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Synthesis of Unsaturated Silyl Heterocycles via an Intramolecular Silyl-Heck Reaction

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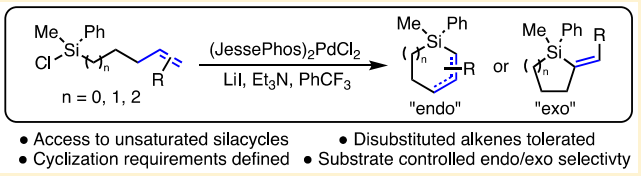
Supporting Information

ABSTRACT: We report the synthesis of unsaturated silacycles via an intramolecular silyl-Heck reaction. Using palladium catalysis, silicon electrophiles tethered to alkenes cyclize to form five- and six-membered silicon heterocycles. The effects of alkene substitution and tether length on the efficiency and regioselectivity of the cyclizations are described. Finally, through the use of an intramolecular tether, the first examples of disubstituted alkenes in silyl-Heck reactions are reported.



INTRODUCTION

Over the past several years our laboratory has developed a general and mild protocol for the direct synthesis of allyl and vinyl silanes directly from unfunctionalized terminal alkenes via the silyl-Heck reaction (Figure 1).[1] Our main studies have focused on palladium-catalyzed reactions, which allow for highly regiospecific terminal silylation of alkenes with good to excellent levels of isomeric and geometric control of the double bond in the product. Moreover, we recently developed a second-generation ligand for these reactions, which allows for lower reaction temperatures, better yields, and greater product selectivity (Figure 1, top).[1e] In 2014, we also reported nickel-catalyzed conditions that allow for the preparation of vinyl silanes.[1d] These methods provide a straightforward means of preparing unsaturated silanes. Most recently, Shimada and Nakajima have also shown similar reactions using chlorosilanes with Lewis acid promotors.[2,3]

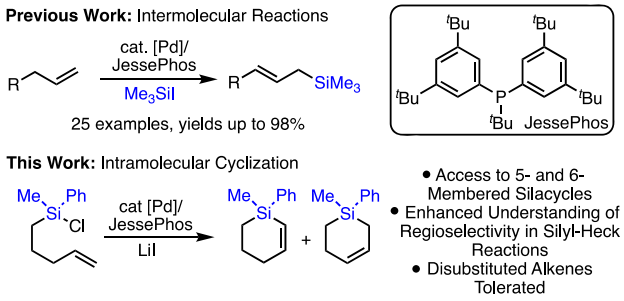


Figure 1. Silyl-Heck reactions.

To date, however, all such studies have focused on bimolecular cross-coupling reactions yielding linear, silicon-containing products. We were interested in investigating an intramolecular silyl-Heck reaction wherein a silyl halide could cyclize onto a pendant alkene.[4] We reasoned that such reactions would allow us to study the reactivity of internal alkenes, which has not been possible in bimolecular reactions. In addition, such a reaction would access new classes of cyclic unsaturated silicon heterocycles.

Silicon-containing heterocycles are important structures in many disciplines of chemistry. Such silacycles are common motifs in silicon derivatives of drugs, known as siladrugs.[5] Silacycles are also important synthetic intermediates[6] and have been utilized in many total syntheses.[7] Most commonly, silicon-containing rings are oxidized to form complex diols.[7,8] Unsaturated silacycles also serve as unique precursors for the formation of silicon-based polymers.[9] Small silacycles, such as silacyclobutanes, have been shown to be excellent nucleophiles for Hiyama−Denmark coupling reactions.[10]

Classically, silacycles have been synthesized from cycloadditions of reactive silenes or silylenes with dienes.[11] Alternatively, intramolecular hydrosilylation is a common strategy for the synthesis of various silacycles. Speier's catalyst (H_2PtCl_6) is commonly used and gives a strong preference for exo cyclizations following the Chalk−Harrod mechanism,[12] while more recently, Yamamoto and Trost have independently demonstrated that endo cyclizations are possible using aluminum trichloride or a cationic ruthenium complex.[13] We envisioned that an intramolecular silyl-Heck reaction could provide an alternative approach for the synthesis of silicon-containing heterocycles.

