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Selective hydrosilylation of alkynes and ketones: contrasting reactivity between cationic 3-iminophosphine palladium and nickel complexes†

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The catalytic hydrosilylation of alkynes and ketones has been explored utilizing palladium- and nickel (allyl) complexes supported by 3-iminophosphine ligands. Palladium and nickel demonstrated distinctly different reactivity profiles, with palladium proving very effective for the hydrosilylation of electron-deficient alkynes, while nickel excelled with ketones and internal alkynes. Additionally, in many cases, regioselective hydrosilylation was observed.

Introduction

Hydrosilylation is a useful catalytic transformation, facilitating access to organosilicon reagents.[1–3] Among the many available organosilicon species, allyl- and vinylsilanes have been key targets in catalytic hydrosilylation reactions because of their indispensable role as substrates in subsequent coupling reactions.[4–8] In addition to the hydrosilylation of carbon–carbon double and triple bonds, the catalytic hydrosilylation of unsaturated carbon–heteroatom systems as a means for selective reduction has grown rapidly.[9–18] While there are many reports of olefin hydrosilylation, common catalysts for use with C=C bonds are second or third row late transition metals, and efforts to take advantage of first row transition metals have only recently proven successful.[7,19–27] This application to olefin chemistry is likely inspired by the very common usage of first row transition metals in the hydrosilylation of carbonyl or imine groups, although selectivity remains an ongoing challenge in this chemistry.

Recently, we reported a very efficient palladium precatalyst for the hydrosilylation of allenes.[28] Mechanistic studies and the observed regioselectivity suggested that primary and secondary unhindered hydrosilanes activated the precatalyst to give a hydridopalladium species that is likely the active catalyst when using [(3-iminophosphine)Pd(allyl)]OTf for the hydrosilylation of allenes. This was further supported by a simple H/D crossover experiment.[28] In addition to allenes, the selective hydrosilylation of imines using this precatalyst was also reported by our group.[13] The simple activation of these complexes in the presence of silanes led us to further expand our study to the hydrosilylation of alkynes, while also investigating the nickel analogues of these palladium complexes in the hydrosilylation of unsaturated systems, as detailed herein.

Results and discussion

In this report, we examine the hydrosilylation of alkynes and carbonyl groups, in particular electron-deficient alkynes and ketones. Additionally, to better understand the role of the metal center, cationic complexes of both palladium and nickel supported by the same 3-iminophosphine ligand were investigated (Fig. 1).

Initially, electron-deficient alkynes were examined, as recent reports of palladium-catalyzed hydrosilylation of these alkynes with tertiary hydrosilanes yielded vinylsilane products

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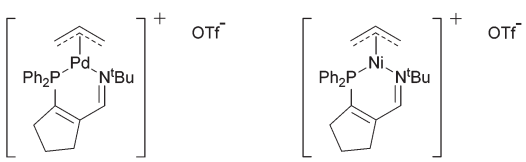
†Electronic supplementary information (ESI) available: Full experimental section, including characterization data and spectra for all hydrosilylation products. Crystallographic data is summarized in the ESI file, while a CIF file provides additional crystallographic data, including bond lengths and angles for compound **1b**. CCDC 1535923. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt00832e



1a **1b**

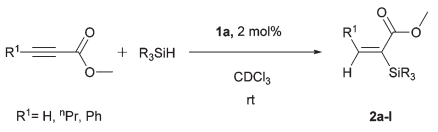
Fig. 1 Palladium and nickel complexes (**1a** and **1b**) utilized.

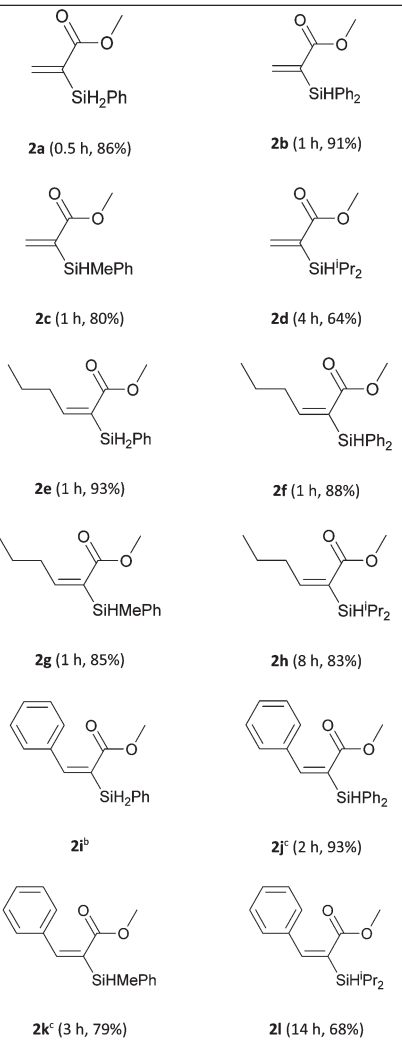
that function as very useful reagents for Hiyama coupling.[29,30] Furthermore, the mechanism invoked in these previous reports centered on the reactivity of a palladium-hydride generated *via* oxidative addition of the hydrosilane to palladium.[29,30] With the belief that our system also proceeds *via* hydrido-palladium intermediates,[28] it seemed a promising candidate for similar catalytic reactions.

