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Tetrahedron 62 (2006) 7560–7566
Tetrahedron

Alkyne hydrosilylation catalyzed by nickel complexes of *N*-heterocyclic carbenes

Mani Raj Chaulagain, Gireesh M. Mahandru and John Montgomery*

Department of Chemistry, University of Michigan, 930 N. University Ave. Ann Arbor, MI 48109-1055, USA

Received 7 December 2005; revised 1 March 2006; accepted 1 March 2006
Available online 19 June 2006

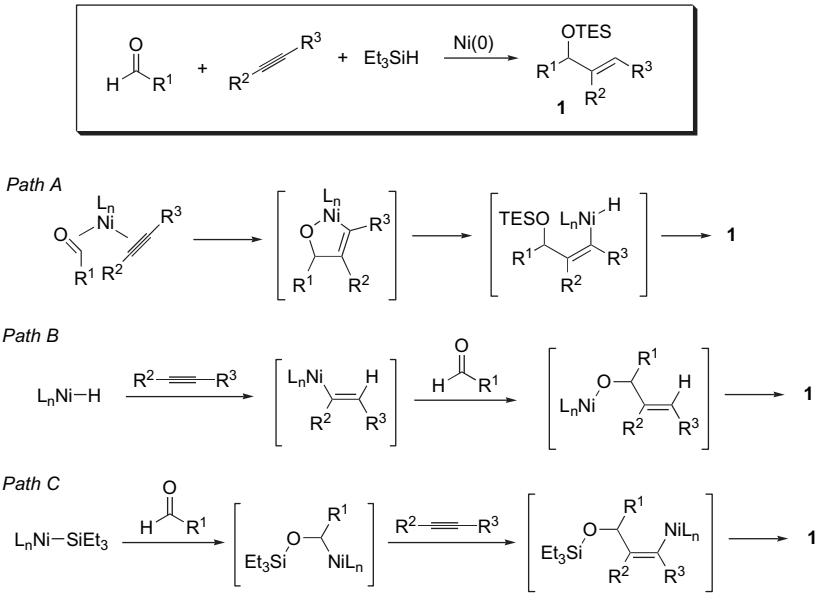
Dedicated to Professor Günther Wilke for his seminal contributions to the field of organonickel chemistry

Abstract—The addition of triethylsilane, triphenylsilane, and triethoxysilane to a variety of alkynes is catalyzed by complexes derived from $Ni(COD)_2$ and *N*-heterocyclic carbenes. A description of the reaction scope and potential mechanistic implications in nickel-catalyzed additions of aldehydes, alkynes, and silanes is provided.

1. Introduction

Vinyl silanes are useful building blocks for a variety of synthetic processes including electrophilic substitutions[1] and palladium-catalyzed cross-couplings.[2] While many methods for preparation of vinyl silanes exist, catalytic additions of silanes to alkynes are perhaps the most powerful.[3] In metal-catalyzed alkyne hydrosilylations, regioselectivity and stereoselectivity issues are both important to control. Regioselectivity is typically highly dependent upon structure of the catalyst, alkyne, and silane, and either cis- or trans-additions may be observed.

We have become interested in the nickel-catalyzed hydrosilylation of alkynes not only because of the synthetic interest in vinyl silanes, but also because we felt that understanding the addition chemistry of silanes and alkynes could potentially shed light on mechanistic issues in the three-component



Scheme 1.

* Corresponding author. Tel.: +1 734 764 4424; fax: +1 734 763 1106; e-mail: jmontg@umich.edu

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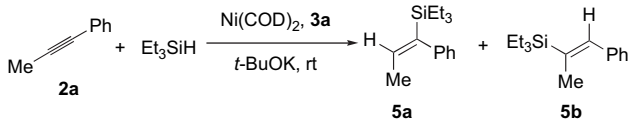
doi:10.1016/j.tet.2006.03.120

coupling of aldehydes, alkynes, and silanes to produce protected allylic alcohols **1** being developed in our laboratory.[4] Prior studies in our lab involving crossover experiments had demonstrated that the mechanism of aldehyde/alkyne/silane couplings catalyzed by nickel phosphine complexes proceeded by a different mechanism than the corresponding couplings involving nickel complexes of *N*-heterocyclic carbenes.[4c,5] The related system developed by Jamison involving triethylborane-mediated aldehyde/alkyne couplings poses similar questions, and evidence for a ligand-based mechanistic switch in alkene-directed couplings of 1,5-enynes was provided.[6] A multitude of mechanistic possibilities for these processes exist, including the formation of metallacycles from Ni(0), aldehydes, and alkynes (path A, Scheme 1), hydrometallation of alkynes followed by aldehyde insertion (path B), and silylmetallation of aldehydes followed by alkyne insertion (path C).[7] In path B, the trialkylsilyl may or may not be directly coordinated to nickel throughout the sequence shown. Similarly, in path C, a hydride may or may not be directly coordinated to nickel throughout the sequence shown. Variation in the active catalyst structure and oxidation state leads to several possibilities within each of these three pathways. Given these mechanistic complexities, we envisioned that understanding the reactivity patterns of simple alkyne hydrosilylations could be useful in further understanding the corresponding three-component couplings with aldehydes.

