OL Organic Letters

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Nickel-Catalyzed Hydrosilylation of Terminal Alkenes with Primary Silanes via Electrophilic Silicon−Hydrogen Bond Activation

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Cite This: *Org. Lett.* 2021, 23, 1434−1439 Read Online

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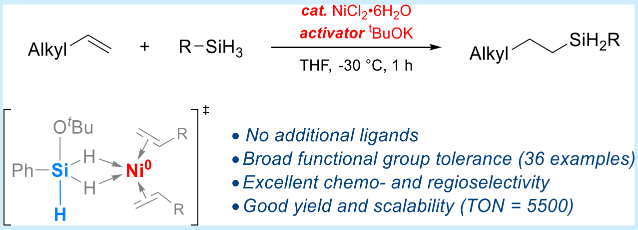
ABSTRACT: We report a simple and effective nickel-based catalytic system, NiCl$_2$·6H$_2$O/^{t}BuOK, for the electrophilically activated hydrosilylation of terminal alkenes with primary silanes. This protocol provides excellent performance under mild reaction conditions: exclusive anti-Markovnikov selectivity, broad functional group tolerance (36 examples), and good scalability (TON = 5500). However, the secondary and tertiary silanes are not suitable. Mechanistic studies revealed that this homogeneous catalytic hydrosilylation includes an electrophilically activated Si−H bond process without the generation of nickel hydrides.

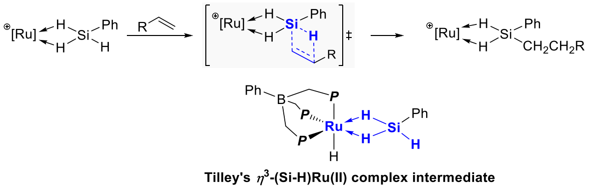


The transition metal-catalyzed hydrosilylation of unsaturated groups, especially olefins, is an important source of commodity organosilicon compounds.[1] Among all hydrosilylation reactions, the activation of the Si−H bond is the most crucial for controlling the reactivity and selectivity.[2] Metal hydrides are the common catalytic species in the classical Chalk−Harrod mechanism, which are generated via various activations mediated by a transition metal, such as oxidative addition, σ-bond metathesis, and [2+2] addition.[3] The highly active metal hydrides also result in many limitations for the application of hydrosilylation, like complex side reactions, the narrow scope of substrates, and the high cost of ligands.[4] Recently, these barriers are gradually overcome with the development of ligand-controlled[5] or heterogeneous[6] protocols based on earth-abundant transition metals. Another solution is to develop new processes avoiding the Chalk−Harrod frame, which has inspired great interest, such as radical hydrosilylation[7] and electrophilic activated hydrosilylation.[8]

Electrophilic activation modes for Si−H bonds have been proposed to explain the reactivity of the main group Lewis acid catalysts in the hydrosilylation of alcohols, carbonyl derivatives, alkenes, CO$_2$, and pyridines.[9] In these processes, the Si−H bond preferentially undergoes η^1-coordination with the strong Lewis acid center, which can render the Si center more electrophilic through electron-withdrawing induction effects and allow attacks from nucleophile. Nonetheless, it is intrinsically challenging for electrophilic Si−H bond activation to occur with transition metal catalysts,[8] because the abundant d orbital electrons of the central transition metal tend to back-donate to the σ* orbital of the Si−H bond and facilitate oxidative addition. Thus, the transition metal center of the catalysts must be extremely electron-deficient in electrophilic hydrosilylation. Recently, Tilley's group demonstrated the hydrosilylation of alkenes with primary and secondary silanes utilizing cationic Ru or Ir complexes as the catalysts (Scheme 1a).[10] The 16e cation metal centers of the catalysts are reluctant to undergo oxidative addition, and the electrophilic η^3-complexes or silylenes were confirmed to be the actual active species to catalyze the direct and fast hydrosilylation. Although similar η^2-(Si−H)M complexes have been synthe-

Scheme 1. η^x-(Si-H)M Complexes (x = 2 or 3)

a) Electrophilically activated hydrosilylation catalyzed by cationic Ru(II) complexes (P = PPh$_2$)



b) Typical η^2-(Si-H)Ni(0) complexes (P = PPh$_2$)

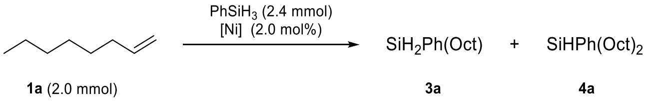
Received: January 12, 2021
Published: January 30, 2021

sized from various silanes and transition metals,[8b,11] their practical reactivity in the hydrosilylation reactions has not been well explored, especially for the first-row transition metals.