Indeed, precatalyst **1a** regioselectively hydrosilylated electron-deficient alkynes *via syn* addition with 100% conversion to produce the corresponding vinylsilane products in moderate to excellent isolated yields (Table 1). For **2j** and **2k**, performing the catalysis at room temperature gave mixtures of *E* and *Z* isomers, although these very rapid reactions were complete in less than 30 minutes. Unfortunately, the ratio of these isomers was not consistent from run to run, likely due to minor changes in ambient temperature and the relatively slow catalyst activation in this system. In order to achieve better selectivity, they were instead performed at 0 °C, which lengthened the reaction time to 2–3 hours, but formed solely the *E* isomer. After reaction completion at 0 °C, giving only the *E* isomer, the catalytic mixture was removed from the ice bath and monitored for 12 hours at room temperature. No signs of isomerization to the *Z* isomer were observed. In previous reports, partial isomerization of the *E* isomer was postulated to occur *via* an insertion and β-hydride elimination sequence in the presence of Pd–H species,[30] but such a mechanism seems absent in our catalytic system. In nearly all previous reports involving the hydrosilylation of electron-deficient alkynes, tertiary silanes were utilized due to unwanted continued hydrosilylation reactivity observed with the resulting primary and secondary hydrosilanes after the first hydrosilylation catalytic turnover, leading to complicated mixtures. Fortuitously, this did not occur with our catalyst, as summarized in Table 1, allowing for clean isolation of the product secondary and tertiary vinylsilanes. In fact, tertiary silanes such as triethylsilane, *tert*-butyldimethylsilane, and dimethylphenylsilane did not undergo hydrosilylation with any of the electron-deficient alkynes at all, consistent with our previously proposed mechanism for precatalyst activation where tertiary silanes react to form the Pd–Si species, rather than the necessary Pd–H catalyst.[28] Other than the usage of these vinylsilane products as substrates in Hiyama coupling, they can also be easily transformed to the corresponding vinyliodides and then utilized in Suzuki–Miyaura coupling.[31] Although hydrosilylation of electron-deficient alkynes with primary and secondary silanes worked very well, internal unactivated alkynes such as 4-octyne, diphenylacetylene and phenylmethylacetylene showed no evidence of reaction after 24 hours under the same catalytic conditions. Simple terminal alkynes, such as phenylacetylene, led to intractable product mixtures.

Having observed excellent results with alkynyl esters, we proceeded on to investigate the electronically similar 1,3-enynes, although cautious of the regioselectivity issues possible in an extended carbon π-system of this sort. In fact, regioselectivity difficulties in the hydrosilylation of 1,3-enynes were recently detailed by Zhou and Moberg, in which reaction optimization by screening different ligands was required to achieve selective internal hydrosilylation of the C–C triple bond.[32] To our surprise, both enynes tested with our system underwent hydrosilylation with diphenylsilane regioselectively to form a single isomer (Scheme 1), although the specific isomer produced depended on the enyne employed. The regioselectivity in these two reactions seems driven entirely by the steric hindrance in the enyne substrate. Similar reactions with phenylsilane, methylphenylsilane and diisopropylsilane were

Table 1 Hydrosilylation of electron-deficient alkynes with primary and secondary silanes catalyzed by **1a**[a]





2a (0.5 h, 86%) **2b** (1 h, 91%)

2c (1 h, 80%) **2d** (4 h, 64%)

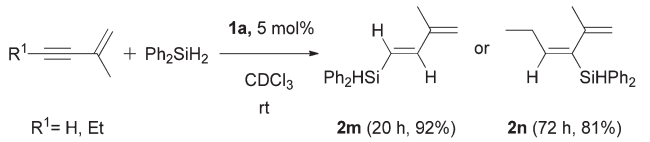
2e (1 h, 93%) **2f** (1 h, 88%)

2g (1 h, 85%) **2h** (8 h, 83%)

2i[b] **2j**[c] (2 h, 93%)

2k[c] (3 h, 79%) **2l** (14 h, 68%)

[a] Catalytic procedure: Reactions were carried out at ambient temperature in NMR tubes prepared in a glovebox using $CDCl_3$ (800 μl), **1a** (0.01 mmol, 2 mol%), hydrosilane (0.5 mmol), and alkyne (0.5 mmol), followed by frequent monitoring of the reaction by ^{1}H NMR spectroscopy. [b] Product was not isolated due to the formation of a complex mixture. [c] Reaction was carried out at 0 °C.



Scheme 1 Hydrosilylation of 1,3-enynes with diphenylsilane catalyzed by **1a**.

unsuccessful due to the formation of complex product mixtures. As before, tertiary silanes were again unreactive in the hydrosilylation of 1,3-enynes, likely due to the formation of Pd–Si intermediates rather than the necessary Pd–H species. These Pd–Si intermediates have much greater steric hindrance at the catalyst center, preventing alkyne insertion.[33]

Since diphenylsilane had proven useful in the hydrosilylation of both substrate classes, it was chosen in order to study the intermediates present in this catalytic system. Reactions utilizing equimolar amounts of palladium precatalyst **1a** and diphenylsilane were monitored over time. Although complete conversion to a distinct palladium intermediate was not observed, the presence of a Pd–H complex was observed *in situ* as a triplet *via* proton NMR spectroscopy (J_{H-P} = 92.4 Hz; Fig. 2). The observation of this resonance as a triplet is consistent with the formation of a dinuclear palladium complex, due to the unsaturated coordination sphere in the resulting monomeric Pd–H species. Interaction with two spin $\frac{1}{2}$ ^{31}P nuclei then gives the observed coupling pattern. Time-resolved ^{31}P NMR analysis of this reaction, as recorded every 15 minutes, supported these same assertions, showing diminishment of the precatalyst ^{31}P resonance in tandem with growth of a new ^{31}P doublet resonance (Fig. 3). Our efforts to isolate this hydride proved unsuccessful. Over time, the hydride decomposed during the attempted workup with formation of palladium black and ligand reduction *via* what appeared to be a hydride attack on the imine carbon atom. Resonances for this same hydride were also observed in equimolar reactions of the palladium precatalyst with either phenylsilane or methylphenylsilane (primary and secondary silanes), but not in stoichiometric reactions with the aforementioned tertiary silanes. Unfortunately, we cannot draw any solid conclusions about the

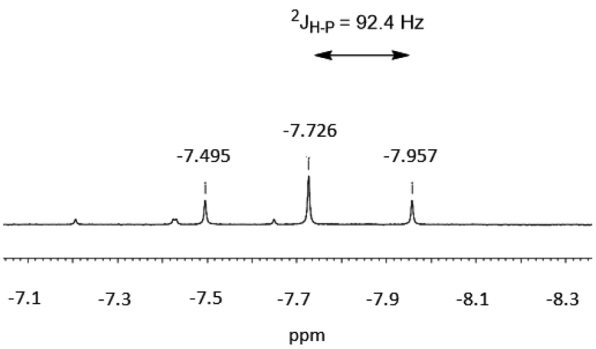


Fig. 2 ^{1}H NMR spectrum for the equimolar reaction of **1a** with diphenylsilane, resulting in the formation of a Pd–H species.