2. Results

The catalyst derived from $Ni(COD)_2$ and tributylphosphine is ineffective in promoting the hydrosilylation of either alkynes or aldehydes with triethylsilane under conditions that are effective in three-component couplings of alkynes, aldehydes, and triethylsilane.[8] This observation was an important feature that led us to propose the metallacycle-based mechanism in the first reports of the nickel-catalyzed reductive coupling of alkynes and aldehydes.[4a,e] The catalyst derived from $Ni(COD)_2$ and *N*-heterocyclic carbenes, however, are effective in alkyne hydrosilylations.[9] Direct treatment of 1-phenyl-1-propyne and triethylsilane in THF with the catalyst derived from $Ni(COD)_2$, *t*-butoxide, and imidazolium salt **3a** provided a 6:1 mixture of adducts derived from the 2:1 coupling of the alkyne and silane in 50% yield (Scheme 2).[10] The major isomer of the 2:1 coupling was determined to be structure **4**. In order to suppress incorporation of the second alkyne, the above experiment was repeated with syringe drive addition of the alkyne, and product **5**, derived from 1:1 coupling of the alkyne and silane, was obtained (Scheme 2). A brief study of solvent effects illustrated that toluene, ether, and *t*-butanol were also effective solvents although yields were highest in THF (Table 1). Only cis addition products were observed, and the regioisomer **5a** was the sole product except for one instance in which **5b** was observed in low yield.

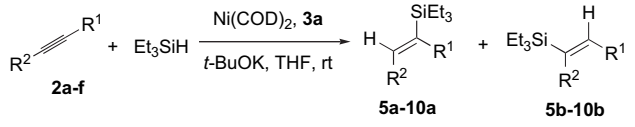
Table 1



Entry	Solvent	Combined yield (%)	**5a**:**5b** Ratio
1	THF	74	>95:5
2	Toluene	56	89:11
3	Ether	49	>95:5
4	*t*-BuOH	37	>95:5

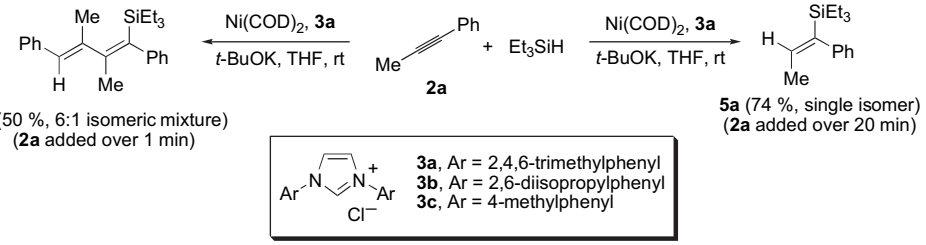
A short study of the range of alkynes tolerated was carried out (Table 2). Hydrosilylation of symmetrical internal alkynes **2b** and **2c** proceeded cleanly to afford products **6** and **7**, respectively, and unsymmetrical alkynes **2a** and **2d**–**2f** underwent efficient couplings with varying degrees of regioselection. As noted above, couplings of phenylpropyne **2a** were completely selective, whereas the regioselectivity with internal doubly aliphatic substituted alkynes **2d** and **2e** varied according to the steric difference in alkyne substituents. Interestingly, terminal alkyne **2f** was an effective participant, but with relatively poor regioselection. In all cases other than activated aromatic alkynes, the silicon unit was preferentially installed at the least hindered alkyne carbon.

Table 2



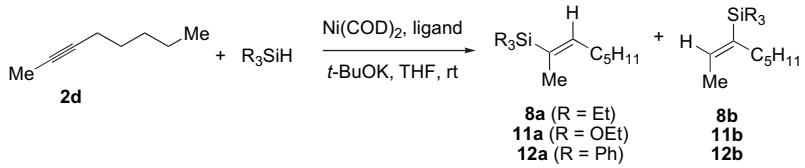
Alkyne	R^1	R^2	Product (% yield)	**a**:**b** Ratio
2a	Ph	Me	**5** (74)	>95:5
2b	*n*-Propyl	*n*-Propyl	**6** (87)	—
2c	Ph	Ph	**7** (92)	—
2d	Me	*n*-Pentyl	**8** (99)	75:25
2e	Me	*t*-Bu	**9** (74)	>95:5
2f	H	*n*-Hexyl	**10** (80)	67:33

Considering the poor regioselection with alkyne **2d**, we examined the impact of varying ligand and silane structures with this alkyne (Table 3). Whereas 3:1 selectivity was noted



Scheme 2.

