 1.7, 1H, HC═C), 6.12 (dd, J = 10.1, 1.8, 0.6H, HC═C), 6.02 (dd, J = 10.3, 1.9, 0.6H, HC═C), 3.01−3.00 (m, 1.2H, CH_2), 2.62−2.55 (m, 1H, CH), 2.51 (dd, J = 13.2, 3.9, 1H, 1 H of CH_2), 2.31 (dd, J = 12.9, 11.5, 1H, 1 H of CH_2), 2.03−2.01 (m, 1.2H, CH_2), 1.89−1.88 (m, 0.6H, HC−Si), 1.20 (s, 5.4H, *t*-Bu), 1.10 (s, 5.4H, *t*-Bu), 1.09 (s, 9H, *t*-Bu), 1.02 (s, 9H, *t*-Bu), 1.00 (s, 5.4H, *t*-Bu), 0.99 (s, 9H, *t*-Bu), 0.95−0.92 (m, 1H, 1 H of H_2C−Si), 0.73 (dd, J = 14.8, 13.7, 1H, 1 H of H_2C−Si), 0.26 (s, 1.8H, H_3C−Si), 0.23 (s, 1.8 H, H_3C−Si), 0.22 (s, 3H, H_3C−Si), 0.18 (s, 3H, H_3C−Si); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.0 (C), 185.6 (C), 153.8 (C), 153.6 (C), 152.4 (CH), 152.1 (CH), 150.6 (CH), 148.5 (CH), 132.4 (C), 130.7 (CH), 130.4 (CH), 129.8 (C), 128.6 (CH), 128.2 (CH), 127.3 (2 CH), 127.2 (CH), 126.2 (CH), 121.3 (CH), 121.2 (CH), 118.9 (CH), 118.8 (CH), 79.3 (C), 75.3 (C), 47.2 (CH), 42.8 (CH_2), 33.3 (CH_2), 30.0 (CH_2), 29.4 (CH), 28.7 (CH_3), 25.3 (CH_3), 28.1 (CH_3), 26.2 (CH_3), 26.1 (CH_3), 25.2 (CH_3), 21.9 (C), 20.63 (C), 20.60 (C), 20.1 (C), 18.6 (C), 18.5 (C), 12.5 (CH_2), −3.6 (CH_3), −3.7 (CH_3), −3.8 (CH_3), −4.0 (CH_3); IR (ATR) 1673, 1632, 1041, 830 cm^{-1}; HRMS (TOF MS ES+) m/z calcd for $C_{29}H_{47}O_3Si_2$ $(M + H)^+$ 499.3058, found 499.3070. Anal. Calcd for $C_{29}H_{46}O_3Si_2$: C, 69.82; H, 9.29. Found: C, 70.00; H, 9.55.

Oxasilacyclopentane 21. To a solution of 1,1-dimethyl-di-*tert*-butylsilacyclopropane **20** (0.030 g, 0.15 mmol) in C_6D_6 (0.50 mL) in a J. Young NMR tube were added a solution of 1,4-benzoquinone **11** (0.50 mL, 0.32 M in C_6D_6, 0.16 mmol) and mesitylene (0.0020 mL, 0.014 mmol, internal standard), and the unpurified reaction mixture was analyzed by NMR spectroscopy after 10 min. Oxasilacyclopentane **21** was formed in 37% yield based on comparison of the standard peak (δ 6.71) and the enone protons: ^{1}H NMR (500 MHz, C_6D_6) δ 6.60 (d, J = 10.2, 2H, HC═C), 6.05 (d, J = 10.1, 2H, HC═C), 1.00 (s, 18H, 2*t*-Bu), 0.84 (s, 6H, $2CH_3$), 0.74 (s, 2H, CH_2); ^{13}C NMR (125 MHz, C_6D_6) δ 185.2 (C), 151.4 (CH), 126.7 (CH), 82.1 (C), 45.6 (C), 31.4 (CH_3), 29.5 (CH_3), 24.8 (CH_2), 20.7 (C).[36]