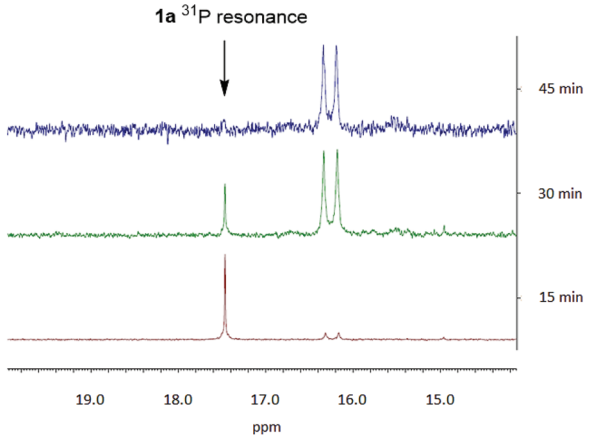


Fig. 3 Time-resolved ^{31}P NMR spectra from equimolar reaction of **1a** and diphenylsilane (recorded every 15 minutes).

catalytic activity of this Pd–H species at this point since other species within the rather complicated reaction mixture could instead serve as the actual functional catalyst.

Following this study of palladium chemistry, the related nickel complex **1b** was also investigated in hydrosilylation reactions. Although we reported **1b** previously, with full characterization by NMR spectroscopy and elemental analysis, during the intervening period crystals of **1b** suitable for X-ray analysis were grown by layering a saturated solution of **1b** in tetrahydrofuran with pentane. Its solid state structure was determined by X-ray crystallography *via* direct methods (Fig. 4) and is included herein. The approximately square planar coordination sphere of the cationic nickel portion, folding of the ligand backbone, and overall metrical parameters were quite similar to the other 3-iminophosphine palladium and nickel complexes previously investigated by the Schmidt group.[34–39]

Unlike the related palladium complex **1a** (Table 1), no catalytic hydrosilylation of methylpropiolate was observed over 24 hours with 5 mol% of nickel complex **1b**. Instead, a complex mixture of products was formed. Moreover, when an

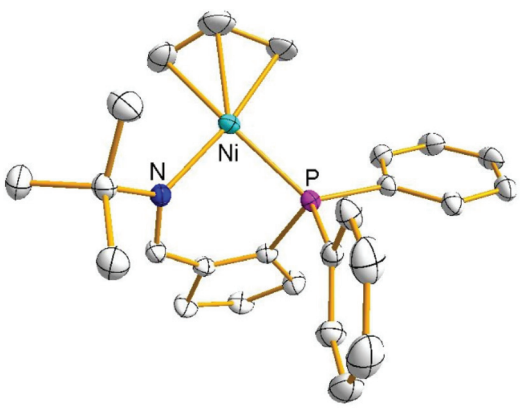


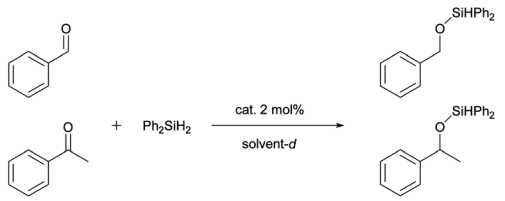
Fig. 4 Crystal structure of complex **1b** (50% thermal ellipsoids; hydrogen atoms and triflate anion omitted for clarity).

equimolar reaction of **1b** with diphenylsilane was monitored by ^{1}H NMR spectroscopy over time, unlike the Pd complex **1a**, no hydride triplet was observed, but instead the resulting mixture gave an uninterpretable ^{1}H NMR spectrum. Thus, it seemed that complex **1b** was ineffective in the hydrosilylation of such alkynes.

Given the recent interest in the hydrosilylation of carbonyls,[40,41] we instead set out to utilize **1b** in the hydrosilylation of aldehydes and ketones, and this nickel complex proved to be quite active for this catalysis. To provide better comparison, both nickel and palladium complexes (**1a** and **1b**) were investigated in the hydrosilylation of benzaldehyde and acetophenone as initial test reactions (Table 2). This data showed quite conclusively that the nickel complex **1b** was far superior to the palladium complex **1a** in the hydrosilylation of C═O derivatives, with quantitative conversion to the silylether product for both benzaldehyde (2 hours) and acetophenone (12 hours), while the palladium complex proved to be almost inactive under these conditions (<5% conversion after 24 hours, even at increased temperature). We attribute the different affinities of Pd and Ni for alkynes and carbonyl groups to their general polarizability and hard–soft acid–base theory, in which the Ni would be expected to form a stronger interaction with the oxygen than Pd, leading to preferred coordination at the Ni center and the subsequent insertion reaction that leads to hydrosilylation.