Table 3



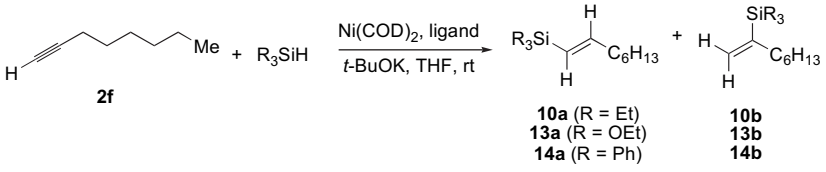
Entry	Ligand	R_3SiH	Product (% yield)	**a**:**b** Ratio
1	**3a**	Et_3SiH	**8** (99)	75:25
2	**3b**	Et_3SiH	**8** (99)	90:10
3	**3c**	Et_3SiH	**8** (75)	67:33
4	**3a**	$(EtO)_3SiH$	**11** (71)	60:40
5	**3a**	Ph_3SiH	**12** (53)	76:24

with **3a**, reactions with more hindered ligand derived from **3b** proceeded in near quantitative yield with very good regioselection (Table 3, entry 2). With smaller *p*-tolyl carbene derived from **3c**, regioselectivity worsened to 2:1 in diminishing yield (Table 3, entry 3). In varying the silane structure, we found with alkyne **2d** that the regioselectivity was only minimally impacted. Triethylsilane and triphenylsilane afforded nearly identical regioselectivities with the carbene derived from **3a**, whereas triethoxysilane participated with lower regioselectivity and yield (Table 3, entries 4–5). Thus, with internal alkynes possessing aliphatic substituents, ligand structure provides the best strategy for controlling regioselection.

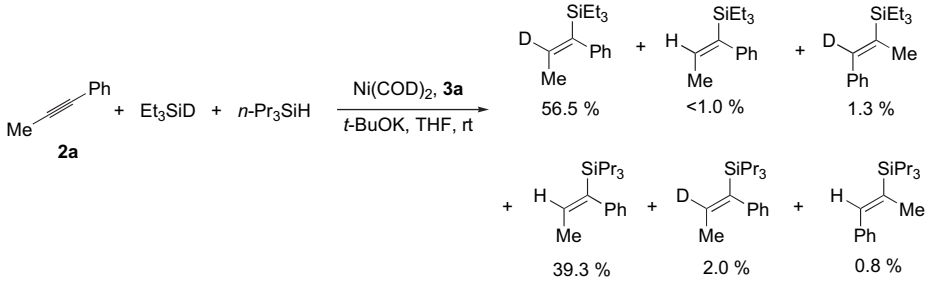
With terminal alkyne **2f**, however, silane structure displayed an enormous impact (Table 4). Whereas reactions with the ligand derived from **3a** afforded a 2:1 ratio of products **10a/10b** with triethylsilane, the corresponding reaction with triphenylsilane afforded the terminal silane **14a** with 7:1 regioselection. In contrast, the coupling of alkyne **2f**, triethoxysilane, and the ligand derived from **3a** favored the internal silane isomer **13b** in 3:1 regioselection. Coupling of **2f** and triphenylsilane with the ligand derived from **3b** afforded improved regioselectivity (relative to reactions with **3a**) in favor of **14a**, whereas the coupling of **2f** and triethoxysilane with the ligand derived from **3b** provided the reversed regioselectivity (relative to reactions with **3a**) in favor of **13a**. Surprisingly, the ligand from **3b** was not effective in couplings of **2f** and triethylsilane. Thus, variation of the silane structure provides a good handle for controlling regioselection in hydrosilylations of terminal alkynes, but the impact of ligand variation is highly substrate dependent.