Herein, we report the first examples of intramolecular silyl-Heck reactions (Figure 1, bottom). These studies not only provide routes to cyclic silanes but also provide insights into the requirements of the silyl-Heck reaction. Specifically, we show that these transformations allow access to a variety of five- and six-membered unsaturated silicon heterocycles with moderate to good yields. Further, through a systematic study of tether length and alkene substitution and their effect on regioselectivity and efficiency, significant insight into the steric

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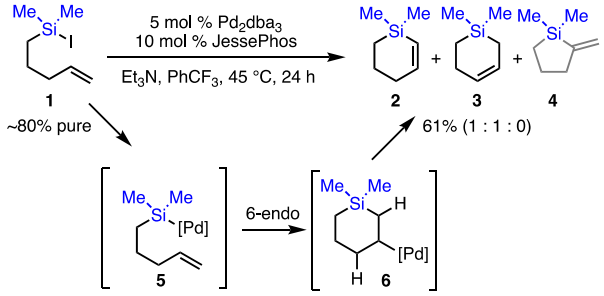
requirements of the silyl-Heck process has been gained. Finally, by tethering the alkene to the silicon electrophile, we have observed the first examples of successful silyl-Heck reactions of 1,1- and 1,2-disubstituted alkenes.

RESULTS

For the initial exploration of an intramolecular silyl-Heck reaction, we sought to design a substrate that closely resembled those of our prior bimolecular reactions, which involved silyl iodides and terminal monosubstituted alkenes. To this end, 4-pentenyldimethyliodosilane (**1**) was identified as a suitable substrate due to minimal steric and electronic bias. However, because of the sensitivity of the molecule toward moisture, and the propensity of trace hydroiodic acid to result in alkene isomerization, **1** could only be prepared in limited purity (ca. 80%, according ^{1}H NMR analysis).[14,15]

Despite those limitations, we decided to explore the cyclization of compound **1** nonetheless. In principle, **1** can undergo either a 6-endo (**2** and/or **3**) or 5-exo (**4**) cyclization (Scheme 1). On the basis of the known selectivities of Heck

Scheme 1. Intramolecular Cyclization of Iodosilane 1

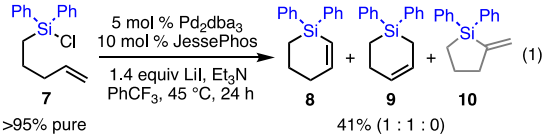


cyclization involving carbon electrophiles,[4] the 5-exo product (**4**) was expected to strongly predominate. However, when **1** was subjected to reaction conditions similar to those employed in our earlier work (Pd_2dba_3/JessePhos),[1f] a surprising result was observed. Instead of the expected 5-exo pathway, **1** underwent cyclization to exclusively provide a mixture of products **2** and **3** in a 1:1 ratio in 61% yield (as determined by ^{1}H NMR against an internal standard). Apparently, these products arise from 6-endo cyclization, followed by non-selective β-hydride elimination from intermediate **6**. Unfortunately, due to their volatility, **2** and **3** proved challenging to isolate and separate. However, samples of sufficient analytical purity for structural characterization were obtained using preparative gas chromatography.[16] In addition, in nearly all cases in prior studies, a strong preference for the allylic isomer has been observed in silyl-Heck transformations where its formation is possible. Here a mixture of allyl and vinyl isomers is obtained. It is unclear in this case if the observed alkene mixture results from kinetic or thermodynamic selectivity.

We wished to understand the origins of the seemingly unusual regioselectivity. On one hand, in all prior examples of silyl-Heck reactions,[17] silylation occurs exclusively at the terminal position of the alkene and the observed selectivity might be due to the same effect. On the other hand, 6-endo intramolecular Heck reactions using carbon-based electrophiles are not unprecedented but typically require electronically biased alkenes[18] or are thought to undergo rearrangements and other nontraditional reaction mechanisms.[19] One notable exception is a recently reported Heck cyclization from the Gevorgyan laboratory involving a silicon-tethered substrate.[20] In that case, 6-endo cyclization was also observed, which presumably is a result of the stereoelectronic effects imparted by the long Si−C bonds contained within the product. To better understand if the observed regioselectivity in the cyclization of **1** was a manifestation of the preference for the silicon center to react at the alkene terminus or is inherent in Heck-type cyclizations involving small silacycles, we undertook a more systemic study.

To facilitate that investigation, substrates that would be easier to prepare and purify and products that would be easier to isolate and analyze were desired. Toward this end, we elected to investigate chlorosilane substrates. We have previously shown that chlorosilanes can participate in palladium-catalyzed silyl-Heck reactions activated in situ by the addition of iodide salts.[21] Moreover, chlorosilanes can be synthesized under mild reaction conditions, potentially allowing for higher yield and purity in substrate synthesis.