Having established the superiority of **1b**, this nickel complex was then utilized for a broad range of ketone hydrosilylation reactions, as summarized in Table 3. The necessary reaction time for these catalyses is highly dependent on the sterics of the ketone, and only a very small amount of product was detected with a bulky mesityl group present (Table 3, entry 6). Entries 7 and 8, with *ortho*-methoxyphenyl and *ortho*-

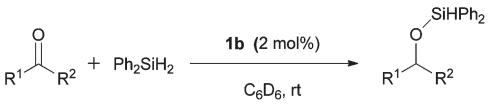
Table 2 Catalytic activity of **1a** and **1b** in the hydrosilylation of benzaldehyde and acetophenone with diphenylsilane[a]



Entry	Substrate	Solvent	Completion time (h) **1a**	Completion time (h) **1b**
1	Benzaldehyde	$CDCl_3$	NR[b]	—[c]
2	Acetophenone	$CDCl_3$	NR[b]	—[c]
3	Benzaldehyde	C_6D_6	NR[b]	2
4	Acetophenone	C_6D_6	NR[b]	12

[a] Catalytic procedure: Reactions were carried out at ambient temperature in NMR tubes prepared in a glovebox using solvent-*d* (800 μl), catalyst **1a** or **1b** (0.01 mmol, 2 mol%), hydrosilane (0.5 mmol), and carbonyl compound (0.5 mmol), followed by frequent monitoring of the reaction by ^{1}H NMR spectroscopy. [b] Trace amount of product detected after 24 h at 60 °C. [c] <5% conversion was observed after 24 h at rt.

Table 3 Hydrosilylation of ketones with diphenylsilane catalyzed by **1b**[a]



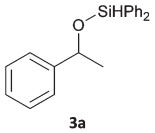
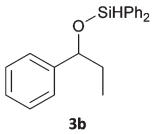
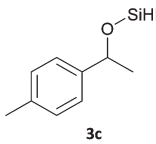
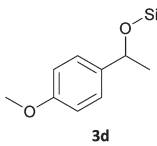
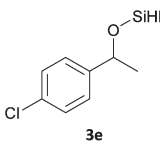
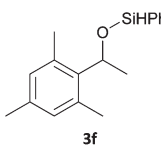
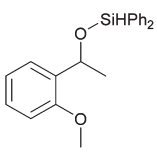
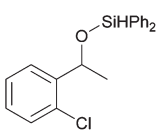
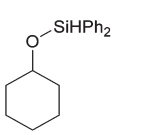
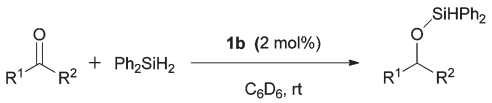
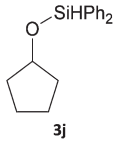
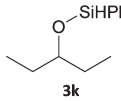
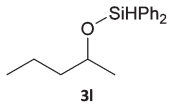
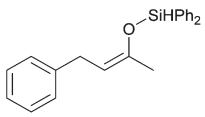
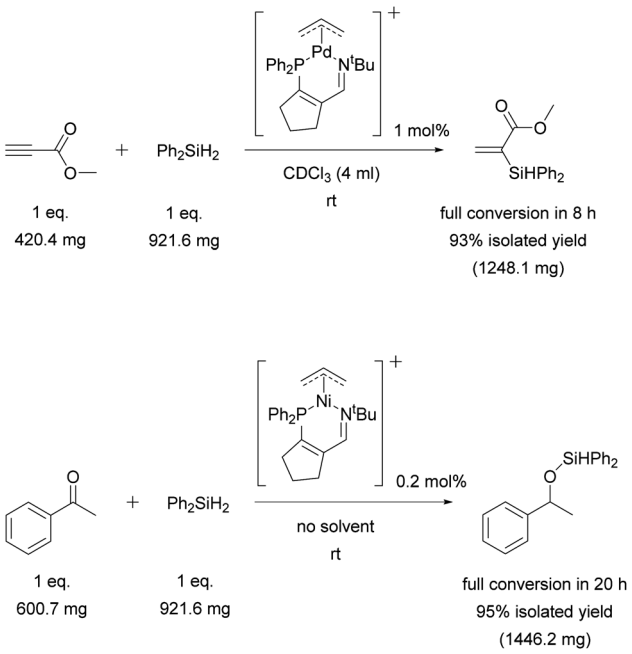
Entry	Product	Completion time (h)	Isolated yield (%)
1	 **3a**	12	94
2	 **3b**	21	85
3	 **3c**	36	71
4	 **3d**	48	86
5	 **3e**	30	66
6	 **3f**	—[b]	
7	 **3g**	44	77
8	 **3h**	—[b]	
9	 **3i**	3	89

Table 3 *(Contd.)*



Entry	Product	Completion time (h)	Isolated yield (%)
10	 **3j**	8	82
11	 **3k**	36[c]	76
12	 **3l**	24[c]	83
13[d]	 **3m**	30[c]	79

[a] Catalytic procedure: Reactions were carried out at ambient temperature in NMR tubes prepared in a glovebox using C_6D_6 (800 μl), **1b** (0.01 mmol, 2 mol%), hydrosilane (0.5 mmol), and ketone (0.5 mmol), followed by frequent monitoring of the reaction by ^{1}H NMR spectroscopy. [b] Trace amount of product was detected by ^{1}H NMR spectroscopy. [c] Reaction was carried out at 60 °C. [d] 2 eq. of diphenylsilane was used due to sluggish reaction with 1 eq. of hydrosilane.



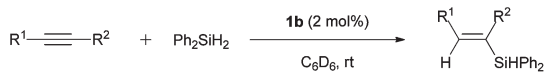
Scheme 2 Gram-scale catalytic reactions of **1a** and **1b**.

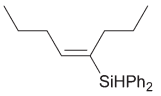
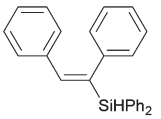
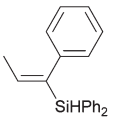
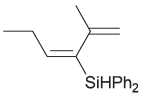
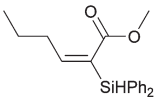
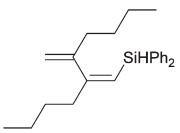
chlorophenyl groups, provide evidence of the advantageous effect of an electron-donating group (OMe) on the rate of the reaction. In general, as previously noted,[40] electron-donating groups on the aryl unit of ketones and imines promote η^2-coordination of the carbonyl or imine to the metal center, a required step for successful insertion of the C═O or C═N group into the metal hydride. The hydrosilylation of *E*-4-phenylbut-3-en-2-one (Table 3, entry 13) resulted in exclusive formation of the conjugate addition 1,4-hydrosilylation product. Previously, 1,4-hydrosilylation of α,β-unsaturated ketones has been obtained with rhodium complexes,[42,43] although nearly all nickel-catalyzed examples favor direct hydrosilylation of the carbonyl functionality, with only a single exception reported recently.[44] Although further investigation of other α,β-unsaturated carbonyl compounds is necessary, entry 13 suggests the strength and capability of nickel as a replacement for more expensive transition metal-catalyzed systems.