Given the utility of a crossover study in illustrating the mechanistic differences between phosphine and *N*-heterocyclic catalyst systems in three-component alkyne, aldehyde, and silane additions,[4c] we examined the crossover reaction of 1-phenyl-1-propyne **2a** with 3.0 equiv each of Et_3SiD and Pr_3SiH in the presence of the catalyst derived from **3a** (Scheme 3). In this experiment, only a small amount

Table 4



Entry	Ligand	R_3SiH	Product (% yield)	**a**:**b** Ratio
1	**3a**	Et_3SiH	**10** (80)	67:33
2	**3a**	Ph_3SiH	**14** (76)	89:11
3	**3a**	$(EtO)_3SiH$	**13** (72)	25:75
4	**3b**	Ph_3SiH	**14** (63)	>95:5
5	**3b**	$(EtO)_3SiH$	**13** (70)	83:17

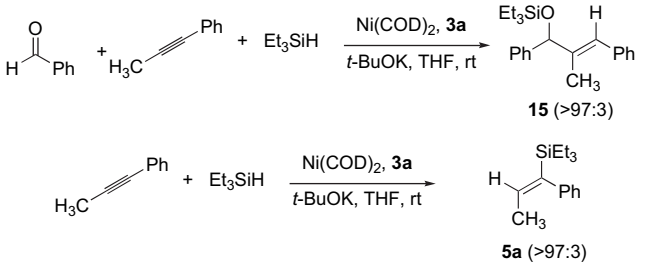


Scheme 3.

(<2%) of crossover products were observed, illustrating that the R_3Si and H units in the product are largely derived from a single molecule of trialkylsilane. Control experiments illustrated that Et_3SiD and Pr_3SiH underwent addition at similar rates.

3. Discussion

Several points from the above study are potentially relevant in analyzing the mechanism of three-component nickel-catalyzed couplings of aldehydes, alkynes, and silanes. In particular, the regioselection of phenylpropyne, benzaldehyde, and triethylsilane with Ni(0)/IMes ligand from **3a** is very clean for the production of isomer **15** (Scheme 4). In contrast, the identical reaction carried out in the absence of benzaldehyde cleanly affords compound **5a**. Notably, the position of introduction of the silane-derived hydrogen atom is reversed in these two reactions. This suggests that hydrometallation of the alkyne (path B, Scheme 1) is not a common first step in both reactions unless coordination of the aldehyde has a dramatic and an unexpected effect on the regioselection.



Scheme 4.

Additionally, since crossover was not observed to an appreciable extent in either the two component couplings of alkynes and silanes or the three-component couplings of alkynes, silanes, and aldehydes, then both reactions involve mechanisms in which the silicon and hydrogen atoms of the Si–H bond are simultaneously delivered to a metal complex.

4. Conclusions

In summary, an efficient method for the hydrosilylation of alkynes involving Ni(0) complexes of *N*-heterocyclic carbenes has been developed. The scope of both alkynes and silanes tolerated is broad, and regioselectivities often depend on the structure of the alkyne, silane, and *N*-heterocyclic carbene ligand. The impact of these variables on the regioselectivity in alkyne hydrosilylations was compared to the regioselectivity of three-component couplings of alkynes, aldehydes, and silanes, and the comparison suggests that alkyne hydrometallation is not a common first step in both groups of reactions.

5. Experimental

5.1. General

All reagents were used as received unless otherwise noted. All alkynes were freshly distilled prior to use. $Ni(COD)_2$, imidazolium salts, and potassium *tert*-butoxide were stored and weighed in an inert atmosphere glove box. All reactions were conducted in flame-dried glassware under argon or nitrogen.

5.2. General procedure for $Ni(COD)_2$/carbene catalyzed hydrosilylation of alkynes

$Ni(COD)_2$ (28 mg, 0.10 mmol), ligand (0.10 mmol), and potassium *tert*-butoxide (11 mg, 0.10 mmol) were weighed together in a 15-mL flask in a glove box. Solvent (8 mL) was added to the mixture under an inert atmosphere at rt. The solution was stirred for 10 min and silane (2.0 mmol) was added dropwise to the stirring mixture and allowed to stir for 10 min. Alkyne (1.00 mmol) was dissolved in 2 mL solvent under nitrogen and was added to the mixture over 20 min via syringe drive. Reactions were usually complete after the addition of alkyne was complete. Solvents were removed in vacuo and the crude product was purified by column chromatography (SiO_2, hexanes, unless otherwise noted) and the vinyl silanes were isolated as colorless oils unless otherwise noted.