Initially, we focused on preparing chlorodiphenylsilane substrates. We reasoned that the added molecular mass of the two phenyl groups would lower the volatility of the products and allow easier isolation. As predicted, we were able to prepare **7** in higher purity (>95% according to ^{1}H NMR analysis, eq 1). Unfortunately, however, this chlorodiphenylsi-

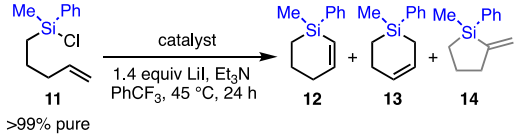


lane substrate proved sluggish in the silyl-Heck reaction. Even with use of lithium iodide as an additive, only a 41% combined yield of products **8** and **9** was obtained.[22] Interestingly, however, like the earlier cyclization, only products arising from a 6-endo cyclization were observed; no 5-exo product (**10**) could be detected.

We suspected that the poor reactivity of **7** was due to the steric demands of the two phenyl groups attached to silicon. As a means of modulating the size of the silicon center, we then turned to chloromethylphenylsilyl substates. Encouragingly, using this electrophilic silicon center, we were able to prepare substrate **11** in an analytically pure fashion. Moreover, using the combination of catalytic Pd_2dba_3 and JessePhos, with LiI additive, **11** underwent smooth cyclization to lead to a 1:1 mixture of **12** and **13** in 81% combined yield (Table 1, entry 1). As before, product **14** (which would arise from 5-exo cyclization) was not observed.

Before continuing to a more exhaustive study, we also wanted to examine the nature of the catalyst. We have previously reported the use of a single-component JessePhos palladium complex as an effective precatalyst for the silyl-Heck

Table 1. Cyclizations of Chloromethylphenyl Silanes



entry	catalyst (mol %)	combined yield (%)	12:13:14
1	Pd_2dba_3 (5), JessePhos (10)	81	1:1:0
2	$(JessePhos)_2PdCl_2$ (5)	88	1:1:0

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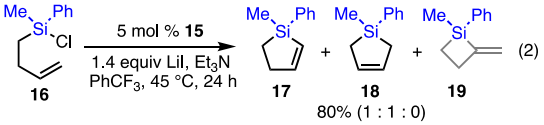
reaction.[23] The use of these precatalysts simplifies reaction setup and often leads to higher and more consistent yields. Using the single-component catalyst $(JessePhos)_2PdCl_2$ (**15**), methyl(phenyl)silane **11** cyclized to yield a 1:1 ratio of **12** and **13** in 88% combined yield (entry 2). This catalyst system was selected for further study.

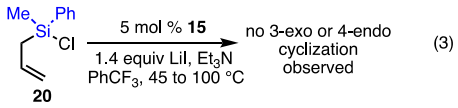
With an isolable and sufficiently reactive class of silicon electrophiles and a proper catalyst identified, we set out to study the effects of both tether length and alkene substitution on the intramolecular silyl-Heck reaction. A series of homologous substrates were prepared[16] and then subjected to the silyl-Heck reaction conditions. The results of those cyclization studies are presented below.

Substrate **16** bearing a four-carbon tether was prepared and subjected to the reaction conditions using catalyst **15** (eq 2).



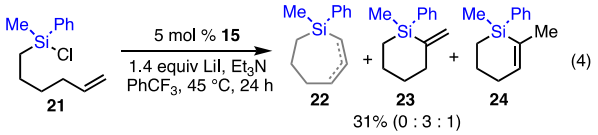
With this butenyl substrate, cyclization occurred to provide a 1:1 mixture of 5-endo products **17** and **18** in 80% combined yield. The observed result is notable, as it again proved dissimilar to Heck cyclizations of carbon electrophiles; 5-endo-trig cyclizations are typically disfavored due to the distortion required for orbital overlap.[24] Although 5-endo products have been observed in Heck reactions[25] to form indoles and related compounds, they are thought react through six-membered palladacycle intermediates.[25i,26] In this case, however, the substrate lacks suitable electronic bias to favor such a pathway. Additionally, although four-membered-ring formation has been observed in Heck cyclizations of carbon electrophiles,[27] in this case silacyclobutane **19** resulting from 4-exo cyclization was not observed.

We also prepared a substrate bearing a tether one atom shorter yet (**20**, eq 3). However, when this allyl substrate was



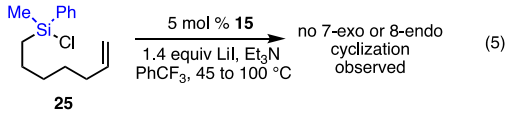
subjected to the optimized reaction conditions, no cyclized product was observed. Even at elevated temperatures, only unreacted or isomerized starting material remained.