Oxasilacyclopentane 23 and Hydroquinone 26. To a solution of vinylsilacyclopropane **22** (0.064 g, 0.17 mmol, from silylene transfer step) in C_6D_6 (0.54 mL) in a J. Young NMR tube were added a solution of 1,4-benzoquinone **11** (0.48 mL, 0.54 mM in C_6D_6, 0.26 mmol) and mesitylene (0.0020 mL, 0.014 mmol, internal standard), and the unpurified reaction mixture was analyzed by ^{1}H NMR spectroscopy after 10 min. Oxasilacyclopentane **23** was formed in 70% yield based on comparison of the standard peak (δ 2.17) and the enone protons. Hydroquinone **26** was also formed in 16% yield after 10 min. The reaction mixture was allowed to sit at room temperature overnight (12 h), and hydroquinone **26** was formed in 78% yield from vinylsilacyclopropane **22** based on comparison of the standard peak (δ 2.17) and the aryl protons.[37]

Oxasilacyclopentane 23. ^{1}H NMR (500 MHz, C_6D_6) δ 6.54 (dd, J = 10.3, 3.1, 1H, HC═C), 6.38 (dd, J = 10.1, 3.1, 1H, HC═C), 6.26 (d, J = 11.7, 1H, HC═C), 6.14 (dd, J = 10.1, 1.9, 1H, HC═C), 6.10 (dd, J = 10.3, 1.9, 1H, HC═C), 4.76 (dd, J = 11.7, 9.3, 1H, HC═C), 2.58 (ddd, J = 13.1, 9.1, 7.1, 1H, CH), 1.06 (br s, 21H, Si(*i*-Pr_3), 0.98 (appar s, 10H, *t*-Bu and 1 H of H_2C−Si), 0.96 (s, 9H, *t*-Bu), 0.73 (dd, J = 14.9, 13.2, 1H, 1 H of H_2C−Si); ^{13}C NMR (125 MHz, C_6D_6) δ 185.2 (C), 151.4 (CH), 147.6 (CH), 142.6 (CH), 129.2 (CH), 129.0 (CH), 111.0 (CH), 80.4 (C), 47.8 (CH), 28.8 (CH_3), 28.5 (CH_3), 20.9 (C), 20.3 (C), 18.3 (CH_3), 15.2 (CH_2), 12.6 (CH).

Hydroquinone 26. ^{1}H NMR (400 MHz, C_6D_6) δ 7.03 (d, J = 8.8, 2H, Ar−H), 6.84 (d, J = 8.9, 2H, Ar−H), 6.18−6.10 (m, 1H, HC═C), 5.97−5.96 (m, 1H, HC), 5.75 (dd, J = 15.2, 5.4, ^{1}H, HC═C), 1.84 (d, J = 8.0, 2H, CH_2), 1.18 (br s, 21H, Si(*i*-$Pr)_3$), 1.10 (s, 18H, 2 *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6) δ 151.4 (C), 151.2 (C), 130.9 (CH), 130.7 (CH), 121.3 (CH), 119.9 (CH), 98.3 (CH), 28.8 (CH_3), 22.32 (C), 22.28 (C), 18.7 (CH_3), 18.6 (CH_3), 18.4 (CH_2), 13.2 (CH).[37]

Radical Clock Experiment with Silacyclopropanes 27. To a solution of silacyclopropanes **27** (0.027 g, 0.074 mmol, from silylene transfer step) in C_6D_6 (0.50 mL) in a J. Young NMR tube were added 1,4-benzoquinone **11** (0.15 mL, 0.5 M in C_6D_6, 0.079 mmol) and mesitylene (0.0020 mL, 0.014 mmol, internal standard), and the unpurified reaction mixture was analyzed by ^{1}H NMR spectroscopy after 10 min. Phenol **31** was formed in 13% yield based on comparison of the standard peak (δ 2.17) and the alkene protons along with a mixture of at least three distinct products. Spectroscopic signatures (listed below) suggest that oxasilacyclopentanes **29** were formed (46% yield based on comparison of the standard peak (δ 2.17) and the quinone protons), but their structures could not be unambiguously assigned. The products (**29**) could not be separated from each other. Spectroscopic data for phenol **31** and diagnostic peaks for the remaining products (**29**) are listed below.