5.2.1. ((1*Z*,3*E*)-2,3-Dimethyl-1,4-diphenylbuta-1,3-dienyl)triethylsilane (4). Following the general procedure (except that alkyne was added over 1 min), $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethylsilane (0.32 mL, 2.0 mmol), and 1-phenylpropyne (116 mg, 1.00 mmol) were employed to give 6:1 mixture of regioisomers of **4** (176 mg, 0.50 mmol, 50%), after column chromatography (SiO_2, hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15–7.42 (m, 8H), 6.97–7.10 (m, 2H), 6.54 (q, J=1.2 Hz, 0.14H, minor regioisomer), 6.44 (m, 0.86H, major regioisomer), 2.06 (d, J=1.6 Hz, 2.59H, major regioisomer), 1.77 (d, J=1.2 Hz, 0.41H, minor regioisomer), 1.71 (s, 0.42H, minor regioisomer), 1.65 (s, 2.58H, major regioisomer), 0.99 (t, J=8.0 Hz, 1.26H, minor regioisomer), 0.89 (t, J=8.0 Hz, 7.74H, major regioisomer), 0.73 (q, J=8.0 Hz, 0.84H, minor regioisomer), 0.51 (q, J=8.0 Hz, 5.16H, major regioisomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 145.3, 142.2, 137.8, 136.2, 129.2, 129.0, 128.47, 128.9, 128.3, 128.2, 128.1, 127.9, 126.3, 126.0, 124.8, 21.0, 20.7, 18.1, 17.5, 7.9, 7.8, 4.6, 4.3; HRMS (EI) *m/z* calculated for $C_{24}H_{32}Si$ 348.2273, found 348.2267 (M^+).

Compound **4** was converted into the previously reported compound ((1*E*,3*E*)-2,3-dimethylbuta-1,3-diene-1,4-diyl)-dibenzene by stirring with $(n\text{-}Bu)_4NF$ for 24 h at rt. Spectroscopic data were identical to that previously reported.[11]

5.2.2. (*E*)-Triethyl(1-phenylprop-1-enyl)silane (5). Following the general procedure, $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethylsilane (0.32 mL, 2.0 mmol), and 1-phenyl-1-propyne (116 mg, 1.00 mmol) were employed to give (*E*)-triethyl(1-phenylprop-1-enyl)silane (171 mg, 0.74 mmol, 74%, single regioisomer), after column chromatography (SiO_2, hexanes) as a colorless oil. Spectroscopic data were identical to that previously reported.[12]

5.2.3. (*E*)-Triethyl(oct-4-en-4-yl)silane (6). Following the general procedure, $Ni(COD)_2$ (28 mg, 0.10 mmol),

imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethylsilane (0.32 mL, 2.0 mmol), and oct-4-yne (110 mg, 1.00 mmol) were employed to give (*E*)-triethyl(oct-4-en-4-yl)silane (197 mg, 0.87 mmol, 87%), after column chromatography (SiO_2, hexanes) as a colorless oil. Spectroscopic data were identical to that previously reported.[13]

5.2.4. (*E*)-(1,2-Diphenylvinyl)triethylsilane (7). Following the general procedure, $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethylsilane (0.32 mL, 2.0 mmol), and 1,2-diphenylethyne (178 mg, 1.00 mmol) were employed to give (*E*)-(1,2-diphenylvinyl)triethylsilane (269 mg, 0.92 mmol, 92%), after column chromatography (SiO_2, hexanes) as a colorless solid. Spectroscopic data were identical to that previously reported.[12]

5.2.5. (*E*)-Triethyl(oct-2-en-2-yl)silane (8a) and (*E*)-triethyl(oct-2-en-3-yl)silane (8b) with 3a. Following the general procedure, $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethylsilane (0.32 mL, 2.0 mmol), and oct-2-yne (110 mg, 1.00 mmol) were employed to give a mixture of (*E*)-triethyl(oct-2-en-2-yl)silane and (*E*)-triethyl(oct-2-en-3-yl)silane (225 mg, 0.99 mmol, 99%, 3:1 mixture of regioisomer), after column chromatography (SiO_2, hexanes) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 5.82 (q, J=6.5 Hz, 0.25H, minor isomer), 5.71 (tq, J=6.5, 1.5 Hz, 0.75H, major regioisomer), 2.07–2.15 (m, 2H), 1.71 (d, J=6.5 Hz, 0.75H, minor regioisomer), 1.66 (m, 2.25H), 1.26–1.43 (m, 6H), 0.89–0.93 (m, 12H), 0.47–0.62 (m, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 141.4, 139.0, 135.5, 132.6, 32.5, 31.8, 29.8, 29.6, 29.2, 28.5, 22.8, 15.1, 14.3, 14.2, 7.6, 6.9, 6.6, 3.3, 2.8; IR (film, cm^{-1}) 2972, 2910, 2860, 1434, 1425, 1332, 1254, 1064, 965, 912, 697, 617; HRMS (EI) *m*/*z* calculated for $C_{14}H_{30}Si$ 226.2116, found 226.2113(M^+).

5.2.6. (*E*)-Triethyl(oct-2-en-2-yl)silane (8a) and (*E*)-triethyl(oct-2-en-3-yl)silane (8b) with 3b. Following the general procedure, $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3b** (43 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethylsilane (0.32 mL, 2.0 mmol), and oct-2-yne (110 mg, 1.00 mmol) were employed to give a mixture of (*E*)-triethyl(oct-2-en-2-yl)silane and (*E*)-triethyl(oct-2-en-3-yl)silane (225 mg, 0.99 mmol, 99%, 9:1 mixture of regioisomer), after column chromatography (SiO_2, hexanes) as a colorless oil.