Next, we next sought to examine longer alkene tether lengths. When substrate **21** (eq 4), bearing a four-carbon



tether, was subjected to the reaction conditions, products **23** and **24** were obtained in 31% combined yield as a 3:1 mixture. Interestingly, both of these products are the result of 6-exo cyclization. These are the first examples of silyl-Heck cyclizations proceeding via an exo pathway. More importantly, however, they are also the first examples of the internal silylation of an alkene using this method and demonstrate that addition of the silicon atom to the internal carbon is possible.[28] Notably, although 7-endo Heck cyclizations have been reported,[20,29] the product from 7-endo cyclization in the silyl-Heck reaction (**22**) was not detected, indicating that the 7-endo pathway is less favorable than internal silylation. However, the overall low yield in this reaction indicates the difficulties associated with both pathways.

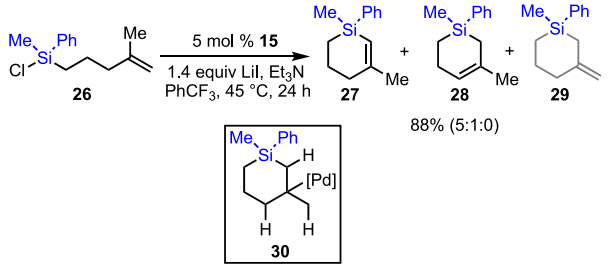
Unfortunately, attempting to drive larger ring cyclization with the five-atom linker of alkene **25** failed to provide a product (eq 5); neither seven- nor eight-membered silacycles were observed.



After determining the range of reactive chain lengths, we next turned our attention to studying the effects of alkene substitution. To date, only monosubstituted alkenes have been found to be suitable substrates in bimolecular silyl-Heck reactions. Tolerance of higher alkene substitution is presumably disfavored due to unfavorable steric interactions. A similar limitation is observed in bimolecular Heck reactions employing carbon electrophiles, wherein the rates of reactivity decrease dramatically with increased olefin substitution under most reaction conditions.[30,31] Related intramolecular Heck cyclizations, however, have been shown to tolerate tri- and tetrasubstituted alkenes.[32] Considering this background, we sought to define the tolerance of alkene substitution in the intramolecular silyl-Heck reaction.

We began with a substrate bearing a tethered 1,1-disubstituted terminal alkene (**26**, Scheme 2). Like other

Scheme 2. 6-Endo Cyclization of 26



disubstituted alkenes, gem-disubstituted olefins have proven to be poor substrates in bimolecular silyl-Heck reactions. Subjecting alkene **26** to the reaction conditions gave rise to products **27** and **28** in 88% yield as a 5:1 ratio of isomers, making this the first successful example of the use of a disubstituted alkene in a silyl-Heck reaction. Consistent with the previous intramolecular cases, the reaction proceeds with exclusive 6-endo selectivity, placing the silicon atom at the terminus of the alkene. However, in contrast to the previous examples the vinyl isomer is largely favored over the allylic isomers.

Next, we investigated the reactivity of several internal alkenes. When the methyl-substituted (*Z*)-alkene **31** was subjected to the optimal reaction conditions, 5-exo product **32** was formed in 18% yield (Scheme 3). Only the (*Z*)-alkene isomer was observed, the configuration of which was established using one- and two-dimensional NMR methods. The geometry of the product is consistent with a Heck-like mechanism involving syn-facial migratory insertion, C−C σ-bond rotation, and syn-periplanar β-hydride elimination (via

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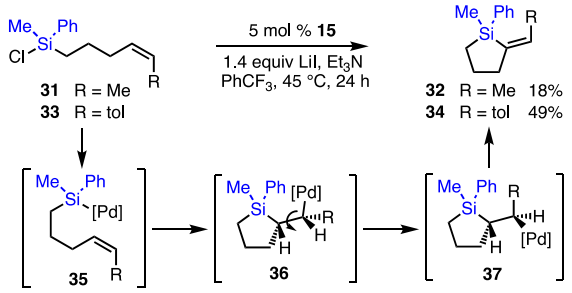
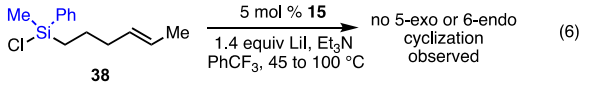
Scheme 3. 5-Exo Cyclizations of 31 and 33



intermediates **35**–**37**). Notably, cyclization of the closely related (*Z*)-styrenyl substrate **33** led to a very similar result in terms of product selectivity (only **34** was observed), but the reaction was considerably more efficient (49% yield). This indicated that the electronic nature of the alkene is also important in the outcome of the silyl-Heck cyclization.

