Published in final edited form as:
Organometallics. 2010 March 3; 29(7): 1661–1669. doi:10.1021/om901042j.

Palladium- and Nickel-Catalyzed Carbon–Carbon Bond Insertion Reactions with Alkylidenesilacyclopropanes

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Abstract

Palladium and nickel catalysts promoted highly selective carbon–carbon bond insertion reactions with di-*tert*-butyl-alkylidenesilacyclopropanes. $Pd(PPh_3)_4$ was demonstrated to be the optimal catalyst, allowing for a variety of carbon–carbon π-bond insertion reactions. Depending on the nature of the carbon–carbon π bond, the insertion reaction proceeded with either direct insertion into the carbon(sp^2)–silicon bond or with allylic transposition. Ring-substituted alkylidenesilacyclopropanes required a nickel catalyst to afford insertion products. Using $Ni(cod)_2$ as the carbon–carbon bond insertion catalyst, new double alkyne insertion products and alkene isomerization products were observed.

Introduction

Strained-ring silanes undergo a variety of ring-expanding reactions. For example, metal-catalyzed insertions with carbon–carbon π bonds have been reported for various three-[1-12] and four-membered ring silacyclic compounds.[13-17] These reactions, however, suffer from low selectivity or limited substrate scope.

In this Article, we report selective and general metal-catalyzed carbon–carbon π-bond insertion reactions with alkylidenesilacyclopropanes (**3**) derived from allenes (**1**) (eq 1).[18] We also report the synthesis of a silacyclopropane derived from an allene ether and its high reactivity that allows subsequent two-atom ring-expansion reactions to occur with high regio- and diastereoselectivity. Electronic effects are examined and mechanistic considerations are discussed.

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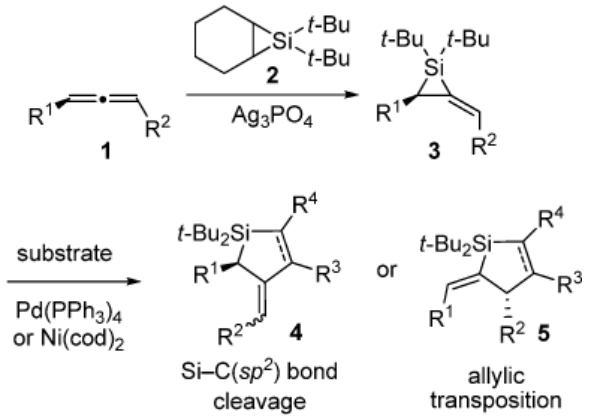
Supporting Information Available. X-ray data for **13a**, additional experimental procedures, spectroscopic and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

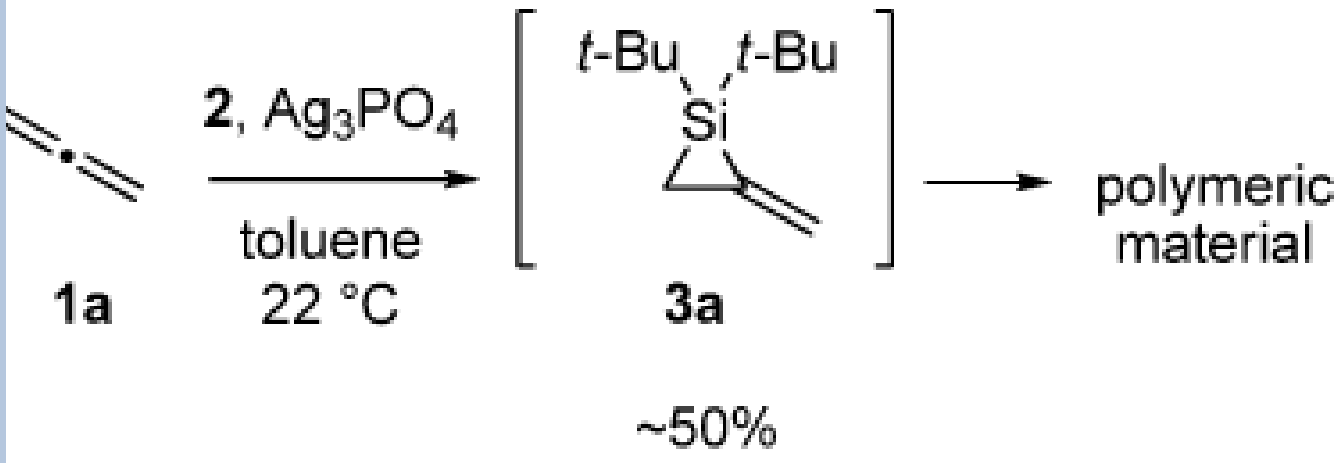


(1)

Results and Discussion

Attempted Synthesis of an Unsubstituted Alkylidenesilacyclopropane

An unactivated alkylidenesilacyclopropane was desired for preliminary experiments. Unsubstituted alkylidenesilacyclopropane **3a** was formed by silylene transfer to allene (**1a**), but it could not be isolated (eq 2).[19] Because monosubstituted alkylidenesilacyclopropane **3b** can be isolated (eq 3),[18] it was employed in the initial carbon–carbon bond insertion reactions.



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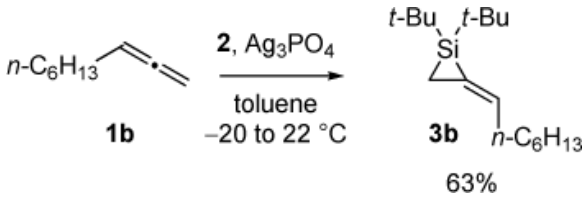

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Pd(0)-Catalyzed Insertion Reaction with a Monosubstituted Alkylidenesilacyclopropane

To determine the potential of metal-catalyzed carbon–carbon π-bond insertion reactions, alkylidenesilacyclopropane **3b** was tested with various substrates in the presence of Pd $(PPh_3)_4$. For all reactions, two equivalents of substrate were required for the reaction to proceed to completion. Insertions of terminal alkynes into substrate **3b** afforded Si–C(sp^2) bond cleavage products selectively, as did the insertion of an allene (Table 1). Instead of direct insertion, allylic transposition products were formed in moderate yields in the presence of both internal alkynes and terminal alkenes (Table 2). Many of the resultant silacyclopentene and -pentane products exhibited moderate instability, so they were difficult to purify. All reactions went to completion at ambient temperature, except for the reaction of substrate **3b** with 1-octene (entry 4), which required heating at 70 °C. Attempts to react alkyl-substituted allenes, internal alkenes, and sterically hindered internal alkynes with alkylidenesilacyclopropane **3b** led to decomposition.

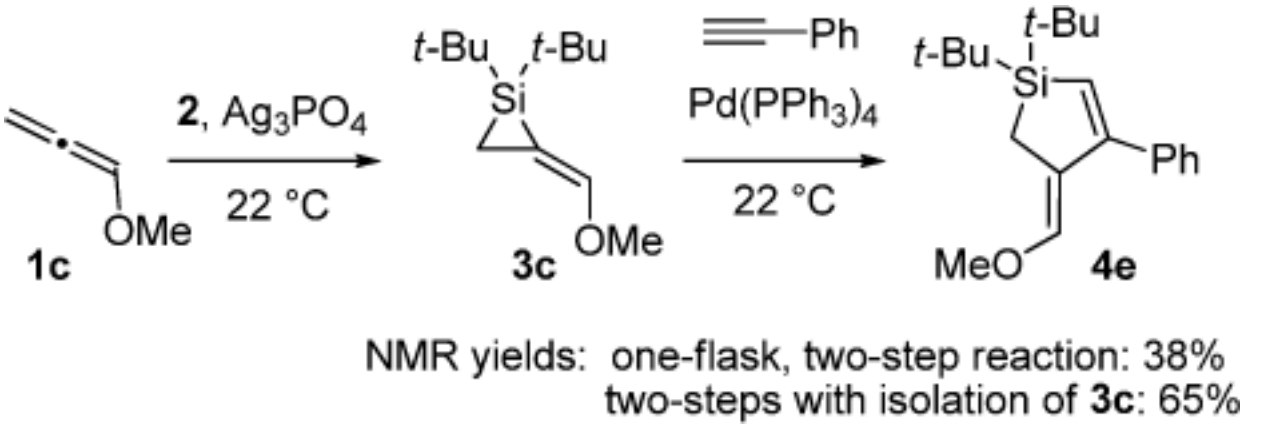
In addition to the observed allylic transposition products, side products were observed for some of the reactions shown in Table 2. Silacyclopentane **6** was observed as the major product in entry 1. The formation of this product results from the formal incorporation of a second equivalent of alkylidenesilacyclopropane **3b** in conjunction with di-*tert*-butylsilylene extrusion.[8,9] Dimeric material[20,21] derived from alkylidenesilacyclopropane **3b** appeared when heating the reaction mixture in entry 4.[5,7,16,22,23] No reactions (including decomposition and byproduct formation) were observed in the absence of catalyst.

Pd(0)-Catalyzed Insertion Reaction with an Electronically Activated Alkylidenesilacyclopropane

Alkylidenesilacyclopropane **3c** was synthesized to investigate possible electronic effects in the Pd(0)-catalyzed reactions. No silylene transfer was observed α- to the methoxy group, which is surprising considering the electrophilic nature of the silver silylenoid generated in situ.[24,25] Control experiments demonstrated that silylene transfer does not occur with enol ether **9** (Scheme 1), although it proceeded readily in the presence of acetylenic ethers.[26,27]

When subjected to the Pd(0)-catalyzed carbon–carbon π-bond insertion reaction, alkylidenesilacyclopropane **3c** was shown to be more reactive than alkyl-substituted analogue **3b** while maintaining high regio- and diastereoselectivity. Terminal alkynes and allenes afforded Si–C(sp^2) bond cleavage products (Table 3), but internal alkynes and terminal alkenes gave allylic transposition products (Table 4). A sterically hindered internal alkyne (Table 4, entry 2) and an alkyl-substituted allene (Table 3, entry 4) were also viable substrates in this reaction. Insertion with 1-octene proceeded to completion at ambient temperature (Table 4, entry 4). Analogously to silacyclopropane **3b**, internal alkenes were unreactive, and a dimeric compound derived from **3c** was observed as a byproduct in the reaction with 1-octene (Table 4, entry 4).[20,21] Although alkylidenesilacyclopropane **3c** exhibited greater reactivity and substrate scope, most of the insertion products were found to be too unstable to isolate and purify.

In an effort to circumvent the isolation of the air-sensitive alkylidenesilacyclopropane, a one-flask, two-step silacyclopropanation/π-bond insertion reaction (eq 4) was attempted with alkylidenesilacyclopropane **3c** in a manner similar to carbonyl insertion reactions.[18] Residual silver salts inhibited the Pd(0)-catalyzed reaction, providing product **4e** in low yield. As a result, all further experiments were conducted using isolated samples of alkylidenesilacyclopropanes.



(4)

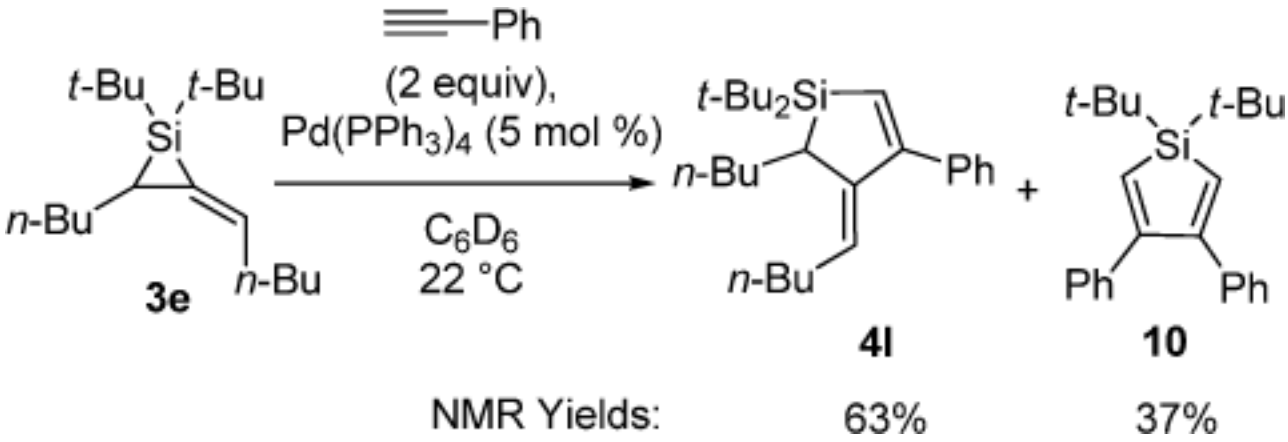
Pd(0)-Catalyzed Insertion Reaction with Disubstituted Alkylidenesilacyclopropanes

To extend these reactions to alkylidenesilacyclopropanes derived from chiral allenes, alkylidenesilacyclopropane **3d** was also subjected to the Pd(0)-catalyzed insertion reaction (Scheme 2). Only the reaction with phenylacetylene led to Si–C(sp^2) bond cleavage product **4i** as a mixture with silole byproduct **10**. Attempted insertion of 1-hexyne gave silole isomers **11a** and **11b** exclusively. Silole product formation has been reported for metal-catalyzed reactions of silacyclopropenes and -propanes, and regeneration of the starting alkyne or alkene was observed.[1,5,6,10-12] In contrast, no allene was observed after silole formation from alkylidenesilacyclopropane **3d**. All other substrates either gave no reaction or resulted in decomposition of the starting materials.