We aimed to develop an efficient and low-cost electrophilic hydrosilylation of alkenes catalyzed by earth-abundant transition metal-based catalysts. Nickel has exhibited a special electrophilic Si−H bond activation ability.[12] Typically, in the work of Iwasawa and Sun,[13] the nickel(0) center has an obviously lower energy barrier to undergo η^2-coordination with Si−H bonds in [PSiP]-pincer complexes, whereas other metals, like Fe and Co, tend to undergo oxidative addition (Scheme 1b). In addition, strong electron-withdrawing ligands are not required for the construction of η^2-(Si-H)Ni(0) complexes.[14] Hence, a nickel-based ligand-free catalytic protocol for the electrophilically activated hydrosilylation is practically possible. Herein, we report a simple and effective Ni-catalyzed electrophilic hydrosilylation of alkenes with primary silanes in the absence of additional ligands.

We began our studies with the reaction between 1-octene (**1a**) and $PhSiH_3$ (**2a**) in THF as the model reaction. We assumed that substrate alkenes serve as the weak electron-withdrawing ligands to provide sufficient stability for the putatively active η^2-(Si-H)Ni(0) complexes, because of the strong coordinating interaction between the Ni(0) center and C═C bonds.[15] Thus, without the addition of any extra ligands, $Ni(COD)_2$, a commercially available nickel(0) precursor, was first examined as a catalyst at room temperature (Table 1, entry 1). However, rapid accumulation of Ni^0 black was observed, and none of the desired product **3a** was detected; **1a** was recovered almost quantitatively (Table 1, entry 1). We next attempted to generate the Ni^0 species *in situ*, and $(DME)NiCl_2$ was added to the model reaction mixture in the presence of ^{t}BuOK, which can activate silane in the reduction and silylation.[16] Surprisingly, although nickel black still precipitated, hydrosilylation product **3a** was obtained in 9% yield with double hydrosilylation byproduct **4a** being obtained in 11% yield (Table 1, entry 2). Moreover, nickel no longer precipitated when the reaction temperature was decreased to 0 °C, and the yield of **3a** was increased to 35% together with a sharp decrease in the level of generation of **4a** to 5% (Table 1, entry 3). This implied that the low temperature is beneficial for the stability of the Ni^0 species and electrophilic interactions with the Si−H bond. Gratifyingly, when the reaction temperature was further decreased to −30 °C, **1a** was converted completely into target product **3a** in quantitative NMR yield without the formation of **4a** [92% isolated yield (Table 1, entry 4)].