The successful cyclizations of **31** and **33** are significant, as these are the first internal alkenes that have been observed to participate in silyl-Heck reactions. Moreover, in contrast to substrates **11** and **26**, which bear identical tether lengths, these substrates cyclize with complete preferential 5-exo selectivity. This indicates that, in the absence of a steric preference, stereoelectronic effects similar to those observed in Heck cyclizations of carbon-based electrophiles predominate.[4a,33]

Successful cyclization of internal alkenes, however, appears to be very substrate dependent. For example, simply switching the alkene geometry of the substrate from cis to trans resulted in no observed cyclization products from substrate **38** (eq 6).



This remained true even with the use of elevated temperatures and longer reaction times. We attribute the lack of reactivity to steric congestion during the migratory insertion between the groups on silicon and the methyl group of the (*E*)-alkene, which indicates the degree of difficulty associated with silyl-palladation of internal alkenes using these methods.

DISCUSSION

Overall, the results presented above paint an initial picture of the steric and stereoelectronic requirements for intramolecular silyl-Heck reactions. The predominant factor in evaluating the facility of a silyl-Heck cyclization appears to depend upon the steric nature of the alkene. With tethered, terminal alkenes, both 5- and 6-endo cyclizations appear to occur readily and are dictated by the ability of the cyclization to place the large silicon group at the nonsterically encumbered terminus of the alkene. Endo-selective cyclizations can also appear to tolerate additional substitution at the internal carbon, so long as the terminal position remains unsubstituted. 3-exo, and 4- and 7-endo cyclizations appear to be much more challenging. In the first two cases, no cyclization products are formed. In the last case, 6-exo cyclization is preferred but is not efficient—presumably due to the challenges of placing the silicon group at the internal carbon of the alkene. Finally, in some cases, through use of an intramolecular tether, 1,2-disubstituted alkenes can participate in silyl-Heck reactions to some extent. However, yields in these cyclizations are low and appear to require the less sterically demanding *cis*-alkene geometry in order to proceed. Finally, unlike bimolecular silyl-Heck reactions where the position of the double bond in the unsaturated organosilane product is readily predicted by the nature of the starting material, intramolecular silyl-Heck reactions provide less predictable and less selective mixtures of allyl and vinyl silane products.

CONCLUSION

In conclusion, for the first time we have explored the feasibility of intramolecular silyl-Heck reactions. We have found that this method is effective for the preparation of both five- and six-membered unsaturated silicon heterocycles, provided that the reaction can proceed to place the silicon atom at the unsubstituted terminus of the tethered alkene. Both endo- and exo-selective reactions are possible. The selectivity between endo and exo modes is best understood by a consideration of both ring size and the steric requirements of the alkene.

These studies have also demonstrated the first examples of more highly substituted alkenes participating in silyl-Heck reactions. Both 1,1- and 1,2-disubstituted alkenes can undergo cyclization, but the success of such reactions is dependent on the geometric and steric considerations of the reaction.

Overall, these studies have provided further insights into the steric requirements of the silyl-Heck reaction and will provide insights into how to further develop silyl-Heck reactions of highly substituted alkenes.

EXPERIMENTAL SECTION

General Procedure for Silyl-Heck Reactions. In a nitrogen-filled glovebox, a 1 dram vial equipped with a magnetic stir bar was charged with $(JessePhos)_2PdCl_2$ (**15**; 13.9 mg, 0.125 mmol, 5 mol %), LiI (47 mg, 0.35 mmol, 1.4 equiv), Et_3N (175 μL, 1.25 mmol, 5.0 equiv), $PhCF_3$ (500 μL, 0.5M), and silyl chloride (0.25 mmol, 1.0 equiv). The vial was sealed, and the contents were stirred at 45 °C for 24 h. The reaction mixture was removed from heat, cooled to room temperature, and opened to air, and 1,3,5-trimethoxybenzene (28 mg, 2/3 equiv) was added. A small aliquot was taken for NMR analysis without concentration; the sample was returned to the crude mixture and then filtered through Celite with Et_2O and concentrated in vacuo. The crude oil was purified via flash silica gel chromatography with the indicated eluent in parentheses.