Electronic Effects in the Pd(0)-Catalyzed Insertion Reactions

To investigate electronic effects, two electronically different alkynes were employed in the carbon–carbon bond insertion reaction with alkylidenesilacyclopropane **3d**. An electron-deficient terminal alkyne required a longer reaction time compared to an electron-rich alkyne (Scheme 3). Although a difference in reactivity was observed, competitive silole formation was still observed.

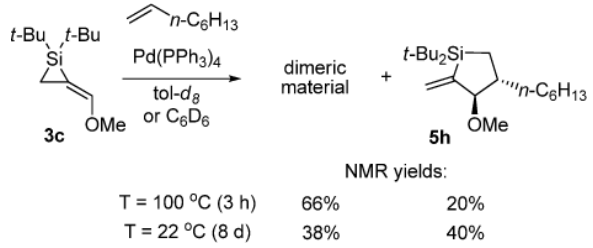
A control experiment demonstrated that steric effects were responsible for the low reactivity of alkylidenesilacyclopropane **3d**. This substrate has both an increase in branching at its allylic carbon as well as additional substitution of its three-membered ring compared to alkylidenesilacyclopropane **3b**. The increased substitution on the ring, not the allylic branching, was found to impede insertion reactions. The insertion reaction was repeated with alkylidenesilacyclopropane **3e** (eq 5), and the results were comparable with those obtained for alkylidenesilacyclopropane **3d**. Because the stereogenic center in the three-membered ring, which is necessary for developing an asymmetric variant of this reaction, also inhibited the reactivity of alkylidenesilacyclopropane **3d** in the Pd(0)-catalyzed reaction, alternative reaction conditions were investigated.



(5)

Optimization and Catalyst Screen

Initial attempts to increase the rate of the insertion reactions and avoid byproduct formation by heating the reaction mixture resulted in increased dimerization of the starting alkylidenesilacyclopropanes (eq 6).[20,21] Control experiments with both alkylidenesilacyclopropanes **3b** and **3c** showed rapid dimerization upon heating in the absence of substrate (eq 7), and suggested that formation of dimeric material is a thermodynamically favored process. An attempt to dimerize disubstituted alkylidenesilacyclopropane **3d** resulted in decomposition of starting material.



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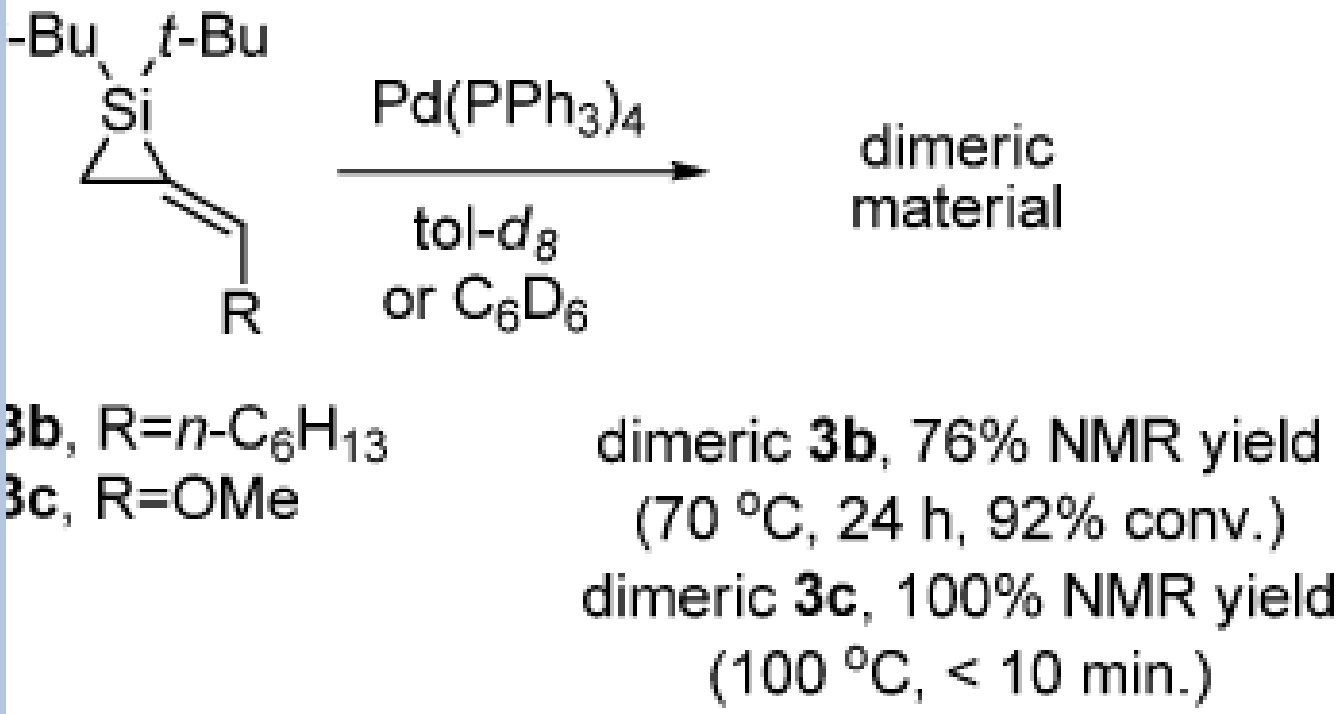
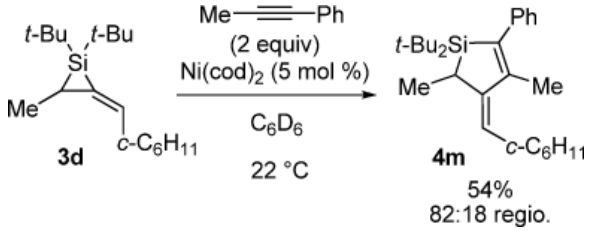


(7)

Because heating the reactions led to an increase in both byproduct formation and decomposition, alternative catalysts were investigated. To find a more reactive catalytic system that remained competent in the carbon–carbon π-bond insertion reaction, we screened a variety of ligands with metal catalysts at various temperatures.[28] Most of the catalyst studies were directed towards the reaction of 1-phenyl-1-propyne with alkylidenesilacyclopropane **3d** in an effort to develop an asymmetric version of the metal-catalyzed carbon–carbon bond insertion reaction. Palladium catalysts did not afford products in this reaction, and all ligands examined were demonstrated to inhibit reactivity. Only $Ni(cod)_2$ gave an insertion product, although in moderate yield (eq 8).

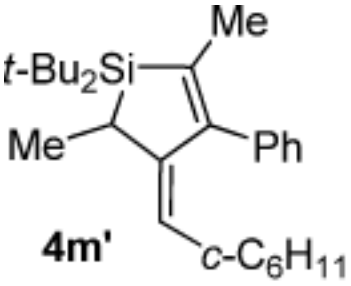


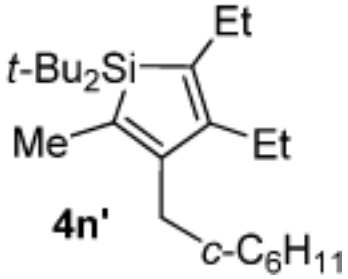
(8)

Ni(0)-Catalyzed Insertion Reaction with a Disubstituted Alkylidenesilacyclopropane

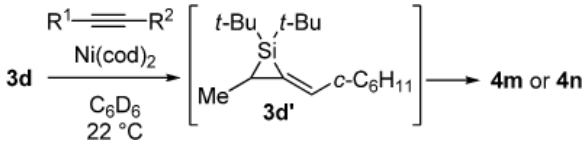
The scope of the Ni(0)-catalyzed carbon–carbon π-bond insertion reaction was investigated with alkylidenesilacyclopropane **3d**. Reactivity was observed with phenylacetylene, 1-phenyl-1-propyne, and 3-hexyne (Scheme 4). All other substrates (e.g., electron-rich terminal alkynes, alkenes, and allenes) led to decomposition of starting material. The increased reactivity exhibited by the Ni(0) catalyst allowed for double insertion[29,30] of phenylacetylene

to give a mixture of silacycloheptadienes **13a** and **13b** (Scheme 4a). If only one equivalent of phenylacetylene were used, decomposition of starting materials was observed. Alkyl-substituted internal alkynes led to Si–C(sp^2) bond cleavage products with isomerization of alkene geometry (Scheme 4b).





For the latter two reactions, alkene isomerization from **3d** to **3d′** was observed prior to insertion of the corresponding alkyne (eq 9).[31] Alkene isomerization did not occur in the absence of alkyne. The general applicability of alkylidenesilacyclopropane **3d** in the carbon–carbon π-bond insertion reaction remains limited.



(9)

Ni(0)-Catalyzed Insertion Reaction with a Monosubstituted Alkylidenesilacyclopropane

For comparison, monosubstituted alkylidenesilacyclopropane **3b** was also examined in the Ni (0)-catalyzed reaction (Table 5). As a result, the carbon–carbon bond insertion reaction gave Si–C(sp^2) bond cleavage product **4a** with phenylacetylene (entry 1) and allylic transposition product **5b** with 3-hexyne (entry 2). These products were analogous to those obtained in the Pd(0)-catalyzed reaction. The insertion of styrene led to acyclic product **14**.[1-3,8,32] Unlike the reaction with alkylidenesilacyclopropane **3d**, neither double insertion nor alkene isomerization products were observed in any of the reactions. In contrast to the Pd(0)-catalyzed reaction, no byproducts were observed.

Reaction Mechanism

Although different products were observed depending on either the substitution pattern of the alkylidenesilacyclopropane or the π-bond substrate, all of the carbon–carbon bond insertion reactions share similar mechanistic characteristics. Regiochemistry can best be explained by insertion to a metal–silicon bond,[33] and each reaction involves oxidative addition and reductive elimination processes.

To explain the substrate-dependent product differentiation that was observed in the Pd(0)-catalyzed reaction, catalytic cycles are proposed (Schemes 5 and 6). Reversible oxidative addition of alkylidenesilacyclopropane **3** provides palladasilacyclobutane **15**.[2,3,5,10,12] For terminal alkynes and allenes, migratory insertion into the palladium–silicon bond[3,8,10,12,14,17,34-36] affords intermediate **16**. Reductive elimination then provides product (*Z*)-**4**. Internal alkynes and terminal alkenes are slow to undergo migratory insertion[37-40] with intermediate **15**, so alkylidenesilacyclopropane **3** instead proceeds through a less favorable and irreversible simultaneous allylic transposition and oxidative addition to afford palladasilacyclobutane **17**.