5.2.7. (*E*)-(4,4-Dimethylpent-2-en-2-yl)triethyl silane (9a). Following the general procedure, $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethylsilane (0.32 mL, 2.0 mmol), and 4,4-dimethylpent-2-yne (96 mg, 1.00 mmol) were employed to give (*E*)-(4,4-dimethylpent-2-en-2-yl)-triethyl silane (157 mg, 0.74 mmol, 74%, single regioisomer), after column chromatography (SiO_2, hexanes) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 5.58 (q, J=1.6 Hz, 1H), 1.74 (d, J=1.6 Hz, 3H), 1.09 (s, 9H), 0.87 (t, J=8.0 Hz, 9H), 0.51 (q, J=8.0 Hz, 6H); ^{13}C (125 MHz, $CDCl_3$) δ 150.1, 131.2, 34.4, 30.7, 15.7, 7.3, 2.5; IR (film, cm^{-1}) 2954, 2910, 2875, 1463, 1362, 1074, 1007, 729; HRMS (EI) *m*/*z* calculated for $C_{13}H_{28}Si$ 212.1954, found 212.1968(M^+).

5.2.8. (*E*)-Triethyl(oct-1-enyl)silane (10a) and triethyl-(oct-1-en-2-yl)silane (10b). Following the general procedure, $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethylsilane (0.32 mL, 2.0 mmol), and oct-1-yne (110 mg, 1.00 mmol) were employed to give a mixture of (*E*)-triethyl(oct-1-enyl)silane and triethyl(oct-1-en-2-yl)silane (181 mg, 0.80 mmol, 80%, 2:1 mixture of regioisomers), after column chromatography (SiO_2, hexanes) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 6.00 (dt, J=18.4, 6.4 Hz, 0.66H, major isomer), 5.58–5.61 (m, 0.34H, minor isomer), 5.50 (dt, J=18.4, 1.6 Hz, 0.66H, major isomer), 5.25 (dt, J=2.7, 0.8 Hz, 0.34H, minor isomer), 2.02–2.12 (m, 2H), 1.22–1.40 (m, 8H), 0.82–0.94 (m, 12H), 0.48–0.60 (m, 6H). Data for **10a** matches those previously reported.[14]

5.2.9. (*E*)-Triethoxy(oct-2-en-2-yl)silane (11a) and (*E*)-triethoxy(oct-2-en-3-yl)silane (11b). Following the general procedure, $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethoxysilane (0.37 mL, 2.0 mmol), and oct-1-yne (110 mg, 1.00 mmol) were employed to give a 1.5:1 mixture of (*E*)-triethoxy(oct-2-en-3-yl)silane and (*E*)-triethoxy(oct-2-en-2-yl)silane, after column chromatography (SiO_2, hexanes) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 6.15 (qt, J=6.4, 0.8 Hz, 0.4H, minor regioisomer), 6.06 (tq, J=6.8, 1.6 Hz, 0.6H, major regioisomer), 3.72–3.80 (m, 6H), 2.03–2.11 (m, 2H), 1.63–1.67 (m, 3H), 1.22–1.38 (m, 6H), 1.13–2.0 (m, 9H), 0.81–0.86 (m, 3H); ^{13}C (125 MHz, $CDCl_3$) δ 146.0, 139.6, 134.0, 126.9, 58.3, 58.2, 32.0, 31.5, 29.0, 28.6, 28.5, 28.2, 22.4, 18.1, 14.1, 14.0, 13.9; IR (film, cm^{-1}) 2973, 2927, 1620, 1442, 1389, 1167, 1104, 1081, 957, 779; HRMS (EI) *m*/*z* calculated for $C_{14}H_{30}O_3Si$ 274.1964, found 274.1759(M^+).