*1,1-Dimethyl-1,2,3,4-tetrahydrosiline (**2**) and 1,1-Dimethyl-1,2,3,6-tetrahydrosiline (**3**).* In a nitrogen-filled glovebox, a 1 dram vial with a magnetic stir bar was charged with tris(dibenzylideneacetone)dipalladium (Pd_2dba_3, 11 mg), JessePhos (12 mg), Et_3N (175 μL), and $PhCF_3$ (500 μL). The vial was capped and heated at 45 °C, and the contents were stirred for 5 min. The vial was removed from heat, and silyl iodide **1** (64 mg) was added in one portion without cooling. The vial was then resealed and stirred at 45 °C for 24 h. The reaction was removed from heat and cooled to room temperature. Mesitylene (35 μL) was added, and a small aliquot was taken for NMR analysis without concentration. The volatile organic compounds (including products) of the crude mixture were vacuum-transferred, to separate them from the catalyst and ligand, and analytical amounts of the two isomeric products were purified to ≥70% purity by preparatory gas chromatography. Data for **2** (vinylsilane): ^1H NMR (400 MHz, C_6D_6) δ 6.63 (dt, J = 14.1, 3.9 Hz, 1H), 5.79 (dt, J = 14.1, 2.1 Hz, 1H), 2.04–1.92 (m, 2H), 1.78–1.64 (m, 2H), 0.68–0.57 (m, 2H), 0.08 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ 149.1, 127.1, 31.2, 21.5, 12.3, −1.6; HRMS (LIFDI) calcd for $[C_7H_{14}Si]$ 126.0865, found 126.0847. Data for **3** (allylsilane): ^1H NMR (400 MHz, C_6D_6) δ 5.86 (dtt, J = 10.1, 5.0, 1.8 Hz, 1H), 5.74 (dtt, J = 10.5, 4.4, 1.8 Hz, 1H), 2.21 (tdt, J = 6.4, 3.8, 1.9 Hz, 2H), 1.17 (dq, J = 4.0, 1.9 Hz, 2H), 0.63 (t, J = 6.9 Hz, 2H), 0.00 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ 130.5, 126.2, 23.2,

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13.3, 10.3, −2.5; HRMS (LIFDI) calcd for [$C_7H_{14}Si$] 126.0865, found 126.0835.

*1-Methyl-1-phenyl-1,2,3,4-tetrahydrosiline (**12**) and 1-Methyl-1-phenyl-1,2,3,6-tetrahydrosiline (**13**).* According to the general procedure, silyl chloride **11** (56 mg, 0.25 mmol), $(JessePhos)_2PdCl_2$ (**15**; 13.9 mg, 0.125 mmol, 5 mol %), LiI (47 mg, 0.35 mmol, 1.4 equiv), Et_3N (175 μL, 1.25 mmol, 5.0 equiv), and $PhCF_3$ (500 μL, 0.5 M) were combined and stirred at 45 °C for 24 h. Analysis of the crude reaction mixture via ^1H NMR revealed an 88% yield. The crude material was purified via silica gel chromatography (hexanes) to afford a mixture of **12** and **13** as a colorless oil (38 mg, 81%). Data for **12** (vinylsilane): ^1H NMR (600 MHz, $CDCl_3$) δ 7.59−7.51 (m, 2H), 7.39−7.32 (m, 3H), 6.91 (dt, *J* = 14.1, 4.0 Hz, 1H), 5.91−5.79 (m, 1H), 2.25−2.18 (m, 2H), 1.90−1.80 (m, 2H), 1.03−0.80 (m, 2H), 0.35 (s, 3H). Data for **13** (allylsilane): ^1H NMR (600 MHz, $CDCl_3$) δ 7.61−7.51 (m, 2H), 7.40−7.32 (m, 3H), 5.91−5.80 (m, 1H), 5.78−5.66 (m, 1H), 2.36−2.27 (m, 2H), 1.63−1.36 (m, 2H), 1.04−0.80 (m, 2H), 0.33 (s, 3H). Data for **12** and **13** (mixture): ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.8, 139.0, 138.9, 134.2, 133.8, 130.7, 129.2, 129.1, 128.0, 127.9, 125.9, 124.7, 31.1, 23.0, 21.2, 12.1, 11.6, 9.4, −3.0, −3.8; FTIR (cm^{-1}) 2907, 1590, 1427, 1251, 1111, 809, 699; HRMS (CI) *m*/*z* calcd for [$C_{12}H_{16}Si$] 188.1021, found 188.1012.