Coordination of an alkyne followed by migratory insertion would afford palladasilacyclohexene **18**. Reductive elimination from intermediate **18** leads to product **5**. Previously, allylic transposition had not been observed for a carbon–carbon bond insertion reaction with an alkylidenesilacyclopropane.[8,9]

For disubstituted alkylidenesilacyclopropane **3d**, the Ni(0)-catalyzed reaction displayed an increase in reactivity[41] that resulted in both alkene isomerization and double alkyne insertion. A possible catalytic cycle to explain the former process is depicted in Scheme 7. In the presence of internal alkynes, alkylidenesilacyclopropane **3d** undergoes alkene isomerization[31] to generate **3d′**. Oxidative addition and migratory insertion afford nickelasilacyclohexene intermediate **21**,[42,43] which undergoes reductive elimination to yield Si–C(sp^2) bond cleavage product (*E*)-**4**. For double insertion, a catalytic cycle is proposed (Scheme 8) comparable to that depicted for the Pd(0)-catalyzed reaction in Scheme 5. Oxidative addition by Ni(0) into alkylidenesilacyclopropane **3d** gives nickelasilacyclobutane intermediate **22**,[6,7,44,45] which undergoes migratory insertion into the nickel–silicon bond.[42,43] A second insertion into the less sterically hindered nickel–carbon(sp^2) bond[46] affords intermediate **24**, which reductively eliminates to yield product **13a**. It is assumed that Ni(0) facilitates the migratory insertion that, with Pd(0) catalysis, would have been inhibited in the transformations leading from intermediates **20** to **21** and from **22** to **23**.[41]

The subtle substrate-ligand effects observed in the Ni(0)-catalyzed reaction suggested that a more electron-rich ligand (either π-bond substrate or alkylidenesilacyclopropane) would lead to an increase in reactivity. For the Ni(0)-catalyzed reaction, we propose that hyperconjugation of $\sigma_{C\text{-}Me}$ into $\pi^*_{C=C}$ makes alkylidenesilacyclopropane **3d** a slightly better ligand for Ni(0) and allows for unusual reactivity not observed for alkylidenesilacyclopropane **3b**.

Conclusion

The reported insertion reactions with alkylidenesilacyclopropanes **3b**, **3c**, and **3d** constitute general and selective examples of metal-catalyzed carbon–carbon π-bond insertion reactions into cyclic organosilicon compounds. New reactivity was observed, and catalytic cycles were proposed to explain these observations.

Experimental Section

General Procedures

General experimental details are provided as Supporting Information.

Palladium-Catalyzed Synthesis of Carbon–Carbon Bond Insertion Products

Method A (isolation): To a solution of alkyne, alkene, or allene (2.0 mmol) and silacyclopropane **3** (1.0 mmol) in toluene (5 mL) was added $Pd(PPh_3)_4$ (0.060 g, 0.05 mmol). When the reaction had proceeded to completion as determined by ^{1}H NMR spectroscopic analysis, the reaction mixture was filtered through SiO_2 and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (hexanes, 1:99 EtOAc/hexanes, or 0.5:1:98.5 NEt_3/EtOAc/hexanes) to afford carbon–carbon bond insertion products. Unless otherwise indicated, all spectral data was obtained using Method A.

Method B (NMR observation): Alkyne, alkene, or allene (0.254 mmol) was added to a solution of silacyclopropane **3** (0.550 mL, 0.127 mmol, 0.230 M solution of 3 and 0.0465 M solution of $PhSiMe_3$ in C_6D_6), followed by the addition of $Pd(PPh_3)_4$ (0.007 g, 0.006 mmol). The progress of the reaction was monitored and yields were determined by ^{1}H NMR spectroscopic analysis (compared to the $PhSiMe_3$ internal standard) using a single scan.

Silacyclopentene 4a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.25 (m, 5H), 5.96 (s, 1H), 5.41 (t, *J* = 7.2, 1H), 2.17 (q, *J* = 7.1, 2H), 1.57 (s, 2H), 1.36–1.27 (m, 8H), 1.04 (s, 18H), 0.90 (t, *J* = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 143.7, 141.9, 129.9, 129.2, 128.5, 127.8, 127.0, 31.8, 30.0, 29.28, 29.26, 28.7, 22.7, 19.6, 14.2, 10.2; IR (neat) 3057, 2931, 2858, 1601, 1577, 1470 cm^{-1}; HRMS (APCI) *m* / *z* calcd for $C_{25}H_{41}Si$ $(M + H)^+$ 369.2978, found 369.2975.

Silacyclopentene 4b: ^{1}H NMR (500 MHz, C_6D_6) δ 5.89 (s, 1H), 5.78 (tt, *J* = 7.2, 2.3, 1H), 2.41 (appar t, *J* = 7.7, 2H), 2.28 (q, *J* = 7.3, 2H), 1.58 (quint, *J* = 7.6, 2H), 1.57 (s, 2H), 1.47 (sext, *J* = 7.5, 2H), 1.34–1.26 (m, 8H), 1.08 (s, 18H), 0.91 (t, *J* = 7.4, 3H), 0.90 (t, *J* = 7.0, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 165.0, 143.3, 125.4, 124.6, 32.4, 31.1, 29.8, 29.6, 29.3, 29.2, 28.5, 28.5, 22.83, 22.77, 19.1, 14.0, 13.9, 10.1; IR (neat) 2957, 2856, 1543, 1469, 1363, 1141 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{23}H_{45}Si$ $(M + H)^+$ 349.3290, found 349.3290.

Silacyclopentene 4c: ^{1}H NMR (500 MHz, C_6D_6) δ 6.38 (s, 1H), 5.68 (t, *J* = 7.2, 1H), 4.36 (s, 2H), 3.97 (d, *J* = 2.4, 2H), 2.23 (q, *J* = 7.3, 2H), 2.00 (t, *J* = 2.4, 1H), 1.57 (s, 2H), 1.37–1.26 (m, 8H), 1.02 (s, 18H), 0.91 (t, *J* = 6.8, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 159.6, 141.6, 128.5, 125.2, 80.0, 74.3, 69.3, 57.1, 31.9, 29.7, 29.5, 29.3, 29.1, 28.4, 22.8, 19.1, 14.0, 10.2; IR (neat) 2957, 2856, 2362, 1553, 1469, 1119 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{23}H_{41}OSi$ $(M + H)^+$ 361.2927, found 361.2925.

Silacyclopentane 4d: [47] **:** ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 6.29 (s, 1H), 5.63 (t, *J* = 7.2, 1H), 3.26 (s, 3H), 2.22 (q, *J* = 7.1, 2H), 1.77 (s, 2H), 1.57 (s, 2H), 1.01 (s, 18H).

Silacyclopentene 4e: ^{1}H NMR (400 MHz, C_6D_6) δ 7.38 (d, *J* = 7.2, 2H), 7.21–7.16 (m, 3H), 6.21 (s, 1H), 5.83 (s, 1H), 3.06 (s, 3H), 1.93 (s, 2H), 1.09 (s, 18H); ^{13}C NMR (125 MHz, C_6D_6) δ 163.8, 147.7, 141.8, 128.3, 127.2, 126.4, 124.3, 59.0, 31.6, 28.5, 19.4, 8.2; HRMS (ESI) *m* / *z* calcd for $C_{20}H_{31}OSi$ $(M + H)^+$ 315.2144, found 315.2141.

Silacyclopentene 4f: ^{1}H NMR (400 MHz, C_6D_6) δ 6.30 (s, 1H), 5.74 (s, 1H), 3.26 (s, 3H), 2.29 (t, *J* = 7.5, 2H), 1.82 (s, 2H), 1.59 (quint, *J* = 7.6, 2H), 1.35 (sext, *J* = 7.5, 2H), 1.07 (s, 18H), 0.92 (t, *J* = 7.4, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 162.4, 143.9, 123.7, 122.3, 59.0, 32.1, 30.9, 28.5, 22.8, 19.2, 14.0, 7.9.

Silacyclopentane 4g: ^{1}H NMR (500 MHz, C_6D_6) δ 6.11 (t, *J* = 2.0, 2H), 3.29 (s, 6H), 1.79 (d, *J* = 2.1, 4H), 1.01 (s, 18H); ^{13}C NMR (125 MHz, C_6D_6) δ 138.0, 120.0, 58.8, 28.1, 19.0, 9.7.

Silacyclopentane 4h: [47] **:** ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 5.90 (t, *J* = 2.0, 1H), 3.26 (s, 3H), 1.95 (s, 3H), 1.82, (s, 3H), 1.75 (d, *J* = 2.0, 2H), 1.01 (s, 18H).

Silacyclopentene 4h′: [48] **:** mp 50–54 °C; ^{1}H NMR (500 MHz, C_6D_6) δ 10.21 (s, 1H), 3.30–3.26 (m, 1H), 1.77 (s, 2H), 1.39 (s, 2H), 0.87 (s, 18H), 0.81 (d, *J* = 6.8, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 188.1, 168.9, 138.2, 28.2, 27.8, 20.9, 18.4, 13.5, 11.3; IR (thin film) 2964, 2931, 2858, 1666, 1595, 1468 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{16}H_{31}OSi$ $(M + H)^+$ 267.2144, found 267.2149.

Silacyclopentene 4i: ^{1}H NMR (500 MHz, C_6D_6) δ 7.41 (dd, *J* = 7.6, 1.4, 2H), 7.21 (t, *J* = 7.3, 2H), 7.15 (td, *J* = 7.5, 1.7, 1H), 6.02 (s, 1H), 5.38 (d, *J* = 10.2, 1H), 2.46–2.39 (m, 2H), 1.78–1.54 (m, 8H), 1.42 (d, *J* = 7.8, 3H), 1.33–1.25 (m, 2H), 1.18 (s, 9H), 1.09 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 165.4, 149.1, 141.7, 133.9, 128.7, 128.1, 128.0, 127.3, 38.4, 33.6, 32.6, 29.6, 28.8, 25.99,[49] 25.95, 21.8, 21.6, 20.2, 18.5; IR (neat) cm^{-1} 3076, 3021, 2929, 1538, 1470, 1363 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{26}H_{41}Si$ $(M + H)^+$ 381.2978, found 381.2982.

Silacyclopentene 4j: [50] **:** ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 6.00 (s, 1H), 5.41 (d, *J* = 10.3, 1H), 3.37 (s, 3H), 1.41 (d, *J* = 7.8, 3H); HRMS (GCMS) *m* / *z* calcd for $C_{27}H_{43}OSi$ $(M + H)^+$ 411.3083, found 411.3093.

Silacyclopentene 4k: [50] **:** ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 5.93 (s, 1H), 5.15 (d, *J* = 10.3, 1H), 1.36 (d, *J* = 7.8, 3H); HRMS (GCMS) *m* / *z* calcd for $C_{27}H_{40}F_3Si$ $(M + H)^+$ 449.2851, found 449.2837.

Silacyclopentene 4l: [47] **:** ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 6.04 (s, 1H), 5.51 (t, *J* = 7.1, 1H), 2.34 (t, *J* = 7.3, 1H).

Silacyclopentene 5a: ^{1}H NMR (400 MHz, C_6D_6) δ 7.21 (t, *J* = 7.7, 2H), 7.11 (t, *J* = 7.5, 1H), 7.07 (d, *J* = 6.8, 2H), 5.90 (t, *J* = 2.2, 1H), 5.73 (t, *J* = 2.5, 1H), 3.55–3.51 (m, 1H), 1.83 (d, *J* = 2.2, 3H), 1.75–1.66 (m, 1H), 1.53–1.44 (m, 1H), 1.39–1.27 (m, 2H), 1.26–1.03 (m, 6H), 1.21 (s, 9H), 1.14 (s, 9H), 0.82 (t, *J* = 7.0, 3H); ^{13}C NMR (125 MHz, C_6D_6, distinctive peaks) δ 129.5, 129.1, 129.0, 128.3, 128.2, 126.9, 126.4, 123.1, 47.9, 36.0; IR (neat) 3057, 2929, 2856, 1581, 1468, 1389 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{26}H_{43}Si$ $(M + H)^+$ 383.3134, found 383.3145.

Silacyclopentene 5b: ^{1}H NMR (500 MHz, C_6D_6) δ 5.85 (t, *J* = 2.1, 1H), 5.68 (t, *J* = 2.4, 1H), 3.16 (br s, 1H), 2.48 (dq, *J* = 13.7, 7.5, 1H), 2.40–2.16 (m, 5H), 2.10, (quint, *J* = 7.2, 1H), 1.91 (dq, *J* = 13.7, 7.5, 1H), 1.84–1.75 (m, 1H), 1.65–1.56 (m, 1H), 1.53–1.34 (m, 4H), 1.19 (s, 9H), 1.10 (s, 9H), 1.08 (appar t, *J* = 5.7, 3H), 0.96 (t, *J* = 7.5, 3H), 0.89 (t, *J* = 7.0, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.9, 151.9, 135.1, 122.4, 50.9, 32.1, 30.4, 29.4, 29.1, 28.8, 26.5, 25.4, 22.7, 21.4, 20.3, 20.0, 15.2, 14.0, 12.7; IR (neat) 2960, 2857, 1580, 1469, 1387, 820 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{23}H_{45}Si$ $(M + H)^+$ 349.3290, found 349.3296.