Mixture of Oxasilacyclopentanes 29. ^{1}H NMR (600 MHz, C_6D_6, diagnostic peaks) δ 6.65 (dd, J = 10.7, 3.2, 1H, HC═C), 6.63 (dd, J = 10.3, 3.1, 1H, HC═C), 6.53 (dd, J = 10.1, 3.1, 1H, HC═C), 6.26 (m, 3H, HC═C), 6.17 (m, 2H, HC═C), 6.13 (dd, J = 10.1, 2.0, 1H, HC═C), 6.09 (dd, J = 10.0, 2.0, 1H, HC═C), 5.88 (dd, J = 10.1, 3.1, 1H, HC═C), 5.85 (dd, J = 10.3, 2.0, 1H, HC═C), 1.93 (dd, J = 13.3, 8.0, 1H, CH_2), 1.85 (m, 2H, CH_2 and HC), 1.62 (m, 1H, CH_2), 1.46 (ddd, J = 9.4, 7.7, 6.2, 1H, HC), 1.30 (m, 1H, CH_2), 1.26 (m, 1H, CH_2), 1.22 (m, 2H, CH_2), 1.11 (m, 1H, CH_2), 1.10 (s, 9H), 1.07 (m, 1H, H_2C−Si), 1.01 (s, 9H), 0.97 (s, 9H and m, 1H, *t*-Bu and H_2C−Si), 0.93 (s, 9H, *t*-Bu), 0.84 (s, 9H, *t*-Bu), 0.81 (m, 1H, H_2C−Si), 0.71 (s,

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9H, *t*-Bu), 0.61 (m, 1H, H_2C−Si), 0.50 (dd, *J* = 14.8, 6.7, 1H, H_2C−Si); ^{13}C NMR (150 MHz, C_6D_6) δ 186.0 (C), 185.8 (C), 185.2 (C), 152.0 (CH), 148.1 (CH), 129.3 (CH), 129.0 (CH), 128.7 (CH), 127.9 (CH), 126.6 (CH), 116.5 (CH), 79.14 (C), 78.99 (C), 75.3 (C), 48.2 (CH), 46.1 (CH), 43.9 (CH_2), 30.0 (CH), 28.9 (CH_3), 28.8 (3 CH_3), 28.4 (CH_3), 28.2 (CH_3), 27.90 (CH), 27.86 (C), 27.3 (CH), 25.8 (CH_2), 20.3 (CH_2), 20.2 (CH_2), 18.02 (CH_2), 17.99 (CH_2), 13.7 (CH_2), 13.4 (CH_2).

Hydroquinone 31. ^1H NMR (600 MHz, C_6D_6) δ 7.46 (d, *J* = 8.0, 2H, Ar−H), 7.11−7.08 (m, 2H, Ar−H), 7.04−7.01 (m, 4H, Ar−H), 6.88−6.79 (m, 4H, Ar−H and hydroquinone Ar−H), 6.72 (br s, 1H, hydroquinone Ar−H), 5.28−5.23 (m, 1H, HC═C), 4.51−4.46 (m, 1H, HC═C), 3.64 (dd, *J* = 12.1, 2.9, 1H, H_2C−C═C), 2.33−2.29 (m, 1H, H_2C−C═C), 1.84−1.80 (m, 1H, H_2C−Si), 1.66−1.62 (m, 1H, H_2C−Si), 1.05 (s, 9H), 0.96 (s, 9H); ^{13}C NMR (150 MHz, C_6D_6) δ 151.4 (C), 146.9 (C), 146.7 (C), 146.1 (C), 136.1 (CH), 133.0 (CH), 132.4 (C), 130.2 (CH), 129.1 (CH), 128.9 (CH), 128.7 (CH), 127.8 (CH), 126.5 (CH), 124.7 (CH), 120.4 (CH), 118.5 (CH), 61.4 (C), 42.1 (CH_2), 28.2 (CH_3), 27.8 (CH_3), 22.7 (C), 21.5 (C), 18.5 (CH_2); IR (ATR) 3527, 3058, 1011, 822 cm^{-1}; HRMS (TOF MS ES +) *m*/*z* calcd for $C_{31}H_{39}O_2Si$ $(M + H)^+$ 471.2714, found 471.2714.

Radical Clock Experiment with Silacyclopropanes 28. To a solution of silacyclopropanes **28** (0.049 g, 0.17 mmol, from silylene transfer step) in C_6D_6 (0.50 mL) in a J. Young NMR tube were added 1,4-benzoquinone **11** (0.19 mL, 0.98 M in C_6D_6, 0.19 mmol) and mesitylene (0.0020 mL, 0.014 mmol, internal standard), and the unpurified reaction mixture was analyzed by ^1H NMR spectroscopy after 10 min. Hydroquinone **32** was formed in 13% yield based on comparison of the standard peak (δ 2.17) and the methylene protons along with a mixture of at least three distinct products. Spectroscopic signatures (listed below) suggest that oxasilacyclopentanes **30** were formed (44% based on comparison of the standard peak (δ 2.17) and the quinone protons), but their structures could not be unambiguously assigned. Upon silica gel chromatography, the reaction mixture completely decomposed, and the products were not fully characterized. Spectroscopic signatures (*in situ* data) are listed below.