*1-Methyl-1-phenyl-2,3-dihydro-1H-silole (**17**) and 1-Methyl-1-phenyl-2,5-dihydro-1H-silole (**18**).* According to the general procedure, silyl chloride **16** (53 mg, 0.25 mmol), $(JessePhos)_2PdCl_2$ (**15**; 13.9 mg, 0.125 mmol, 5 mol %), LiI (47 mg, 0.35 mmol, 1.4 equiv), Et_3N (175 μL, 1.25 mmol, 5.0 equiv), and $PhCF_3$ (500 μL, 0.5 M) were combined and stirred at 45 °C for 24 h. Analysis of the crude reaction mixture via ^1H NMR revealed an 80% yield. The crude material was purified via silica gel chromatography (pentane) to afford a mixture of **17** and **18** as a colorless oil (31 mg, 71%). Data for **17** (vinylsilane): ^1H NMR (600 MHz, $CDCl_3$) δ 7.55−7.48 (m, 2H), 7.42−7.32 (m, 3H), 7.00 (dt, *J* = 10.1, 2.7 Hz, 1H), 6.07 (dt, *J* = 10.1, 2.3 Hz, 1H), 2.70−2.51 (m, 2H), 1.06−0.82 (m, 2H), 0.48 (s, 3H). Data for **18** (allylsilane): ^1H NMR (600 MHz, $CDCl_3$) δ 7.61−7.55 (m, 2H), 7.43−7.31 (m, 3H), 5.97 (s, 2H), 1.69−1.43 (m, 4H), 0.48 (s, 3H). Data for **17** and **18** (mixture): ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 138.9, 138.3, 134.0, 133.8, 131.2, 129.4, 129.2, 128.7, 128.0, 127.9, 32.4, 17.7, 8.8, −3.0, −3.7; FTIR (cm^{-1}) 3019, 2905, 1114; HRMS (CI) *m*/*z* calcd for [$C_{11}H_{14}Si$] 174.0865, found 174.0858.

*1-Methyl-2-methylene-1-phenylsilinane (**23**) and 1,6-Dimethyl-1-phenyl-1,2,3,4-tetrahydrosiline (**24**).* According to the general procedure, silyl chloride **21** (240 mg, 1.0 mmol), $(JessePhos)_2PdCl_2$ (**15**; 56 mg, 0.5 mmol, 5 mol %), LiI (188 mg, 1.4 mmol, 1.4 equiv), Et_3N (700 μL, 5.0 mmol, 5.0 equiv) and $PhCF_3$ (2 mL, 0.5 M) were combined and stirred at 45 °C for 24 h. Analysis of the crude reaction mixture via ^1H NMR revealed a 31% yield. The crude material was purified via silica gel chromatography (hexanes) to afford a mixture of **23** and **24** as a colorless oil (23 mg, 12%). Data for **23** (exo): ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.51 (m, 3H), 7.40−7.33 (m, 3H), 5.60 (dd, *J* = 3.3, 1.6 Hz, 1H), 5.19 (dt, *J* = 3.6, 1.2 Hz, 1H), 2.49−2.27 (m, 2H), 1.96−1.83 (m, 1H), 1.70−1.60 (m, 1H), 1.54−1.39 (m, 1H), 1.20−1.09 (m, 1H), 0.86−0.72 (m, 1H), 0.34 (s, 3H). Data for **24** (endo): ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.49 (m, 2H), 7.43−7.30 (m, 3H), 6.49 (dq, *J* = 4.2, 1.8 Hz, 1H), 2.23−2.12 (m, 2H), 1.84−1.76 (m, 2H), 1.71 (q, *J* = 2.0 Hz, 3H), 1.00−0.89 (m, 1H), 0.86−0.71 (m, 1H), 0.37 (s, 3H). Data for **23** and **24** (mixture): ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 143.9, 138.2, 137.0, 134.4, 134.3, 131.9, 129.2, 129.1, 127.9, 127.9, 123.5, 40.0, 31.0, 30.6, 24.5, 21.9, 21.4, 13.7, 11.9, −4.3, −4.9; FTIR (cm^{-1}) 2921, 2852, 1653; HRMS (CI) *m*/*z* calcd for [$C_{13}H_{18}Si$] 202.1178, found 202.1176.

*1,5-Dimethyl-1-phenyl-1,2,3,4-tetrahydrosiline (**27**) and 1,5-Dimethyl-1-phenyl-1,2,3,6-tetrahydrosiline (**28**).* According to the general procedure, silyl chloride **26** (60 mg, 0.25 mmol), $(JessePhos)_2PdCl_2$ (**15**; 13.9 mg, 0.125 mmol, 5 mol %), LiI (47 mg, 0.35 mmol, 1.4 equiv), Et_3N (175 μL, 1.25 mmol, 5.0 equiv), and $PhCF_3$ (500 μL, 0.5 M) were stirred at 45 °C for 24 h. Analysis of the crude reaction mixture via ^1H NMR revealed an 88% yield. The crude material was purified via silica gel chromatography (pentane) to afford a mixture of **27** and **28** as a colorless oil (42 mg, 82%). Data for **27** (vinylsilane): ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.50 (m, 2H), 7.41−7.31 (m, 3H), 5.51 (s, 1H), 2.11 (t, 2H), 1.89 (d, 3H), 1.88−1.79 (m, 2H), 0.94−0.69 (m, 2H), 0.31 (s, 3H). Data for **28** (allylsilane): ^1H NMR (400 MHz, $CDCl_3$) δ 7.60−7.49 (m, 2H), 7.41−7.31 (m, 3H), 5.51 (s, 1H), 2.29−2.21 (m, 2H), 1.79 (d, *J* = 1.8 Hz, 3H), 1.53−1.29 (m, 2H), 0.97−0.68 (m, 2H), 0.31 (s, 3H). Data for **27** and **28** (mixture): ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 139.6, 134.2, 133.8, 129.1, 128.9, 127.9, 127.8, 124.3, 118.4, 100.1, 35.3, 29.5, 28.5, 22.8, 21.6, 17.4, 10.7, 9.0, −2.8; FTIR (cm^{-1}) 2924, 1608, 1427, 1250, 1111, 815, 731, 698; HRMS (CI) *m*/*z* calcd for [$C_{13}H_{18}Si$] 202.1178, found 202.1174.