Silacyclopentane 5c: ^{1}H NMR (400 MHz, C_6D_6) δ 7.24–7.22 (m, 4H), 7.14–7.10 (m, 1H), 5.80 (t, *J* = 2.5, 1H), 5.65 (t, *J* = 2.7, 1H), 2.76 (td, *J* = 12.6, 6.4, 1H), 2.53 (dtd, *J* = 12.5, 4.7, 1.6, 1H), 1.68–1.60 (m, 1H), 1.53–1.44 (m, 1H), 1.39–1.30 (m, 2H), 1.26–1.16 (m, 8H), 1.11 (s, 9H), 1.09 (s, 9H), 0.83 (t, *J* = 6.9, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 153.3, 147.8, 128.5, 127.1, 126.0, 121.2, 53.4, 49.2, 31.7, 30.0, 28.7, 28.5, 27.9, 24.7, 22.7, 19.6, 18.9, 18.7, 14.0; IR (neat) 3026, 2929, 2856, 1601, 1470, 1363 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{25}H_{43}Si$ $(M + H)^+$ 371.3134, found 371.3135. Anal. Calcd for $C_{25}H_{42}Si$: C, 81.00; H, 11.42. Found: C, 80.87; H, 11.49.

Silacyclopentane 5d: ^{1}H NMR (500 MHz, C_6D_6) δ 5.78 (d, *J* = 2.2, 1H), 5.61 (d, *J* = 1.0, 1H), 2.33–2.27 (m, 1H), 2.00–1.92 (m, 2H), 1.84 (appar t, *J* = 11.8, 2H), 1.78–1.71 (m, 2H), 1.63–1.58 (m, 4H), 1.45–1.33 (m, 13H), 1.10 (s, 9H), 1.07 (s, 9H), 0.93–0.89 (m, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.3, 120.3, 52.9, 41.3, 36.4, 32.1, 31.9, 30.4, 29.8, 28.7, 28.5, 27.5, 27.3, 24.2, 22.85, 22.82, 19.5, 18.7, 14.1, 14.0, 13.4; IR (neat) 3041, 2927, 1468, 1387, 1363 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{25}H_{51}Si$ $(M + H)^+$ 379.3760, found 379.3764.

Silacyclopentene 5e: ^{1}H NMR (400 MHz, C_6D_6) δ 7.30–7.21 (m, 5H), 6.10 (dd, *J* = 2.9, 1.8, 1H), 5.78 (t, *J* = 2.5, 1H), 5.01 (q, *J* = 1.9, 1H), 3.02 (s, 3H), 1.84 (d, *J* = 1.9, 3H), 1.17 (s, 9H), 1.08 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 156.5, 146.7, 139.4, 137.7, 128.7, 128.7, 126.7, 126.2, 87.6, 52.7, 29.0, 28.6, 20.2, 19.8, 17.5; HRMS (ESI) *m* / *z* calcd for $C_{21}H_{32}OSiNa$ $(M + Na)^+$ 351.2120, found 351.2118.

Silacyclopentene 5f: [47] **:** ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 6.10 (s, 1H), 5.74 (s, 1H), 4.87 (s, 1H), 3.11 (s, 3H), 2.05 (t, *J* = 6.2, 2H).

Silacyclopentene 5f′: ^{1}H NMR (500 MHz, C_6D_6, distinctive peaks) δ 7.23 (s, 1H), 5.68 (d, *J* = 2.6, 1H), 5.42 (d, *J* = 2.3, 1H), 2.20 (t, *J* = 7.4, 2H), 1.58 (m, 2H), 1.07 (s, 18H), 0.83 (t, *J* = 7.0, 3H); ^{13}C NMR (125 MHz, C_6D_6, distinctive peaks) δ 172.9, 157.2, 154.2, 144.3, 125.3, 35.6, 27.8, 24.9, 18.7, 13.7; HRMS (ESI) *m* / *z* calcd for $C_{17}H_{30}SiONa$ $(M + Na)^+$ 301.1964, found 301.1962.

Silacyclopentane 5g: ^{1}H NMR (500 MHz, C_6D_6) δ 7.33 (d, *J* = 7.1, 2H), 7.24 (t, *J* = 7.6, 2H), 7.14 (t, *J* = 7.3, 1H), 6.16 (t, *J* = 2.9, 1H), 5.65 (t, *J* = 3.0, 1H), 4.04 (dt, *J* = 11.4, 2.7, 1H), 3.06 (s, 3H), 2.95 (ddd, *J* = 12.7, 11.5, 7.0, 1H), 1.050 (s, 9H), 1.045 (s, 9H), 0.89 (appar t, *J* = 6.8, 1H), 0.83 (dd, *J* = 15.2, 13.0, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 149.5, 146.2, 128.3, 127.4, 126.2, 122.4, 91.2, 57.9, 50.0, 28.34, 28.33, 19.3, 18.7, 14.1; IR (neat) 3059, 3028, 2931, 2858, 1470, 1105 cm^{-1}; HRMS (ESI) *m* / *z* calcd for $C_{20}H_{32}OSiNa$ $(M + Na)^+$ 339.2120, found 339.2126.

Silacyclopentane 5h: ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 6.01 (t, *J* = 2.8, 1H), 5.57 (t, *J* = 3.2, 1H), 3.49 (dt, *J* = 11.2, 2.7, 1H), 3.34 (s, 3H), 1.03 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6, distinctive peaks) δ 151.3, 121.2, 91.2, 56.9, 42.9, 35.9, 32.1, 27.4, 14.0; HRMS (APCI) *m* / *z* calcd for $C_{14}H_{28}OSi$ $(M + H)^+$ 325.2927, found 325.2932.

Silacyclopentane 6: ^{1}H NMR (500 MHz, C_6D_6) δ 5.78 (t, *J* = 1.5, 1H), 5.53 (t, *J* = 2.2, 1H), 5.26 (td, *J* = 7.2, 1.8, 1H), 2.97–2.95 (m, 1H), 2.44 (q, *J* = 6.8, 1H), 2.29 (q, *J* = 7.6, 1H), 2.25–2.12 (m, 3H), 1.81 (d, *J* = 15.6, 1H), 1.65–1.56 (m, 4H), 1.52–1.44 (m, 8H), 1.41–1.36 (m, 4H), 1.10 (s, 9H), 1.09 (s, 9H), 0.93–0.91 (m, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.7, 142.6, 122.88, 122.86, 58.3, 36.6, 32.1, 31.9, 30.0, 29.5, 29.3, 29.0, 28.9, 28.5, 28.1, 27.5, 22.8, 20.0, 18.9, 14.03, 14.02, 11.3; IR (neat) 3037, 2927, 2856, 1468, 1389, 1363 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{26}H_{51}Si$ $(M + H)^+$ 391.3760, found 391.3756.

Silole 10: mp 103–104 °C; ^{1}H NMR (400 MHz, C_6D_6) δ 7.13–7.11 (m, 4H), 7.00–6.97 (m, 6H), 6.16 (s, 2H), 1.18 (s, 18H); ^{13}C NMR (125 MHz, C_6D_6) δ 162.1, 141.3, 130.7, 128.01, 128.00, 126.8, 28.8, 19.3; IR (thin film) 3061, 2958, 1597, 1470, 1387, 1190 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{24}H_{31}Si$ $(M + H)^+$ 347.2195, found 347.2193. Anal. Calcd for $C_{24}H_{30}Si$: C, 83.17; H, 8.72. Found: C, 83.09; H, 8.89.

Silole 11a: ^{1}H NMR (500 MHz, C_6D_6) δ 5.74 (s, 2H), 2.25 (t, *J* = 7.6, 4H), 1.51 (quint, *J* = 7.3, 4H), 1.34 (sext, *J* = 7.3, 4H), 1.18 (s, 18H), 0.91 (t, *J* = 7.4, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 162.7, 122.3, 32.8, 32.4, 29.0, 26.5, 22.6, 14.0; IR (neat) 2956, 2856, 1543, 1512, 1468, 1363 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{20}H_{39}Si$ $(M + H)^+$ 307.2821, found 307.2824.

Silole 11b: ^{1}H NMR (500 MHz, C_6D_6) δ 5.88 (s, 1H), 5.74 (s, 1H), 2.38 (t, *J* = 7.6, 2H), 2.21 (t, *J* = 7.3, 2H), 1.60–1.55 (m, 4H), 1.46 (sext, *J* = 7.4, 4H), 1.07 (s, 18H), 0.96 (t, *J* = 7.3, 3H), 0.91 (t, *J* = 7.4, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 165.0, 143.5, 125.4, 124.3, 32.4, 31.8, 28.5, 26.2, 22.82, 22.78, 19.1, 18.9, 13.94, 13.92.

Silole 12a: [50] **:** ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 6.13 (s, 2H), 3.25 (s, 6H); HRMS (GCMS) *m* / *z* calcd for $C_{26}H_{35}O_2Si$ $(M + H)^+$ 407.2406, found 407.2391.

Silole 12b: [50] **:** ^{1}H NMR (400 MHz, C_6D_6, distinctive peaks) δ 6.09 (s, 2H); HRMS (GCMS) *m* / *z* calcd for $C_{26}H_{29}F_6Si$ $(M + H)^+$ 483.1943, found 483.1923.

Nickel-Catalyzed Synthesis of Carbon–Carbon Bond Insertion Products

Method A (isolation): To a solution of alkyne, alkene, or allene (2.0 mmol) and silacyclopropane **3** (1.0 mmol) in toluene (5 mL) was added $Ni(cod)_2$ (0.014 g, 0.05 mmol). When the reaction had proceeded to completion as determined by ^1H NMR spectroscopic analysis, the reaction mixture was filtered through SiO_2 and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (hexanes) to afford carbon–carbon bond insertion products. Unless otherwise indicated, all of the spectral data was obtained using Method A.

Method B (NMR observation): Alkyne, alkene, or allene (0.254 mmol) was added to a solution of silacyclopropane **3** (0.550 mL, 0.127 mmol, 0.230 M solution of 3 and 0.0465 M solution of $PhSiMe_3$ in C_6D_6), followed by the addition of $Ni(cod)_2$ (0.002 g, 0.006 mmol). The progress of the reaction was monitored and yields were determined by ^1H NMR spectroscopic analysis (compared to the $PhSiMe_3$ internal standard) using a single scan.

Silacyclopentene 4m: ^1H NMR (500 MHz, C_6D_6) δ 7.23–7.19 (m, 4H), 7.08–7.03 (m, 1H), 5.10 (dd, *J* = 9.7, 2.1, 1H), 2.74 (qt, *J* = 10.2, 3.4, 1H), 2.19 (qd, *J* = 7.1, 2.1, 1H), 2.07 (s, 3H), 1.90–1.41 (m, 10H), 1.43 (d, *J* = 7.2, 3H), 1.11 (s, 9H), 1.09 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 155.2, 146.0, 145.1, 144.0, 128.7, 128.4, 128.2, 125.3, 37.5, 34.5, 34.2, 29.5, 29.3, 27.0, 26.2, 26.2, 26.1, 23.0, 20.5, 18.9, 14.4; IR (neat) 3020, 2925, 1597, 1541, 1468, 1365 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{27}H_{43}Si$ $(M + H)^+$ 395.3134, found 395.3129.

Silacyclopentene 4m′: ^1H NMR (400 MHz, C_6D_6, distinctive peaks) δ 4.97 (d, *J* = 8.9, 1H).

Silacyclopentene 4n: ^1H NMR (500 MHz, C_6D_6, distinctive peaks) δ 4.90 (dd, *J* = 9.4, 2.1, 1H), 1.36 (d, *J* = 7.1, 3H), 1.10 (s, 9H), 1.09 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.9, 144.3, 142.4, 124.4, 37.4, 34.3, 34.2, 29.3, 29.0, 28.2, 23.1, 22.71, 22.68, 22.4, 20.0, 14.0, 13.8, 13.7; IR (neat) 2927, 2854, 1470, 1448, 1363, 820 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{22}H_{45}Si$ $(M + H)^+$ 361.3290, found 361.3285.

Silacyclopentene 4n′: ^1H NMR (500 MHz, C_6D_6) δ 2.35 (q, *J* = 7.3, 2H), 2.34 (q, *J* = 7.5, 2H), 2.23 (d, *J* = 7.0, 2H), 1.96 (s, 3H), 1.79–1.37 (m, 11H), 1.16 (s, 18H), 1.14 (t, *J* = 7.6, 3H), 1.01 (t, *J* = 7.5, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 157.9, 153.4, 134.7, 131.1, 39.1, 35.3, 33.7, 29.0, 26.6, 26.5, 22.6, 21.1, 19.3, 16.6, 15.3, 14.4; IR (neat) 2927, 2854, 1468, 1448, 1363, 820cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{24}H_{45}Si$ $(M + H)^+$ 361.3290, found 361.3287.