5.2.10. (*E*)-Oct-2-en-2-yltriphenylsilane (12a) and (*E*)-oct-2-en-3-yltriphenylsilane (12b). Following the general procedure (with the modification in silane stoichiometry), $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triphenylsilane (260 mg, 1.0 mmol in 2 mL THF), and oct-2-yne (110 mg, 1.00 mmol) were employed to give a 3.2:1 mixture of regioisomers (*E*)-oct-2-en-2-yltriphenylsilane and (*E*)-oct-2-en-3-yltriphenylsilane (196 mg, 0.53 mmol, 53%), after column chromatography (SiO_2, hexanes) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.58 (m, 6H), 7.32–7.42 (m, 9H), 6.05 (q, J=6.4 Hz, 0.24H, minor regioisomer), 5.94 (tq, J=6.8, 1.6 Hz, 0.76H, major regioisomer), 2.16–2.25 (m, 2H), 1.81–1.84 (m, 0.24H, minor regioisomer), 1.79 (d, J=6.4 Hz, 0.76H, major regioisomer), 1.24–1.42 (m, 4H), 1.05–1.11 (m, 2H), 0.88 (t, J=6.8 Hz, 2.27H, major regioisomer), 0.72 (t, J=6.8 Hz, 0.73H, minor regioisomer); ^{13}C (125 MHz, $CDCl_3$) δ 147.3, 141.0, 136.3, 136.2, 134.9, 134.5, 129.9, 129.5, 129.2, 127.7, 127.6, 32.0, 31.6, 29.9, 29.1, 28.8, 28.7, 22.5, 16.1, 14.8, 14.1, 13.9; IR (film, cm^{-1}) 3068, 2955, 2927, 2856, 1613, 1428, 1188, 1108, 741, 512; HRMS (EI) *m*/*z* calculated for $C_{26}H_{30}Si$ 370.2116, found 370.2120(M^+).

5.2.11. (*E*)-Triethoxy(oct-1-enyl)silane (13a) and triethoxy(oct-1-en-2-yl)silane (13b) with 3a. Following the general procedure, $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethoxysilane (0.37 mL, 2.0 mmol), and oct-1-yne (110 mg, 1.00 mmol) were employed to give a 3:1 mixture of regioisomers triethoxy(oct-1-en-2-yl)silane and (*E*)-triethoxy(oct-1-enyl)silane (196 mg, 0.72 mmol, 72%), after column chromatography (SiO_2, ethyl acetate/hexanes, 1:19) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 6.38 (dt, J=18.8, 6.4 Hz, 0.25H, minor regioisomer), 5.65–5.68 (m, 0.75H, major regioisomer), 5.56–5.59 (m, 0.75H, major regioisomer), 5.36 (dt, J=18.8, 1.6 Hz, minor regioisomer), 3.77 (q, J=7.2 Hz, 6H), 2.06–2.12 (m, 2H), 1.32–1.44 (m, 2H), 1.21–1.27 (m, 6H), 1.18 (t, J=7.2 Hz, 9H), 0.80–0.86 (m, 3H); ^{13}C (125 MHz, $CDCl_3$) δ 154.0, 143.7, 128.9, 118.6, 58.3, 36.5, 35.9, 31.7, 31.6, 29.0, 28.7, 28.6, 28.1, 22.6, 22.5, 18.2, 18.1, 14.0, 13.9; IR (film, cm^{-1}) 2925.8, 1389.5, 1074.7, 956.2, 734.4; HRMS (EI) *m*/*z* calculated for $C_{14}H_{30}O_3Si$ 274.1964, found 274.1963(M^+).

5.2.12. (*E*)-Triethoxy(oct-1-enyl)silane (13a) and triethoxy(oct-1-en-2-yl)silane (13b) with 3b. Following the general procedure, $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3b** (43 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triethoxysilane (0.37 mL, 2.0 mmol), and oct-1-yne (110 mg, 1.00 mmol) were employed to give a 1:5 mixture of regioisomers triethoxy(oct-1-en-2-yl)silane and (*E*)-triethoxy(oct-1-enyl)silane (192 mg, 0.70 mmol, 70%, single regioisomer), after column chromatography (SiO_2, ethyl acetate/hexanes, 1:19) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 6.37 (dt, J=18.8, 6.4 Hz, 0.83H, major regioisomer), 5.64–5.67 (m, 0.17H, minor regioisomer), 5.55–5.58 (m, 0.17H, minor regioisomer), 5.35 (dt, J=18.8, 1.6 Hz, 0.83H, major regioisomer), 3.77 (m, 6H), 2.06–2.13 (m, 2H), 1.30–1.40 (m, 2H), 1.12–1.28 (m, 15H), 0.80–0.86 (m, 3H); ^{13}C (125 MHz, $CDCl_3$) δ 154.0, 143.7, 118.6, 59.0, 58.3, 36.5, 31.7, 31.6, 28.7, 28.1, 22.6, 22.5, 18.2, 18.1, 14.0, 13.9; IR (film, cm^{-1}) 2925.8, 1389.5, 1074.7, 956.2, 734.4; HRMS (EI) *m*/*z* calculated for $C_{14}H_{30}O_3Si$ 274.1964, found 274.1963(M^+).