To test the scale-up robustness of **1a** and **1b** in the hydrosilylation of π-compounds, representative gram scale hydrosilylation reactions with each catalyst were performed, resulting in excellent isolated yields in both cases (Scheme 2).

In addition to carbonyl hydrosilylation, it was found that nickel complex **1b** also worked well in the *cis*-hydrosilylation of internal alkynes to form the corresponding vinylsilane products (Table 4). Although a few other examples of first row transition metal-catalyzed hydrosilylation of alkynes have been reported to date,[19,25,27] overall selectivity is variable in all cases, often yielding more than one product isomer. These previous reports include a cobalt system by Mo and coworkers that works perfectly for terminal alkynes, but lacks regioselectivity with unsymmetric internal alkynes.[25] Additionally, recent reports of nickel-catalyzed hydrosilylation by Srinivas and coworkers form two regioisomers in the hydrosilylation of an unsymmetric alkyne (1-phenyl-1-propyne).[19,26] This contrasts with our observation of strong regioselectivity with the same substrate, where a 92 : 8 ratio of regioisomers was formed. Another interesting result using our catalyst involved the telomerization of 1-hexyne when treated with an equimolar amount of diphenylsilane. For the result given (Table 4, entry 6), the reaction was repeated with 2 eq. of 1-hexyne in order to reflect the product stoichiometry, since the initial equimolar reaction had yielded telomerized product and unreacted diphenylsilane. Unfortunately, other terminal alkynes (phenylacetylene, trimethylsilylacetylene, methyl propiolate, and 2-methylbut-1-en-3-yne) did not form the telomerized product, but rather gave intractable mixtures. As discussed above, hydrosilylation of electron-deficient alkynes was effective utilizing palladium (Table 1). Although the nickel complex **1b** was not successful in hydrosilylation of methylpropiolate, it did show moderate reactivity for the hydrosilylation of methyl hept-2-ynoate. As with most organotransition metal chemistry, it should be emphasized that the reactivity and selectivity observed in catalytic hydrosilylation is highly dependent on

Table 4 Substrate scope of alkyne hydrosilylation catalyzed by **1b**[a]



Entry	Alkyne	Product	Completion time (h)	Isolated yield (%)
1	$R^1 = R^2 = {}^n$Pr	 **4a**	22 (12[b])	84
2	$R^1 = R^2$ = Ph	 **4b**	30 (16[b])	77
3	R^1 = Me R^2 = Ph	 **4c**	14 (10[b])	80
4	R^1 = Et R^2 = 2-Propenyl	 **2n**	24 (14[b])	81
5	$R^1 = {}^n$Pr R^2 = Methyl formate	 **2f**	16 (12[b])	71
6[c]	$R^1 = {}^n$Bu R^2 = H	 **4e**	36 (24[b])	86

[a] Catalytic procedure: Reactions were carried out at room temperature in NMR tubes prepared in a glovebox using C_6D_6 (800 μl), **1b** (0.01 mmol, 2 mol%), hydrosilane (0.5 mmol), and ketone (0.5 mmol), followed by frequent monitoring of the reaction by ^{1}H NMR spectroscopy. [b] Reaction was carried out at 60 °C. [c] 2 eq. of alkyne was used.

the combination of metal and ligand used in the catalyst as well as the electronic and steric parameters of the hydrosilane.[28,45,46]

Conclusions

In summary, efficient systems for the hydrosilylation of alkynes and ketones were developed using cationic complexes of palladium and nickel supported by the 3-iminophosphine ancillary ligand. The palladium precatalyst showed satisfactory reactivity in the hydrosilylation of activated alkynes. The mechanism for this system involved reactive palladium-hydride intermediates formed after treatment of the precatalyst with primary or secondary silanes. Our previous experiments, along with the time-resolved ^{1}H NMR data in this work, provide supporting evidence for the proposed mechanism. On the other hand, the nickel analogue of the palladium complex showed poor reactivity for hydrosilylation of electron-deficient alkynes, but performed regio- and stereoselectively in the hydrosilylation of unactivated internal alkynes with diphenylsilane. Additionally, the nickel precatalyst functioned well in ketone hydrosilylation. Although the mechanism involved in activation of the nickel precatalyst remains unknown at present, continued mechanistic investigations and expansion of reaction substrate scope are ongoing research avenues in this project.

Experimental

General methods and instrumentation

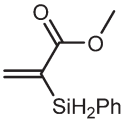
All NMR-scale reactions were set up in a nitrogen-filled glovebox. $CDCl_3$ and C_6D_6 were purchased from Cambridge Isotope Laboratories and for air-sensitive usage, dried over calcium hydride and sodium, respectively, freeze–pump–thawed three times, vacuum-transferred, and stored over molecular sieves in a nitrogen-filled glovebox. Precatalysts **1a** and **1b** were synthesized *via* the previously reported procedures.[36,39] Hydrosilanes for catalytic hydrosilylation reactions were purchased from Gelest, AK Scientific, or Acros, dried neat over calcium hydride and distilled under nitrogen, freeze–pump–thawed, and transferred to the glovebox. All aromatic aldehydes and ketones were supplied from Alfa Aesar, AK Scientific, Sigma-Aldrich, and Acros. Alkynes were purchased from either Sigma-Aldrich or AK Scientific. ^{1}H and ^{13}C NMR data were obtained either on a 400 MHz Varian VXRS NMR spectrometer at 399.95 MHz for ^{1}H and 100.56 MHz for ^{13}C NMR spectroscopy or on a 600 MHz Bruker Avance III at 599.9 MHz for ^{1}H and 150.8 MHz for ^{13}C NMR spectroscopy. High resolution mass spectrometry data were determined by the University of Illinois Mass Spectrometry Laboratory, Urbana, IL, USA.