Silacycloheptadiene 13a: mp 64–67 °C; ^1H NMR (500 MHz, C_6D_6) δ 7.41–7.37 (m, 4H), 7.03 (s, 1H), 7.00 (appar t, *J* = 7.5, 4H), 6.90–6.85 (m, 2H), 6.58 (s, 1H), 5.21 (d, *J* = 9.9, 1H), 3.18 (q, *J* = 7.7, 1H), 2.42 (appar q, *J* = 10.8, 1H), 1.84–1.53 (m, 10H), 1.48 (d, *J* = 7.8, 3H), 1.21 (s, 9H), 1.15 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 155.7, 144.3, 144.1, 140.6, 140.1, 136.0, 131.6, 129.0, 128.13, 128.06, 126.92,[49] 126.89, 126.8, 37.5, 34.4, 33.1, 30.6, 30.0, 28.6, 26.2, 26.0, 25.9, 23.0, 20.1, 17.1; IR (thin film) 2926, 2854, 1599, 1566, 1470, 1444 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{34}H_{47}Si$ $(M + H)^+$ 483.3447, found 483.3439.

Silacycloheptadiene 13b: mp 68–70 °C; ^1H NMR (500 MHz, C_6D_6) δ 7.74 (d, *J* = 7.4, 2H), 7.47 (d, *J* = 7.0, 2H), 7.27–7.11 (m, 6H), 6.65 (s, 1H), 6.45 (s, 1H), 5.11 (d, *J* = 9.8, 1H), 3.33 (q, *J* = 8.1, 1H), 2.56–2.48 (m, 1H), 1.73–1.57 (m, 10H), 1.22 (d, *J* = 8.2, 3H), 1.18 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.6, 147.1, 144.4, 141.2, 138.6, 131.7, 129.3, 128.3, 128.3, 128.2, 128.2, 127.4, 126.5, 126.2, 37.8, 32.0, 30.6, 28.7, 26.2, 26.0, 25.8, 22.4, 19.9, 17.3; IR (thin film) 3078, 2926, 1597, 1562, 1491, 1470 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{34}H_{47}Si$ $(M + H)^+$ 483.3447, found 483.3445. Anal. Calcd for $C_{34}H_{46}Si$: C, 84.58; H, 9.60. Found: C, 84.36; H, 9.75.

Diene 14: ^{1}H NMR (400 MHz, C_6D_6) δ 7.37 (d, *J* = 7.9, 2H), 7.17 (d, *J* = 19.2, 1H), 7.13–7.06 (m, 3H), 6.60 (d, *J* = 19.3, 1H), 5.81 (appar q, *J* = 9.0, 1H), 5.43 (dt, *J* = 10.9, 7.7, 1H), 2.22 (q, *J* = 6.9, 2H), 1.93 (d, *J* = 9.0, 2H), 1.47–1.40 (m, 2H), 1.38–1.26 (m, 6H), 1.13 (s, 18H), 0.89 (t, *J* = 6.7, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 146.3, 138.6, 128.5, 128.1, 128.0, 126.48, 126.45, 123.7, 31.9, 29.7, 29.2, 28.8, 27.4, 22.7, 19.9, 14.0, 10.9; IR (neat) 3059, 2958, 1603, 1575, 1495, 1464 cm^{-1}; HRMS (GCMS) *m* / *z* calcd for $C_{25}H_{43}Si$ $(M + H)^+$ 371.3134, found 371.3130. Anal. Calcd for $C_{25}H_{42}Si$: C, 81.00; H, 11.42. Found: C, 80.80; H, 11.61.

Supplementary Material

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Acknowledgments

This research was supported by the National Institute of General Medical Sciences of the National Institutes of Health (GM-54909). K.M.B. thanks the Department of Education (GAANN) for a predoctoral fellowship. K.A.W. thanks Amgen and Lilly for awards to support research. We thank Dr. P. Dennison (UCI) for assistance with NMR spectroscopy, Dr. J. W. Ziller and M. K. Takase (UCI) for X-ray crystallography, and Dr. J. Greaves and S. Sorooshian (UCI) for mass spectrometry.

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19. Silacyclopropane **3a** was observed by ^{1}H NMR spectroscopic analysis of the crude reaction mixture. The yield was calculated relative to an internal standard ($PhSiMe_3$).
20. The dimeric material could not be isolated due to its instability and its structure could not be determined in the reaction mixture. The exact mass of the dimer was determined by HRMS (GCMS). Additional details are provided as Supporting Information.
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28. Metals included in the screen were Pd(0), Pd(II), Ni(0), Ni(II), Rh(I), and Pt(0). Also included were a variety of bimetallic systems with gold catalysts. Ligands included a series of mono-, di-, and tridentate ligands containing some combination of either phosphorous, nitrogen, or oxygen chelation. $Pd(PPh_3)_4$ and $Ni(cod)_2$ proved to be the best catalysts in our catalytic system by consistently giving products in modest to high yields. $PdCl_2(PPh_3)_2$, $Pt(PEt_3)_4$, and $[RhCl(CO)_2]_2$ were each observed to give products in low yields (<10%). All other catalysts gave no reaction or decomposition of starting materials.
29. Nickel-catalyzed incorporation of two equivalents of a terminal alkyne has been reported for an acyclic example. See reference [30].
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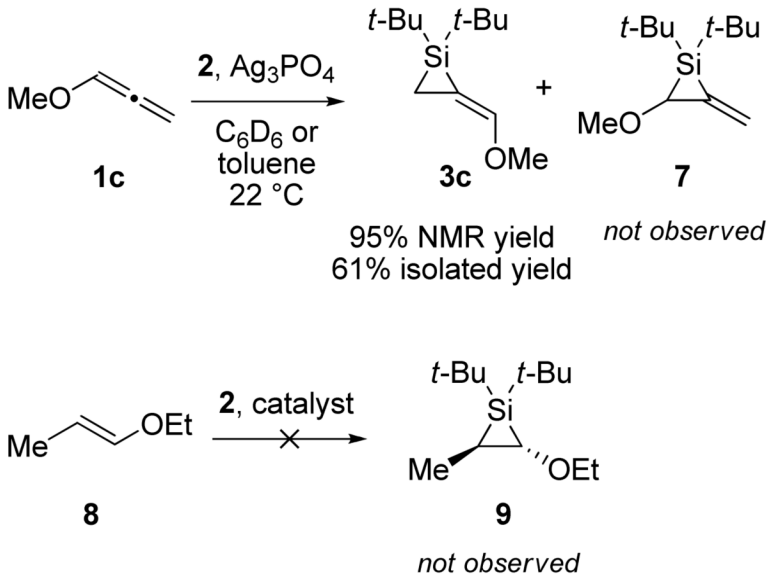
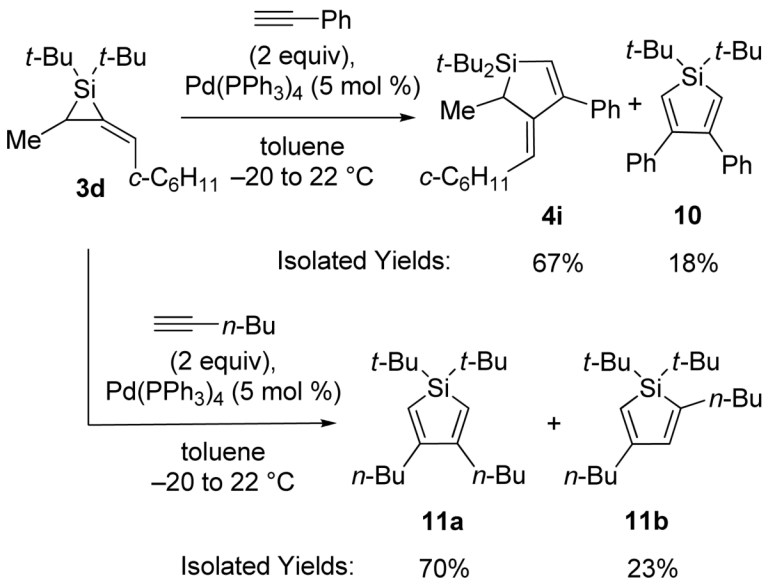
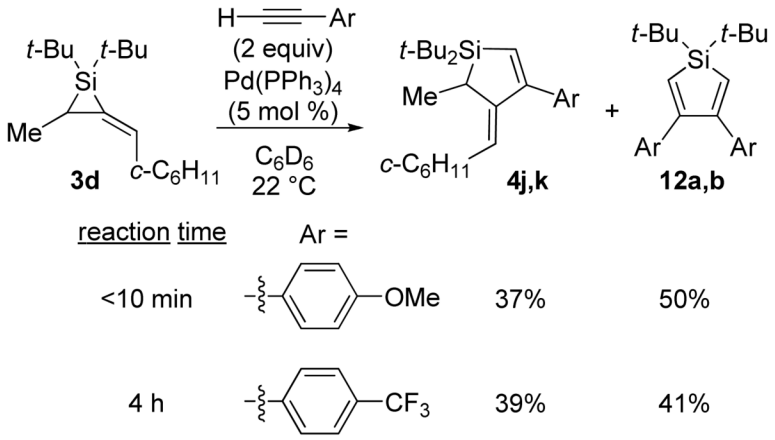
46. The latter migratory insertion suffers from low regioselectivity, which ultimately leads to products **13a** and **13b** in a 72:28 mixture. The catalytic cycle is shown for the major regioisomer.
47. Spectrum for material obtained from Method B.
48. Obtained upon attempted chromatography of the desired product.
49. Corresponds to two chemically unequivalent carbons.
50. Spectra for material obtained from Method B.



Scheme 1.
Silacyclopropanation of Allene Ether **1c** and a Control Experiment with Enol Ether **8**

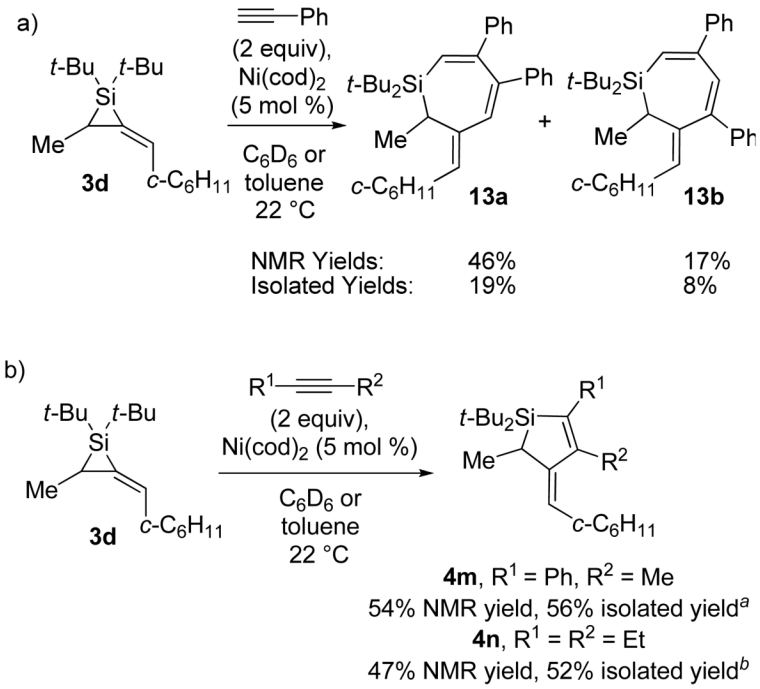


Scheme 2.
Pd(0)-Catalyzed Carbon–Carbon Bond Insertion with **3d**



Scheme 3.