*(Z)-2-Ethylidene-1-methyl-1-phenylsilolane (**32**).* According to the general procedure, silyl chloride **31** (240 mg, 1.0 mmol), $(JessePhos)_2PdCl_2$ (**15**; 56 mg, 0.5 mmol, 5 mol %), LiI (188 mg, 1.4 mmol, 1.4 equiv), Et_3N (700 μL, 5.0 mmol, 5.0 equiv) and $PhCF_3$ (2 mL, 0.5 M) were combined and stirred at 45 °C for 24 h. Analysis of the crude reaction mixture via ^1H NMR revealed a 18% yield. The crude material was purified via silica gel chromatography (pentane) to afford **32** as a colorless oil (36 mg, 17%): ^1H NMR (600 MHz, $CDCl_3$) δ 7.61−7.52 (m, 2H), 7.40−7.30 (m, 3H), 6.29 (qt, *J* = 6.6, 2.0 Hz, 1H), 2.39−2.33 (m, 2H), 1.85−1.69 (m, 2H), 1.64 (dt, *J* = 6.7, 1.9 Hz, 3H), 0.98−0.81 (m, 2H), 0.50 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.5, 138.1, 134.3, 133.8, 129.1, 127.9, 39.2, 25.5, 19.8, 15.0, −3.9; FTIR (cm^{-1}) 2916, 1428, 1250, 1112, 732, 698; HRMS (CI) *m*/*z* calcd for [$C_{13}H_{18}Si$] 202.1178, found 202.1177.

*(Z)-1-Methyl-2-(4-methylbenzylidene)-1-phenylsilolane (**34**).* According to the general procedure, silyl chloride **33** (158 mg, 0.5 mmol), $(JessePhos)_2PdCl_2$ (**15**; 28 mg, 0.25 mmol, 5 mol %), LiI (94 mg, 0.7 mmol, 1.4 equiv), Et_3N (350 μL, 2.5 mmol, 5.0 equiv), and $PhCF_3$ (1.0 mL, 0.5M) were combined and stirred at 45 °C for 24 h. Analysis of the crude reaction mixture via ^1H NMR revealed a 49% yield. The crude material was purified via silica gel chromatography (hexanes) to afford **34** as a colorless oil (57 mg, 41%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.58−7.52 (m, 2H), 7.37−7.31 (m, 3H), 7.26 (s, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 2H), 2.66−2.58 (m, 2H), 2.25 (s, 3H), 1.98−1.85 (m, 1H), 1.76−1.63 (m, 1H), 0.97 (dd, *J* = 7.8, 6.6 Hz, 2H), 0.38 (s, 3H); ^1H NMR (400 MHz, C_6D_6) δ 7.62−7.53 (m, 2H), 7.35 (s, 1H), 7.26−7.21 (m, 2H), 7.22−7.17 (m, 3H), 6.79 (d, *J* = 7.8 Hz, 2H), 2.66−2.52 (m, 2H), 1.98 (s, 3H), 1.94−1.79 (m, 1H), 1.71−1.57 (m, 1H), 0.99−0.84 (m, 2H), 0.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 139.1, 138.4, 136.6, 136.6, 134.2, 129.2, 128.8, 128.0, 127.9, 42.8, 24.8, 21.3, 15.8, −5.0 (15_C); ^{13}C NMR (101 MHz, C_6D_6) δ 143.6, 140.0, 138.6, 137.1, 136.8, 134.5, 129.5, 129.1, 128.3, 43.0, 25.1, 21.1, 16.1, −4.9; FTIR (cm^{-1}) 2920, 1510, 1428, 1110, 809, 699; HRMS (CI) *m*/*z* calcd for [$C_{19}H_{22}Si$] 278.1491, found 278.1493.

■ ASSOCIATED CONTENT

Supporting Information

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NMR spectra (PDF)

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Notes

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