Catalytic reactions and isolation of hydrosilylation products

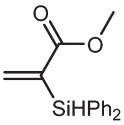
For the hydrosilylation reactions of alkynes, unless otherwise noted, **1a** or **1b** was suspended in $CDCl_3$ or C_6D_6, followed by addition of hydrosilane (1 eq.) and alkyne (1 eq.). In the case of carbonyl hydrosilylation, the carbonyl derivative was added before the hydrosilane. Then, the resulting solution was transferred to an NMR tube, sealed and reaction progress was monitored by acquiring ^{1}H NMR data frequently. Gram scale reactions were set up in 20 ml vials, sealed with gentle stirring, and reaction completion was monitored by TLC analysis of the reaction mixture. After detection of reaction completion by ^{1}H NMR spectroscopy (based on diminishing starting material peaks), all volatiles were removed under vacuum, and the crude reaction mixture was extracted with hexanes and passed through a short plug of silica gel to remove inorganics. This mixture was concentrated and purified by flash chromato-

graphy (hexanes for vinylsilane products and 90 : 10 hexanes : ethylacetate for silylether products) as a colorless oily liquid. Isolated yields are calculated based on unsaturated substrate (alkyne or carbonyl derivative). For silylether products, due to partial hydrolysis of the product on silica gel, yields are based on total of silylether and corresponding alcohol. All vinylsilanes were characterized by ^{1}H and ^{13}C NMR spectroscopy and high resolution mass spectrometry. Silylether products were characterized only by ^{1}H and ^{13}C NMR spectroscopy. Hydrosilylation products **3a**,[47] **3b**,[48] **3d**,[49] **3i**,[49] **3j**,[50] **3k**,[49] **3l**,[51] **3m**,[52] **4a**,[53] **4b**,[54] and **4c**[54] were identified by comparison to previously reported NMR spectral data.

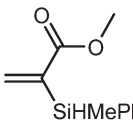
Characterization of hydrosilylation products



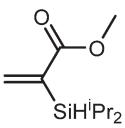
Methyl 2-(phenylsilyl)acrylate (2a). 86% isolated yield (83 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.64–7.61 (m, 2H), 7.44–7.37 (m, 3H), 7.03 (d, ^{2}J = 2.0 Hz, 1H), 6.26 (d, ^{2}J = 2.0 Hz, 1H), 4.69 (s, 2H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 168.5, 144.6, 137.2, 135.7, 130.5, 130.2, 128.2, 52.1; HRMS (EI) (*m*/*z*): $[M - H]^+$ calc. for $C_{10}H_{11}O_2Si$, 191.0528; found, 191.0530.



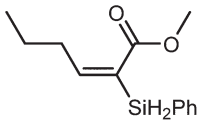
Methyl 2-(diphenylsilyl)acrylate (2b). 91% isolated yield (122 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.66–7.63 (m, 4H), 7.47–7.41 (m, 6H), 7.15 (d, ^{2}J = 2.8 Hz, 1H), 6.25 (d, ^{2}J = 2.8 Hz, 1H), 5.31 (s, 1H), 3.73 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 168.9, 145.0, 138.9, 135.7, 132.4, 130.1, 128.2, 52.0; HRMS (EI) (*m*/*z*): $[M - H]^+$ calc. for $C_{16}H_{15}O_2Si$, 267.0841; found, 267.0841.



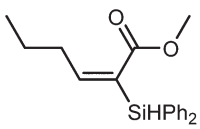
Methyl 2-(methyl(phenyl)silyl)acrylate (2c). 80% isolated yield (83 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.60–7.58 (m, 2H), 7.42–7.37 (m, 3H), 6.96 (d, ^{2}J = 2.8 Hz, 1H), 6.16 (d, ^{2}J = 2.8 Hz, 1H), 4.72 (q, ^{3}J = 4.0 Hz, 1H), 3.75 (s, 3H), 0.57 (d, ^{3}J = 4.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 169.0, 142.9, 140.3, 134.8, 133.5, 129.8, 128.0, 51.9, −5.3; HRMS (EI) (*m*/*z*): $[M - H]^+$ calc. for $C_{11}H_{13}O_2Si$, 205.0685; found, 205.0684.



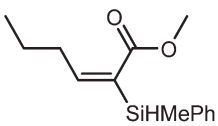
Methyl 2-(diisopropylsilyl)acrylate (2d). 64% isolated yield (64 mg), ^{1}H NMR ($CDCl_3$, 600 MHz): 6.92 (d, ^{2}J = 3.6 Hz, 1H), 6.17 (d, ^{2}J = 3.6 Hz, 1H), 3.75 (s, 3H), 3.65 (t, ^{3}J = 3.6 Hz, 1H), 1.20–1.15 (m, 2H), 1.05 (d, ^{3}J = 7.2 Hz, 6H), 0.98 (d, ^{3}J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz): 169.6, 143.3, 139.0, 51.8, 18.9, 18.8, 10.7; HRMS (CI) (*m*/*z*): $[M + H]^+$ calc. for $C_{10}H_{21}O_2Si$, 201.1311; found, 201.1313.



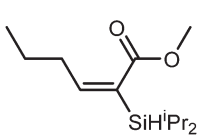
Methyl (*E*)-2-(phenylsilyl)hex-2-enoate (2e). 93% isolated yield (109 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.62–7.60 (m, 2H), 7.42–7.36 (m, 3H), 6.68 (t, ^{3}J = 6.8 Hz, 1H), 4.66 (s, 2H), 3.70 (s, 3H), 2.62 (q, ^{3}J = 6.8 Hz, 2H), 1.53–1.47 (m, 2H), 0.95 (t, ^{3}J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 168.7, 162.9, 135.6, 131.5, 129.9, 128.1, 127.5, 51.4, 33.9, 22.2, 13.9; HRMS (EI) (*m*/*z*): $[M - H]^+$ calc. for $C_{13}H_{17}O_2Si$, 233.0998; found, 233.0990.