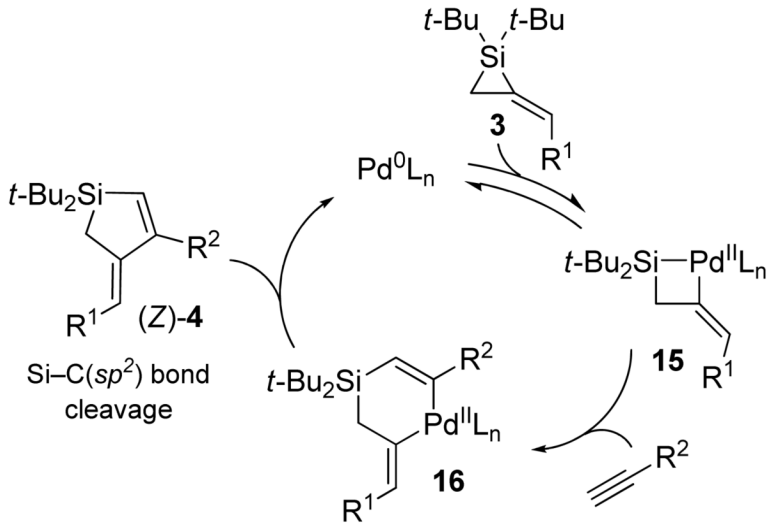
Electronic Effects in the Pd(0)-Catalyzed Carbon–Carbon Bond Insertion Reaction with **3d**



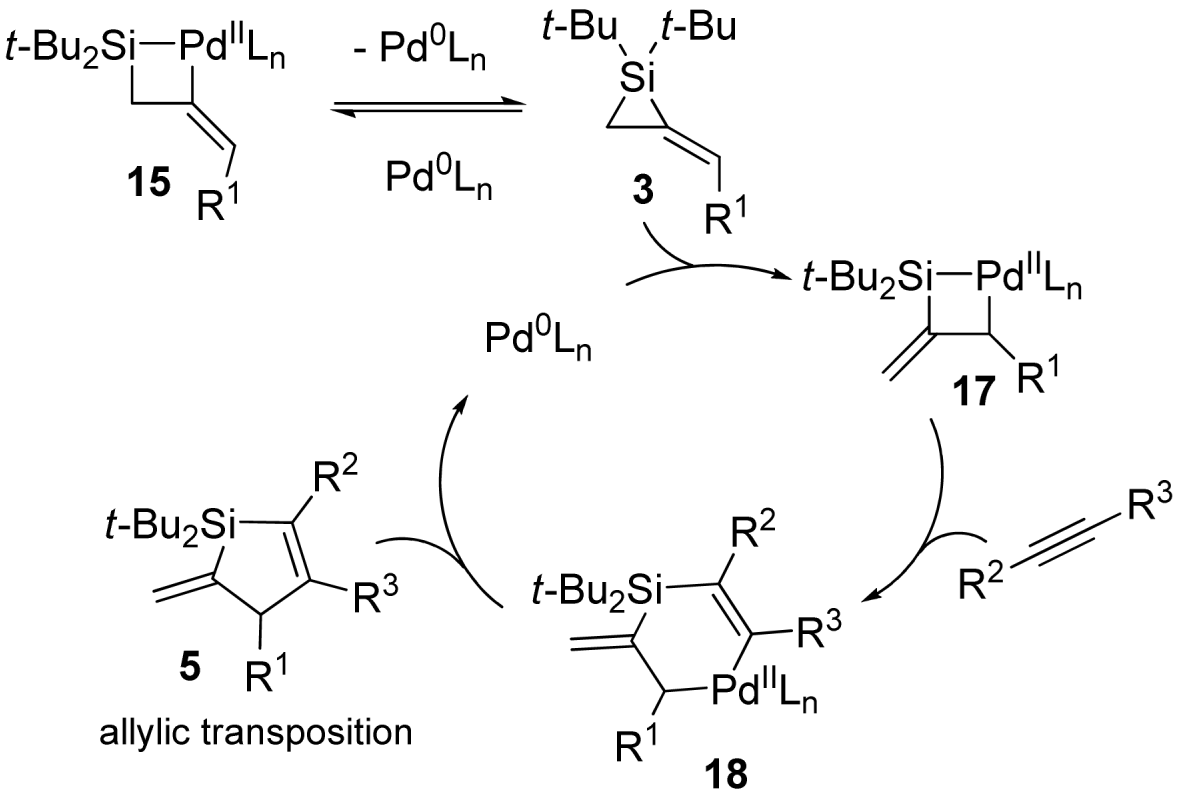
Scheme 4.

Ni(0)-Catalyzed Carbon–Carbon Bond Insertion with **3d**

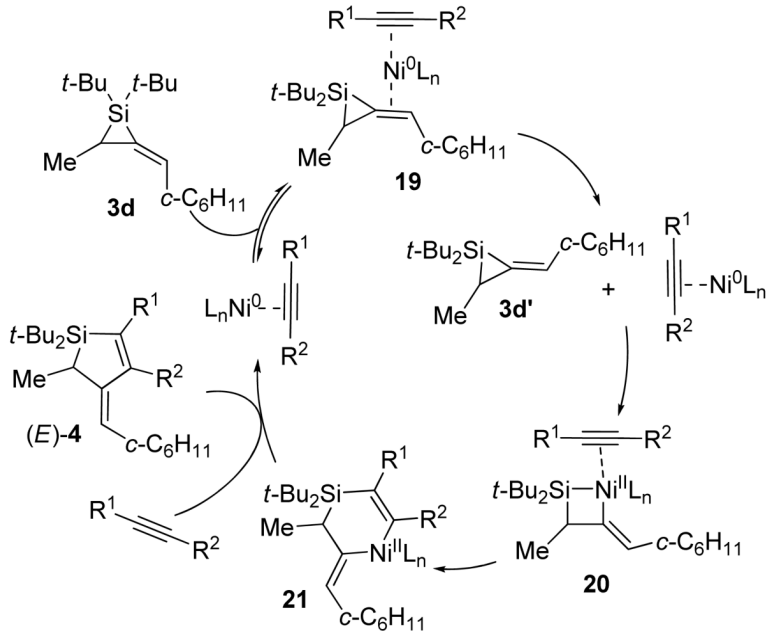
[a]Formed as an 82:18 mixture of regioisomers with **4m′** (R^1 = Me, R^2 = Ph). [b]Alkene migration occurred during purification to give silole **4n′** in 52% yield. Silacyclopentene **4n** could be obtained in 10% yield if purified in the presence of NEt_3.



Scheme 5.
Proposed Catalytic Cycle for the Pd(0)-Catalyzed Carbon–Carbon π-Bond Insertion Reaction with Terminal Alkynes

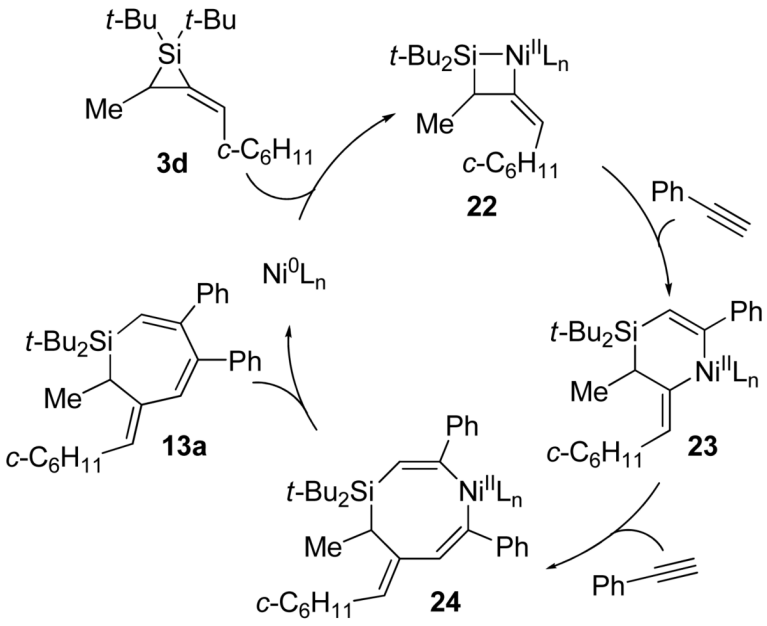


Scheme 6.
Proposed Catalytic Cycle for the Pd(0)-Catalyzed Carbon–Carbon π-Bond Insertion Reaction with Internal Alkynes



Scheme 7.

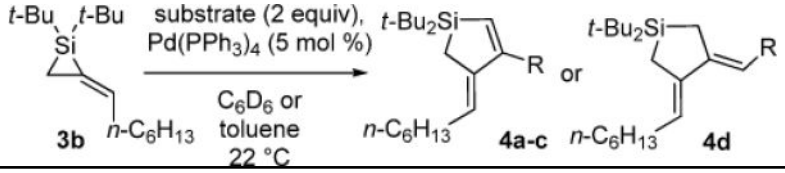
Proposed Catalytic Cycle for the Ni(0)-Catalyzed Carbon–Carbon Bond Insertion with **3d** and Internal Alkynes

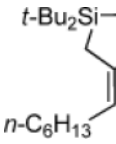
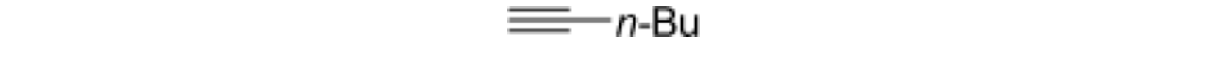
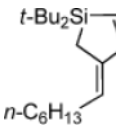
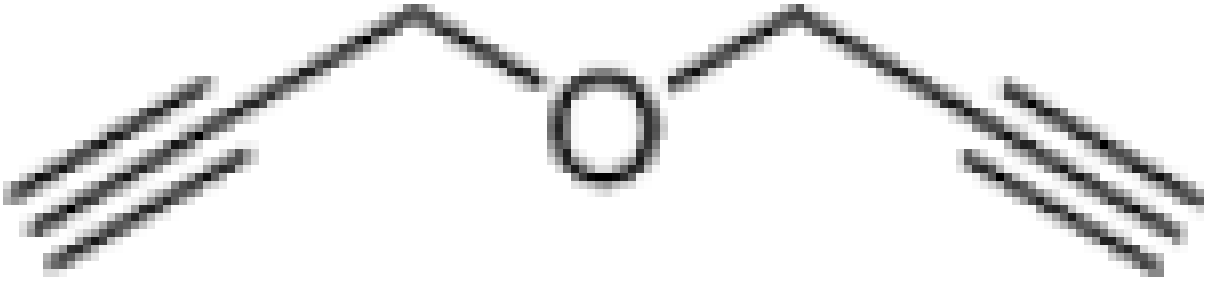
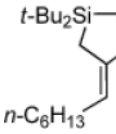
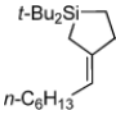


Scheme 8.
Proposed Catalytic Cycle for the Ni(0)-Catalyzed Carbon–Carbon Insertion Reaction with **3d** and Phenylacetylene

Table 1

Pd(0)-Catalyzed Carbon–Carbon Bond Insertion with **3b** to Yield Si–C(sp^2) Bond Cleavage Products