Mixture of Oxasilacyclopentanes 30. ^1H NMR (600 MHz, C_6D_6, diagnostic peaks) δ 2.24 (m, 1H, CH), 1.98 (m, 2H, CH_2), 1.75 (m, 4H, H_2C and HC), 1.42 (m, 4H, H_2C and HC), 0.79 (m, 2H, CH_2), 0.73 (m, 2H, CH_2), 0.56 (m, 5H, H_2C and HC), 0.51 (m 1H, H_2C−Si), 0.46 (m, 1H, H_2C−Si); ^{13}C NMR (150 MHz, C_6D_6, diagnostic peaks) δ 185.7 (C), 185.4 (C), 185.2 (C), 184.9 (C), 79.3 (C), 77.2 (C), 75.4 (C), 75.3 (C), 53.7 (CH), 53.4 (CH), 44.0 (CH), 43.6 (CH), 14.6 (CH_2), 14.0 (CH_2), 13.7 (CH_2), 12.9 (CH_2).

Hydroquinone 32. ^1H NMR (600 MHz, C_6D_6, diagnostic peaks) δ 6.45 (d, *J* = 2.9, 1H, HC═C), 5.44−5.40 (m, 1H, HC═C), 5.33−5.32 (m, 1H, HC═C), 4.55−4.50 (m, 1H, HC═C), 3.21−3.17 (m, 1H, H_2C−C═C), 2.06−2.05 (m, 1H, H_2C−C═C), 1.91 (m, 1H, overlaps with cyclohexene from silylene transfer step, H_2C−Si), 1.51 (m, 1H, overlaps with cyclohexene from silylene transfer step, H_2C−Si); ^{13}C NMR (150 MHz, C_6D_6, diagnostic peaks) δ 149.6 (C), 143.2 (C), 135.8 (CH), 131.8 (CH), 125.7 (CH), 45.7 (CH), 38.0 (CH_2), 28.8 (CH_2).

Oxasilacyclopentanes 37. To a solution of dienone **36** (0.016 g, 0.13 mmol) in C_6D_6 (0.30 mL) in a J. Young NMR tube were added a solution of cyclohexene silacyclopropane **13** (0.11 mL, 1.3 M in C_6D_6, 0.14 mmol) and mesitylene (0.0020 mL, 0.014 mmol, internal standard). The reaction mixture was monitored by ^1H NMR spectroscopy. After 2 weeks, all of silacyclopropane **13** was consumed and the reaction mixture was concentrated *in vacuo*. Purification by flash chromatography (3:97 EtOAc/hexanes) provided oxasilacyclopentanes **37** as a colorless oil (80:20 mixture of diastereomers, 0.030 g, 66%): ^1H NMR (400 MHz, $CDCl_3$) δ 6.06 (d, *J* = 10.4, 0.2H, HC═C), 5.95 (dd, *J* = 2.3, 10.3, 1H, HC═C), 5.65−5.52 (m, 4H, HC═C), 2.13−2.09 (m, 1H, HC−C), 1.80−1.67 (m, 3.6H, HC−C minor and 3 CH_2 minor, 3 CH_2 major), 1.64−1.60 (m, 2H, CH_2), 1.54−1.44 (m, 3.6H, HC−Si minor and 3 CH_2 minor, 3 CH_2 major), 1.40−1.34 (m, 1.4H, HC−Si major and CH_2 minor), 1.19 (s, 9H, *t*-Bu), 1.14 (s, 1.8H, *t*-Bu), 1.11 (s, 1.8H, *t*-Bu), 1.08 (s, 9H, *t*-Bu), 1.00 (s, 3H, CH_3), 0.993 (s, 0.6H, CH_3), 0.990 (s, 0.6H, CH_3), 0.98 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5 (CH), 137.3 (CH), 136.8 (CH), 136.2 (CH), 131.8 (CH), 130.7 (CH), 129.8 (CH), 127.6 (CH), 80.2 (C), 77.8 (C), 53.2 (CH), 46.2 (CH), 34.3 (C), 33.8 (C), 30.7 (CH_3), 30.6 (CH_3), 30.3 (CH_2), 30.0 (CH_3), 29.6 (CH_3), 29.5 (CH_3), 29.34 (CH_3), 29.29 (CH), 29.2, (CH_3), 28.72 (CH_2), 28.69 (CH_2), 28.5 (CH_3), 27.5 (CH_2), 27.3 (CH_2), 26.9 (CH_2), 25.3 (CH_2), 25.0 (CH), 23.1 (CH_2), 22.2 (C), 21.9 (C), 21.4 (C), 20.7 (C); IR (ATR) 2928, 1012, 820 cm^{-1}; HRMS (TOF MS ES+) *m*/*z* calcd for $C_{22}H_{39}OSi$ $(M + H)^+$ 347.2765, found 347.2772. Anal. Calcd for $C_{22}H_{38}OSi$: C, 76.23; H, 11.05. Found: C, 75.97; H, 11.01.