Methyl (*E*)-2-(diphenylsilyl)hex-2-enoate (2f). (Same regio- and stereoisomers from either **1a** or **1b**) 88% isolated yield (137 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.64–7.62 (m, 4H), 7.45–7.39 (m, 6H), 6.60 (t, ^{3}J = 7.2 Hz, 1H), 5.23 (s, 1H), 3.63 (s, 3H), 2.62 (q, ^{3}J = 7.2 Hz, 2H), 1.55–1.49 (m, 2H), 0.97 (t, ^{3}J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 169.3, 161.7, 135.6, 133.1, 129.9, 129.5, 128.0, 51.3, 33.9, 22.3, 13.9; HRMS (EI) (*m*/*z*): $[M - H]^+$ calc. for $C_{19}H_{21}O_2Si$, 309.1311; found, 309.1306.

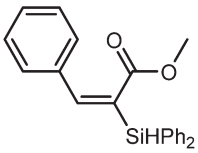


Methyl (*E*)-2-(methyl(phenyl)silyl)hex-2-enoate (2g). 85% isolated yield (106 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): 7.60–7.57 (m, 2H), 7.41–7.38 (m, 3H), 6.52 (t, ^{3}J = 7.2 Hz, 1H), 4.67 (q, ^{3}J = 4.0 Hz, 1H), 3.69 (s, 3H), 2.54 (q, ^{3}J = 7.2 Hz, 2H), 1.49 (sext, ^{3}J = 7.2 Hz, 2H), 0.95 (t, ^{3}J = 7.2 Hz, 3H), 0.54 (d, ^{3}J = 4.0 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 400 MHz): 169.5, 159.2, 134.9, 134.7, 131.0, 129.6, 127.9, 51.2, 33.8, 22.3, 13.9, −5.0; HRMS (EI) (*m*/*z*): $[M - H]^+$ calc. for $C_{14}H_{19}O_2Si$, 247.1154; found, 247.1153.

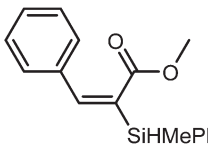


Methyl (*E*)-2-(diisopropylsilyl)hex-2-enoate (2h). 83% isolated yield (101 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): 6.38 (t, ^{3}J = 7.6 Hz, 1H), 3.68 (s, 3H), 3.56 (t, ^{3}J = 3.2 Hz, 1H), 2.42 (q, ^{3}J = 7.6 Hz, 2H), 1.50–1.41 (m, 2H), 1.13–1.05 (m, 2H), 1.01 (d, ^{3}J = 6.8 Hz, 6H), 0.97 (d, ^{3}J = 6.8 Hz, 6H), 0.90

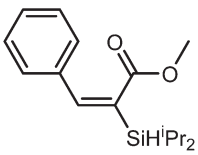
(t, ^3J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): 170.4, 158.1, 129.9, 51.1, 33.8, 22.4, 18.8, 18.7, 13.8, 11.0. HRMS (EI) (*m*/*z*): $[M - H]^+$ calc. for $C_{13}H_{25}O_2Si$, 241.1624; found, 241.1624.



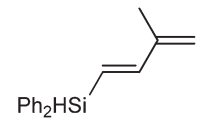
Methyl (*E*)-2-(diphenylsilyl)-3-phenylacrylate (2j). 93% isolated yield (160 mg), ^1H NMR ($CDCl_3$, 600 MHz): 7.69–7.68 (m, 4H), 7.48–7.45 (m, 2H), 7.43–7.41 (m, 4H), 7.38–7.32 (m, 5H), 7.10 (s, 1H), 5.34 (s, 1H), 3.58 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 600 MHz): 171.2, 148.8, 136.2, 135.8, 132.0, 131.7, 130.3, 129.3, 128.7, 128.5, 128.2, 51.8; HRMS (EI) (*m*/*z*): $[M]^+$ calc. for $C_{22}H_{20}O_2Si$, 344.1233; found, 344.1238.



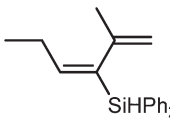
Methyl (*E*)-2-(methyl(phenyl)silyl)-3-phenylacrylate (2k). 79% isolated yield (112 mg), ^1H NMR ($CDCl_3$, 400 MHz): 7.66–7.64 (m, 2H), 7.44–7.31 (m, 8H), 7.03 (s, 1H), 4.81 (q, ^3J = 3.6 Hz, 1H), 3.67 (s, 3H), 2.62 (d, ^3J = 3.6 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): 171.5, 146.6, 136.3, 134.9, 133.4, 130.8, 130.1, 129.0, 128.53, 128.50, 128.2, 51.8, −5.3; HRMS (EI) (*m*/*z*): $[M]^+$ calc. for $C_{17}H_{18}O_2Si$, 282.1076; found, 282.1079.



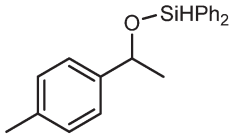
Methyl (*E*)-2-(diisopropylsilyl)-3-phenylacrylate (2l). 68% isolated yield (94 mg), ^1H NMR ($CDCl_3$, 600 MHz): 7.33–7.24 (m, 5H), 7.05 (s, 1H), 3.77–3.75 (m, 1H), 3.69 (s, 3H), 1.24–1.19 (m, 2H), 1.12 (d, ^3J = 7.6 Hz, 6H), 1.10 (d, ^3J = 7.6 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 600 MHz): 172.3, 158.8, 146.4, 136.5, 128.8, 128.5, 128.4, 51.7, 18.61, 18.56, 11.1; HRMS (EI) (*m*/*z*): $[M - H]^+$ calc. for $C_{16}H_{23}O_2Si$, 275.1467; found, 275.1471.