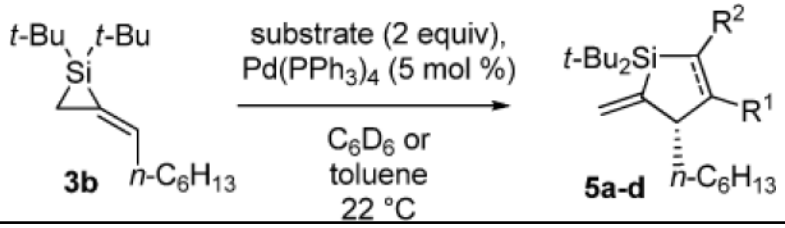
entry	substrate	product
1		
2		
3		
4		

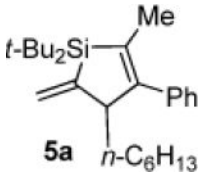
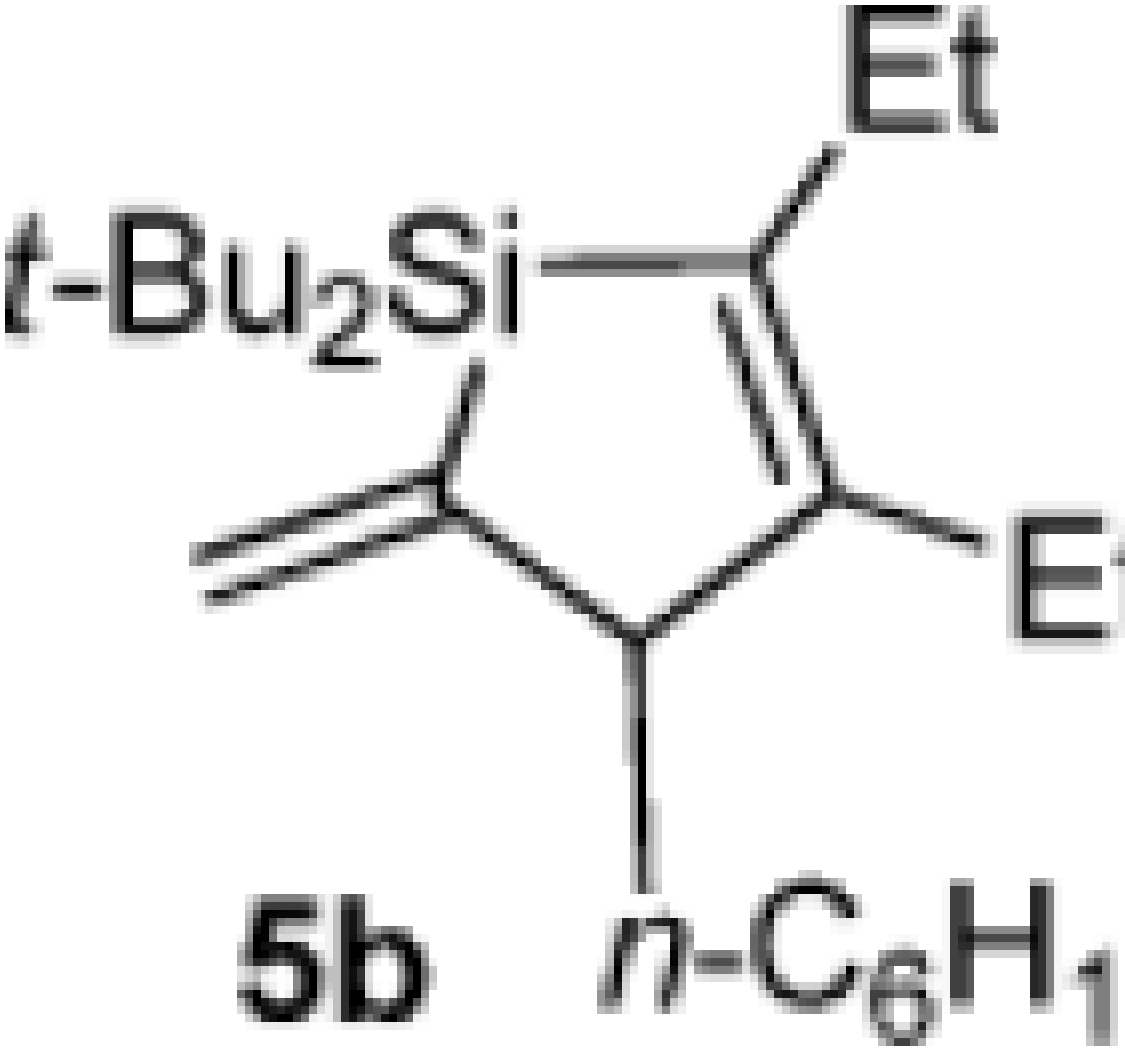
[a] As determined by ^{1}H NMR spectroscopic analysis relative to an internal standard ($PhSiMe_3$). Isolated yields are shown in parentheses.

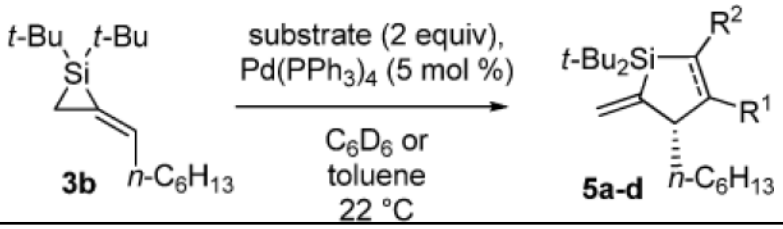
[b] Unstable towards isolation attempts.

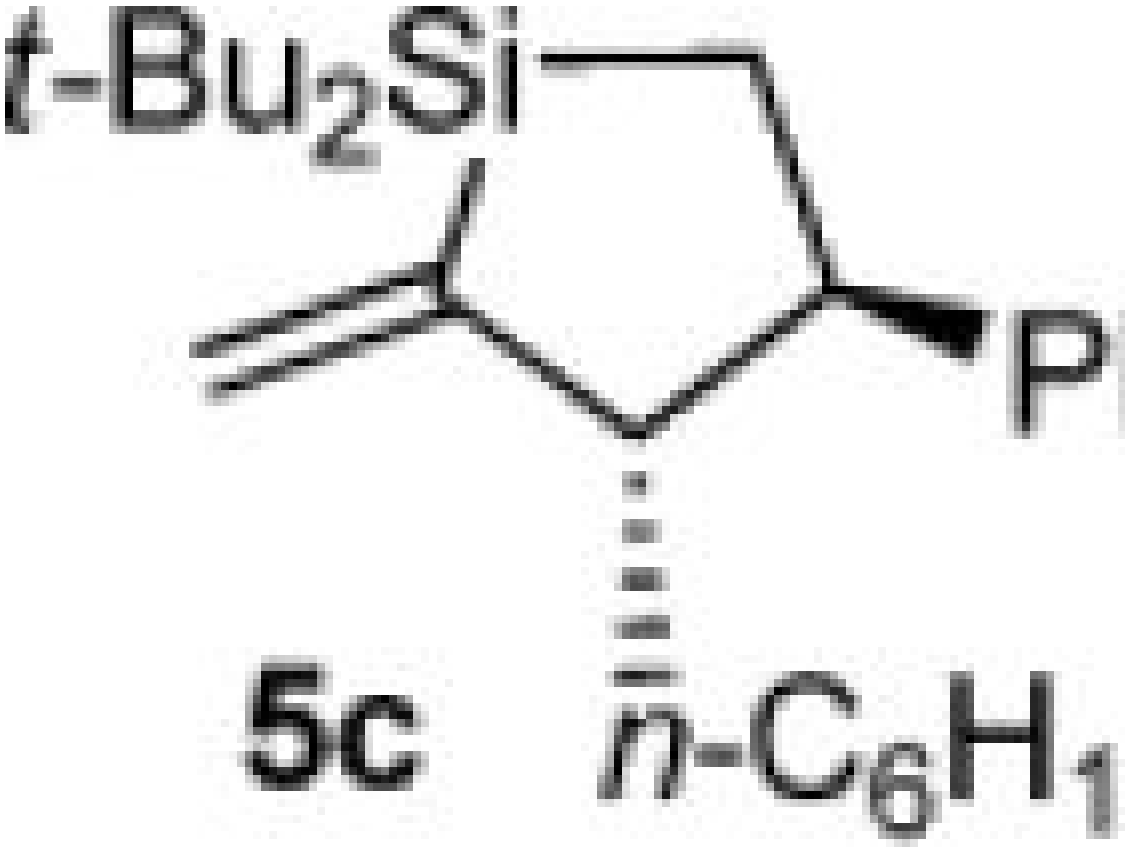
Table 2

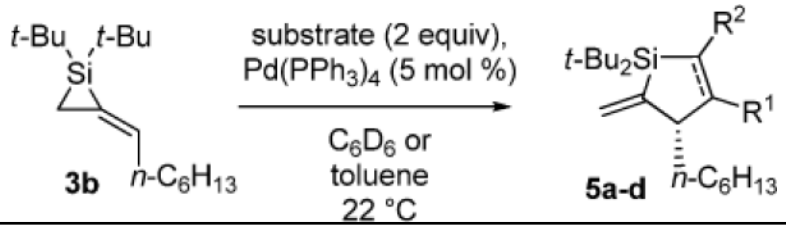
Pd(0)-Catalyzed Carbon–Carbon Bond Insertion with **3b** to Yield Allylic Transposition Products

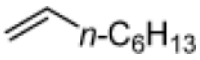
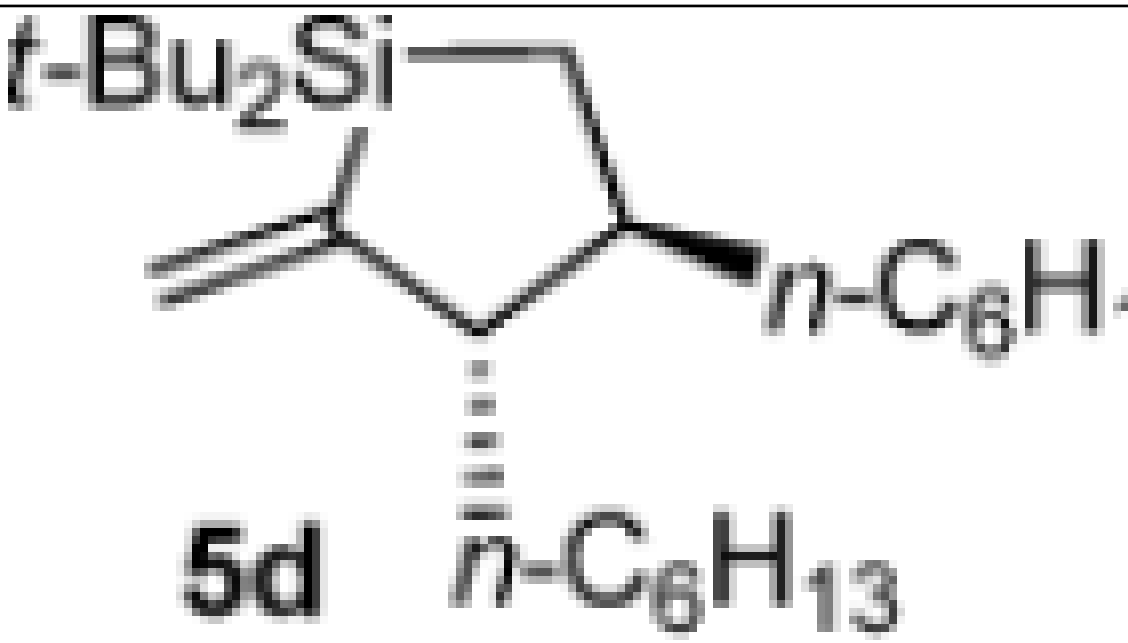


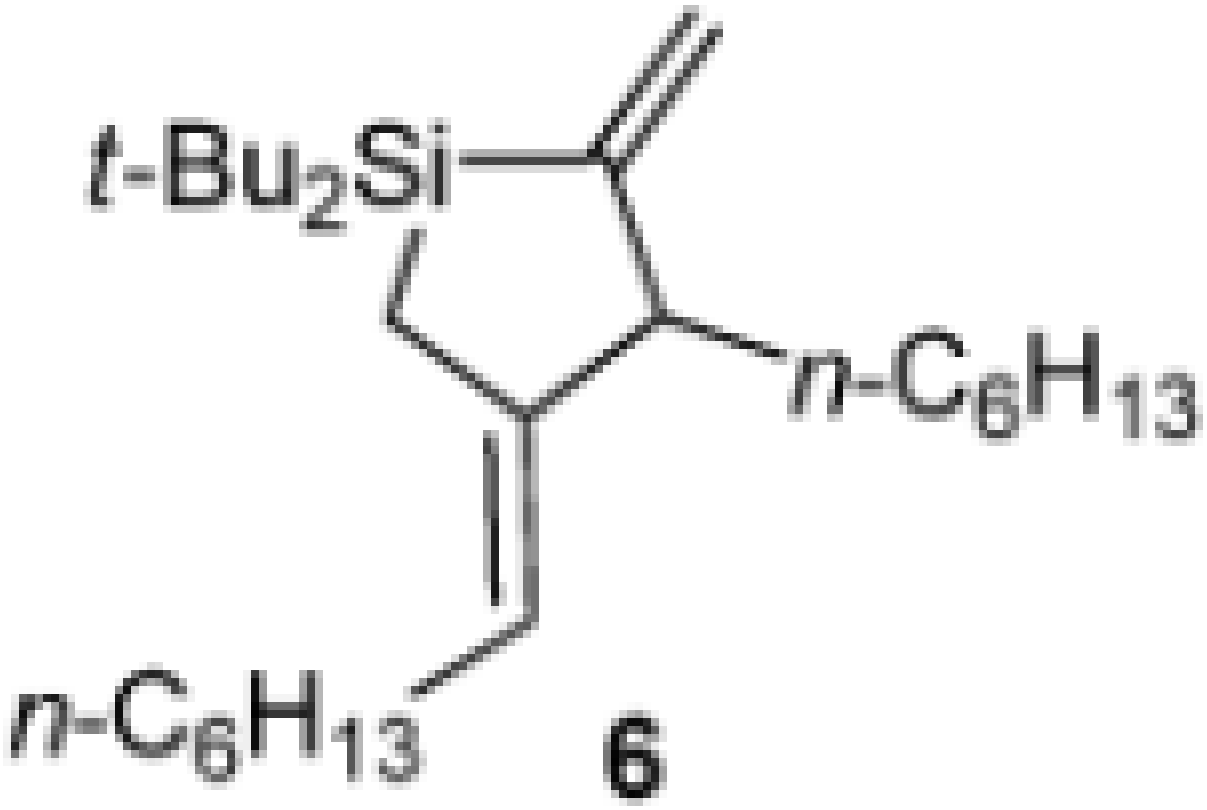
entry	substrate	product[a]
1	Me—≡—Ph	
2	Et—≡—Et	



entry	substrate	product[a]
3		



entry	substrate	product[a]
4		



6

[a]The stereo- and regiochemistry of the products were assigned by nOe analyses. Details are provided as Supporting Information.