Dioxasilacyclopentane 38. To a solution of benzaldehyde **2** (0.10 mL, 0.10 mmol) in C_6D_6 (0.3 mL) in a J. Young NMR tube were added a solution of cyclohexene silacyclopropane **13** (0.10 mL, 1.3 M in C_6D_6, 0.13 mmol) and mesitylene (0.0020 mL, 0.014 mmol, internal standard). The reaction was monitored by ^1H NMR spectroscopy. After 4 h, the reaction mixture was concentrated *in vacuo*. Purification by flash chromatography (3:97 EtOAc/hexanes) provided dioxasilacyclopentane **38** as a colorless oil (0.023 g, 100%). Dioxasilacyclopentane **38** is known, but the data were previously collected in $CDCl_3$.[38] ^1H NMR (600 MHz, C_6D_6) δ 7.27−7.26 (m, 4H, Ar−H), 7.11−7.09 (6H, Ar−H), 4.96 (s, 2H, 2 CH), 1.24 (s, 18H, 2 *t*-Bu); ^{13}C NMR (150 MHz, C_6D_6) δ 140.4, 128.8, 128.5, 127.6, 85.4, 27.9, 14.7; HRMS (TOF MS ES+) *m*/*z* calcd for $C_{22}H_{31}O_2Si$ $(M + H)^+$ 355.2088, found 355.2086.

Dioxasilacyclopentane 40 and Oxasilacyclopentene 41. To a solution of *trans*-4-phenyl-3-buten-2-one (0.030 g, 0.21 mmol) in C_6D_6 (0.30 mL) in a J. Young NMR tube were added a solution of cyclohexene silacyclopropane **13** (0.21 mL, 1.3 M in C_6D_6, 0.27 mmol) and mesitylene (0.0020 mL, 0.014 mmol, internal standard), and the unpurified reaction mixture was analyzed by ^1H NMR spectroscopy after 20 min. Dimer **40** was formed in 54% yield, and oxasilacyclopentene **41** was formed in 30% yield based on comparison of the standard peak (δ 2.17) and the alkene protons. The products were inseparable.

Dioxasilacyclopentane 40. ^1H NMR (500 MHz, C_6D_6, diagnostic peaks) δ 7.07−7.05 (m, 1H, HC═C), 6.81 (d, *J* = 16.1, 1H, HC═C), 6.49 (d, *J* = 16.1, 1H, HC═C), 6.21 (d, *J* = 15.6, 1H, HC═C), 1.48 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.19 (s, 9H, *t*-Bu), 1.01 (s, 9H, *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6, diagnostic peaks) δ 138.12 (CH), 138.09 (CH), 137.0 (CH), 85.3 (C), 84.5 (C), 23.6 (CH_3).

Oxasilacyclopentene 41. Oxasilacyclopentene **41** is a known compound, but data were collected in $CDCl_3$. The data below were collected *in situ* due to difficulty separating oxasilacyclopentene **41** from dioxasilacyclopentane **40**:[33] ^1H NMR (500 MHz, C_6D_6, diagnostic peaks) δ 4.89−4.87 (m, 1H, HC═C), 3.54−3.52 (m, 1H, HC−Ar), 1.87−1.86 (m, 3H, CH_3), 1.12 (s, 9H, *t*-Bu), 0.85 (s, 9H, *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6, diagnostic peaks) δ 158.3 (C), 103.4 (CH), 28.2 (CH_3), 27.8 (CH_3), 18.6 (CH_3).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00469.

Additional experimental procedures with analytical and spectroscopic data, NMR spectra, and stereochemical proof for oxasilacyclopentane **16** (PDF)

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Notes

The authors declare no competing financial interest.

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