5.2.13. (*E*)-Oct-1-enyltriphenylsilane (14a) and oct-1-en-2-yltriphenylsilane (14b). Following the general procedure (with the modification in silane stoichiometry), $Ni(COD)_2$ (28 mg, 0.10 mmol), imidazolium salt, **3a** (34 mg, 0.10 mmol), *t*-BuOK (11 mg, 0.10 mmol), triphenylsilane (260 mg, 1.0 mmol in 2 mL THF), and oct-1-yne (110 mg, 1.00 mmol) were employed to give a 8:1 mixture of regioisomers (*E*)-oct-1-enyltriphenylsilane and oct-1-en-2-yltriphenylsilane (280 mg, 0.74 mmol, 74%), after column chromatography (SiO_2, hexanes) as a colorless solid (mp 53–55 °C). ^1H NMR (400 MHz, C_6D_6) δ 7.58–7.66 (m, 6H), 7.10–7.14 (m, 9H), 6.25 (dt, J=18.4, 5.6 Hz, 0.89H, major isomer), 6.19 (d, J=18.8 Hz, 0.89H, major isomer), 5.93–5.96 (m, 0.11H, minor isomer), 5.64–5.66 (d, J=2.8 Hz, 0.11H, minor isomer), 2.26 (t, J=7.8 Hz, 0.22H, minor regioisomer), 2.00–2.08 (m, 1.78H, major regioisomer), 1.20–1.34 (m, 8H), 0.72–0.84 (m, 3H); ^{13}C (125 MHz, C_6D_6) δ 153.7, 136.3, 136.0, 135.1, 129.3, 127.8, 123.6, 36.9, 31.5, 28.8, 28.4, 22.5, 13.8; IR (film, cm^{-1}) 3068, 2926, 2855, 1615, 1465, 1428, 1187, 1110, 998, 784, 737; HRMS (EI) *m*/*z* calculated for $C_{26}H_{30}Si$ 370.2117, found 370.2103(M^+).

5.3. Crossover reaction

$Ni(COD)_2$ (3 mg, 0.01 mmol), ligand, **3a** (4 mg, 0.01 mmol), and *t*-BuOK (1 mg, 0.01 mmol) were weighed in glove box and 1.5 mL THF was added to the mixture under argon. The dark green solution obtained was stirred for 10 min at rt. Triethylsilane-*d* (48 μL, 0.30 mmol) and tripropylsilane (56 μL, 0.30 mmol) were added simultaneously and stirred for 10 more minutes. Alkyne (12 mg, 0.10 mmol) was dissolved in 0.5 mL THF under argon and was added to the reaction mixture over 20 min via syringe drive. The progress of the reaction was monitored in 10 and 20 min in GCMS.

5.3.1. Analysis of the crossover experiment. Pure samples of products derived from Et_3SiH (MW 232), Et_3SiD (MW 233), and Pr_3SiH (MW 274) were independently prepared and GCMS analysis was performed. Based on the similarity of the molecular ion regions of the Et_3SiH and Et_3SiD-derived product, the molecular ion region of the Pr_3SiD-derived product was assumed to appear as the molecular ion region of the Pr_3SiH-derived product, shifted by one mass unit. Relative peak heights in the molecular ion region of the spectra of each pure compound were normalized, with a value of 1 assigned to the base peak.

In the crude product of an experiment that employed 1 equiv each of Et_3SiD and Pr_3SiH, the ratio of Et_3Si products to Pr_3Si products was determined by GC. From the crude GCMS, the relative intensity of the 232 and 233 products were normalized, with the value of 1 assigned to the base peak. The ratio of the Et_3Si-(H) product to Et_3Si-(D) product was determined as follows:

$$\frac{\text{intensity of 232 peak in crossover experiment}}{\text{intensity of 233 peak in crossover experiment}} = \frac{[X]\times[\text{rel height of 232 peak in pure } Et_3Si\text{-(H) product}] + [Y]\times[\text{rel height of 232 peak in pure } Et_3Si\text{-(D) product}]}{[X]\times[\text{rel height of 233 peak in pure } Et_3Si\text{-(H) product}] + [Y]\times[\text{rel height of 233 peak in pure } Et_3Si\text{-(D) product}]}$$

$X = 1/100\times$relative % of Et_3Si-(H) product

$Y = 1/100\times$relative % of Et_3Si-(D) product $= 1-X$

In the above equation, after substitution of $[1-X]$ for $[Y]$, the experimental values were inserted and the equation was solved for $[X]$. The ratio of Pr_3Si-(H) product to the

Pr_3Si-(D) products was determined in a similar fashion. Merging the GC ratios of Et_3Si products to Pr_3Si products with the data calculated from the above equation, an overall ratio of the six products were obtained.

Acknowledgements

We thank the National Institutes of Health (GM57014) for support of this research. Beth Knapp-Reed and Kanicha Sa-ei are thanked for helpful discussions.

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