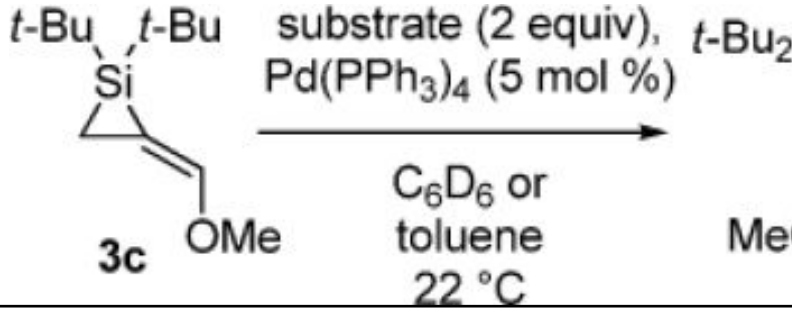
[b]As determined by ^{1}H NMR spectroscopic analysis relative to an internal standard ($PhSiMe_3$). Isolated yields are shown in parentheses.

[c]Formed as a minor product in a 29:71 mixture with silacyclopentane **6**.

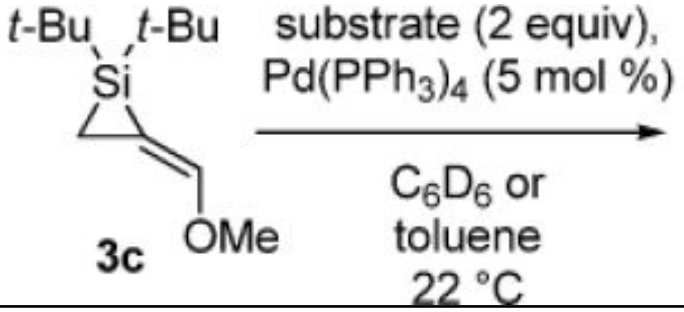
[d]Required heating at 70 °C to go to completion, and was formed as a 56:44 mixture with dimeric material derived from **3b**.

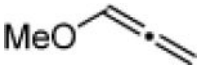
Table 3

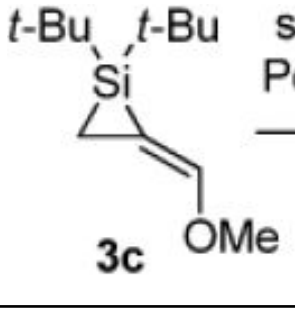
Pd(0)-Catalyzed Carbon–Carbon Bond Insertion with **3c** to Yield Si–C(sp^2) Bond Cleavage Products



entry	substrate
1	
2	



entry	substrate
3	

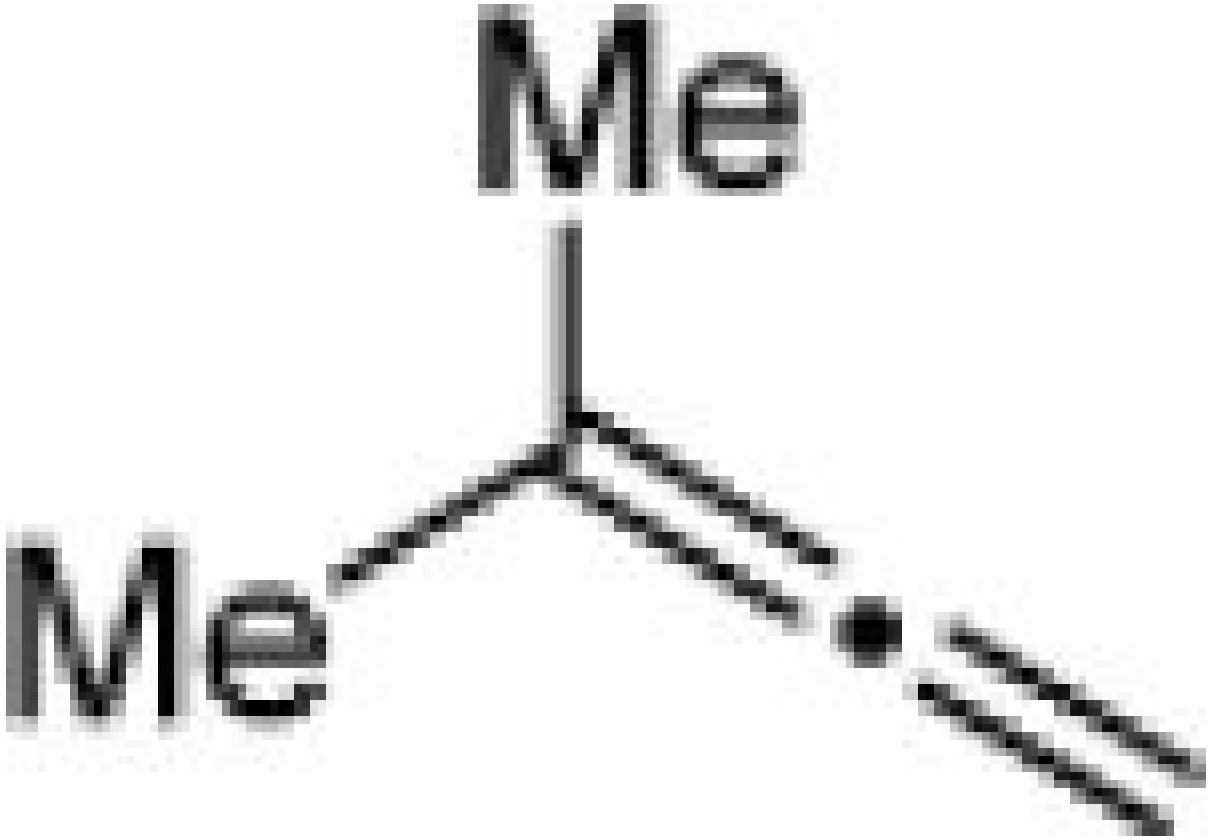


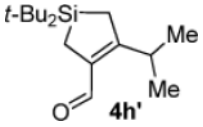
substrate (2 equiv), $Pd(PPh_3)_4$ (5 mol %)

C_6D_6 or toluene 22 °C

t-Bu_2

Me

entry	substrate
4	

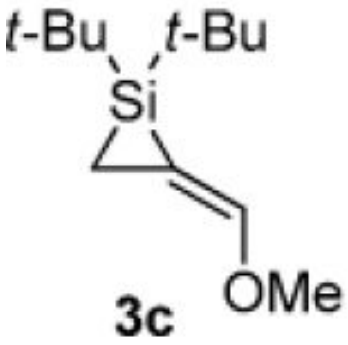


[a] As determined by ^{1}H NMR spectroscopic analysis relative to an internal standard ($PhSiMe_3$). Isolated yields are shown in parentheses.

[b] Hydrolysis gave (α,β-unsaturated aldehyde **4h′** when subjected to chromatography.

Table 4

Pd(0)-Catalyzed Carbon–Carbon Bond Insertion with **3c** to Yield Allylic Transposition Products

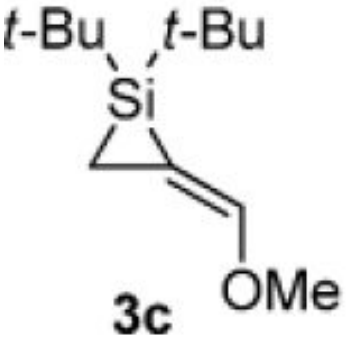


3c

substrate (2 equ
$Pd(PPh_3)_4$ (5 mo

C_6D_6 or
toluene
22 °C

entry	substrate
1	

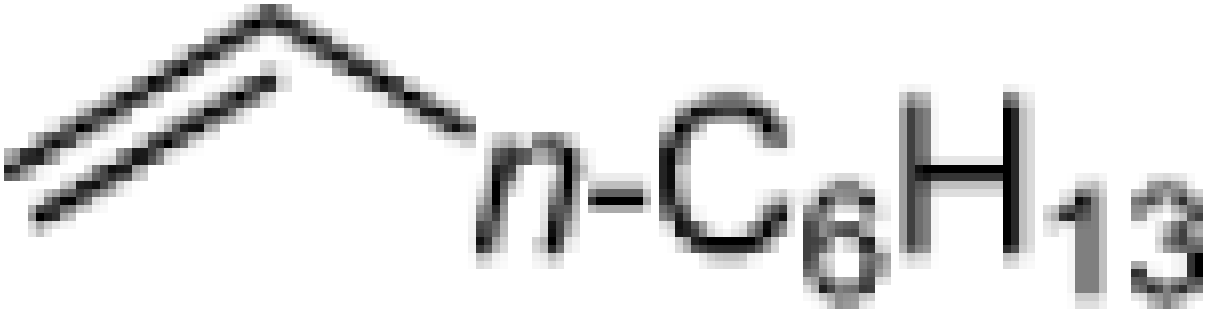


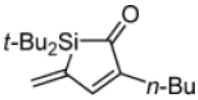
3c

substrate (2 equ

$Pd(PPh_3)_4$ (5 mo

C_6D_6 or
toluene
22 °C

entry	substrate
2	
3	
4	



5f'

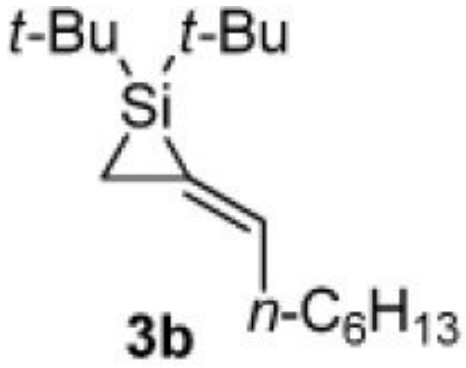
[a] As determined by ^{1}H NMR spectroscopic analysis relative to an internal standard ($PhSiMe_3$). Isolated yields are shown in parentheses.

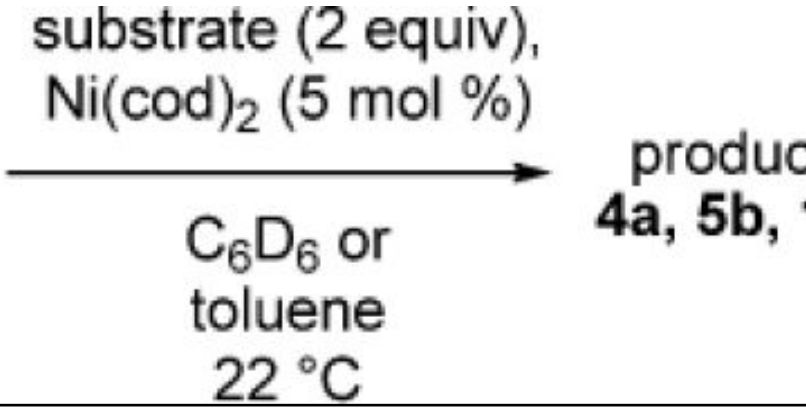
[b] Hydrolysis and elimination gave α,β,γ,δ-unsaturated acyl silane **5f′** upon attempted chromatography. Difficulties with purification prevented accurate determination of the isolated yield.

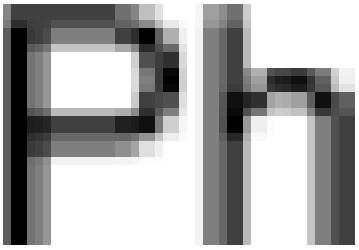
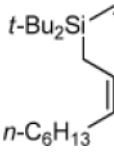
[c] Formed as a 68:32 mixture with dimeric material derived from **3c**.

Table 5

Ni(0)-Catalyzed Carbon–Carbon Bond Insertion with **3b**





entry	substrate	produ
1		 4a
2		5b
3		

[a] As determined by ^{1}H NMR spectroscopic analysis relative to an internal standard (PhSiMe3). Isolated yields are shown in parentheses.

[b] In the ^{1}H NMR spectra of the reaction mixture, diagnostic peaks corresponding to **14** overlapped with peaks from residual styrene, making accurate determination of the NMR yield difficult.