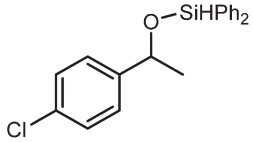
(3-Methylbuta-1,3-dien-1-yl)diphenylsilane (2m). 92% isolated yield (115 mg), ^1H NMR ($CDCl_3$, 400 MHz): 7.60–7.58 (m, 4H), 7.43–7.37 (m, 6H), 6.83 (d, ^4J = 18.8 Hz, 1H), 6.09 (dd, ^4J = 18.8 Hz, ^2J = 3.2 Hz, 1H), 5.17 (d, ^2J = 3.2 Hz, 1H), 5.14 (s, 1H), 5.06 (s, 1H), 1.92 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): 152.1, 143.3, 135.6, 133.9, 129.8, 128.2, 121.4, 119.0, 18.1; HRMS (EI) (*m*/*z*): $[M]^+$ calc. for $C_{17}H_{18}Si$, 250.1178; found, 250.1172.



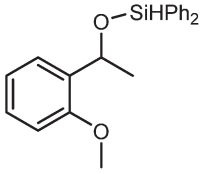
(*E*)-(2-Methylhexa-1,3-dien-3-yl)diphenylsilane (2n). (Same regio- and stereoisomers from either **1a** or **1b**) 81% isolated yield (113 mg), ^1H NMR ($CDCl_3$, 600 MHz): 7.60 (dd, ^3J = 7.8 Hz, ^4J = 1.4 Hz, 4H), 7.42–7.26 (m, 6H), 5.89 (t, ^3J = 7.1 Hz, 1H), 5.09 (s, 1H), 4.86 (d, ^2J = 1.3 Hz, 1H), 4.53 (d, ^3J = 1.3 Hz, 1H), 2.20 (quint, ^3J = 7.1 Hz, 2H), 1.71 (s, 3H), 0.99 (t, ^3J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 600 MHz): 147.5, 145.4, 139.2, 135.9, 133.9, 129.7, 128.0, 112.2, 24.5, 23.8, 14.4; HRMS (EI) (*m*/*z*): $[M]^+$ calc. for $C_{19}H_{22}Si$, 278.1491; found, 278.1491.



Diphenyl(1-(*p*-tolyl)ethoxy)silane (3c). 71% isolated yield (113 mg), ^1H NMR ($CDCl_3$, 400 MHz): 7.72 (d, ^3J = 7.6 Hz, 2H), 7.67 (d, ^3J = 7.2 Hz, 2H), 7.52–7.41 (m, 6H), 7.33 (d, ^3J = 8.0 Hz, 2H), 7.21 (d, ^3J = 8.0 Hz, 2H), 5.51 (s, 1H), 5.07 (q, ^3J = 6.0 Hz, 1H), 2.42 (s, 3H), 1.59 (d, ^3J = 6.0 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): 142.4, 136.8, 135.9, 134.83, 134.79, 134.4, 130.41, 130.36, 129.0, 128.1, 128.0, 125.6, 72.7, 26.4, 21.4.

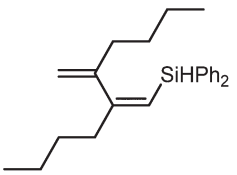


(1-(4-Chlorophenyl)ethoxy)diphenylsilane (3e). 66% isolated yield (112 mg), ^1H NMR ($CDCl_3$, 400 MHz): 7.62 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2H), 7.57 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2H), 7.46–7.33 (m, 6H), 7.27 (s, 4H), 5.40 (s, 1H), 4.96 (q, ^3J = 6.4 Hz, 1H), 1.48 (d, ^3J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): 143.9, 134.81, 134.76, 134.1, 133.9, 132.9, 130.6, 130.5, 128.5, 128.2, 128.1, 127.1, 72.2, 26.4.



(1-(2-Methoxyphenyl)ethoxy)diphenylsilane (3g). 77% isolated yield (129 mg), ^1H NMR ($CDCl_3$, 400 MHz): 7.64 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2H), 7.59 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2H), 7.45–7.34 (m, 6H), 7.23 (t, ^3J = 8.4 Hz, 1H), 6.93–6.90 (m, 2H), 6.79 (dm, ^3J = 8.4 Hz, 1H), 5.42 (s, 1H), 4.99 (q, ^3J = 6.4 Hz, 1H), 3.77 (s, 3H), 1.51 (d, ^3J = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 400 MHz): 159.7, 147.1, 134.84, 134.82, 134.3, 134.1,

130.5, 130.4, 129.4, 128.14, 128.07, 118.1, 112.8, 111.1, 72.7, 55.3, 26.4.



(*E*)-(2-Butyl-3-methylenehept-1-en-1-yl)diphenylsilane (4e). 86% isolated yield (150 mg, 2,3-di^{n}butyl/2,4-di^{n}butyl isomer: 1/0.27 from crude mixture), ^{1}H NMR ($CDCl_3$, 600 MHz): 7.56–7.54 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 4H), 7.37–7.33 (m, 6H), 5.64 (d, ^3J = 5.7 Hz, 1H), 5.14 (d, ^3J = 5.7 Hz, 1H), 4.80 (d, ^2J = 2.0 Hz, 1H), 4.77 (d, ^2J = 2.0 Hz, 1H), 2.28 (t, ^3J = 7.6 Hz, 2H), 2.05 (t, ^3J = 7.1 Hz, 2H), 1.44–1.24 (m, 8H), 0.92 (t, ^3J = 7.3 Hz, 3H), 0.86 (t, ^3J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 600 MHz): 166.3, 150.9, 136.3, 135.1, 128.0, 127.9, 118.1, 113.1, 38.8, 34.6, 30.4, 29.6, 22.8, 22.4, 14.11, 14.08; HRMS (EI) (*m*/*z*): $[M]^+$ calc. for $C_{24}H_{32}Si$, 348.2273; found, 348.2269.

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