Table 1. Optimization of the Hydrosilylation Reaction of 1-Octene with $PhSiH_3$



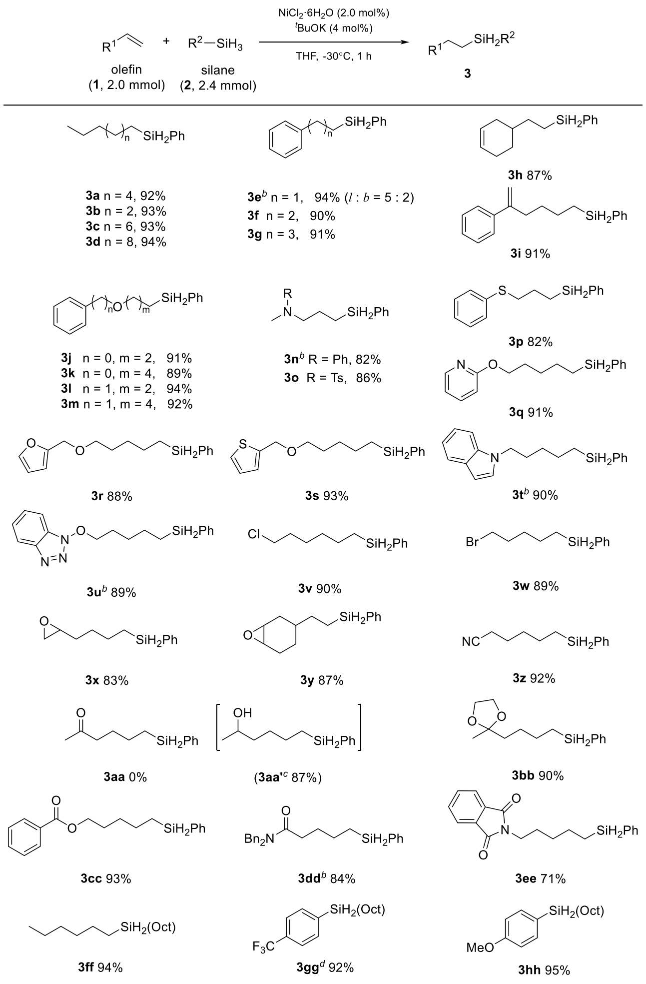
entry[a]	catalyst	activator	conversion (%)	yield (%) 3a	yield (%) 4a
1[b]	$Ni(COD)_2$	–	<1	0	0
2[b]	$(DME)NiCl_2$	^{t}BuOK	31	9	11
3[c]	$(DME)NiCl_2$	^{t}BuOK	47	35	5
4	$(DME)NiCl_2$	^{t}BuOK	99	99	0
5	$(DME)NiBr_2$	^{t}BuOK	40	33	0
6	$NiCl_2{\cdot}6H_2O$	^{t}BuOK	99	99	0
7	$Ni(O^tBu)_2{\cdot}x$KCl	–	55	54	0
8	$FeCl_2{\cdot}4H_2O$	^{t}BuOK	2	0	0
9	$MnCl_2{\cdot}4H_2O$	^{t}BuOK	4	0	0
10	$CuCl_2{\cdot}2H_2O$	^{t}BuOK	8	0	0
11	$CoCl_2{\cdot}6H_2O$	^{t}BuOK	2	0	0
12	$ZnCl_2$	^{t}BuOK	4	0	0
13	$NiCl_2{\cdot}6H_2O$	^{t}BuONa	40	40	0
14	$NiCl_2{\cdot}6H_2O$	^{t}BuOLi	5	0	0
15	–	^{t}BuOK	7	0	0
16	$NiCl_2{\cdot}6H_2O$	—	8	0	0

[a] General reaction conditions: 1-octene (**1a**, 224 mg, 2.0 mmol), $PhSiH_3$ (**2a**, 260 mg, 2.4 mmol), catalyst (2.0 mol %), activator (4.0 mol %), THF (3.0 mL), −30 °C, 12 h. Conversions and yields were determined by ^{1}H NMR analysis (internal standard, benzyl ether). [b] The reaction temperature was 25 °C. [c] The reaction temperature was 0 °C.

Other nickel precatalysts, except $(DME)NiBr_2$, exhibited excellent activity and selectivity for the hydrosilylation (Table 1, entries 5 and 6, and Table S2). Even with $NiCl_2{\cdot}6H_2O$ as a precatalyst, the reaction gave **3a** in 99% yield (Table 1, entry 6). Upon replacement of the catalytic system, $NiCl_2{\cdot}6H_2O/^tBuOK$, with the reported nanocatalyst $Ni(O^tBu)_2{\cdot}x$KCl,[6e] the conversion was decreased to 55%, and the selectivity was maintained (Table 1, entry 7). Moreover, 10% conversion of 1-octene was observed in the hydrosilylation catalyzed by nano $Ni(O^tBu)_2{\cdot}x$KCl at room temperature (Table S2, entry 8). It is worth noting that other first-row metals, such as Fe, Mn, Cu, Co, and Zn, are not suitable for this reaction (Table 1, entries 8−12, respectively). Indeed, nickel shows excellent suitability for the electrophilic hydrosilylation as it allows for η^2-coordination with the Si−H bond to activate Si−H bond electrophilically as we hypothesized. Switching ^{t}BuOK to ^{t}BuONa or ^{t}BuOLi resulted in a marked decrease in reactivity (Table 1, entry 13 or 14, respectively), which is in agreement with literature reports.[16b,17] This is caused by the quite different ionizations of the alkoxides in an organic solvent. The activities can be improved partly by adding appropriate crown ethers (Table S3, entries 3 and 5). Solvent and reaction time are also screened (Tables S4 and S5). In addition, control experiments showed that the nickel precatalyst and ^{t}BuOK are both required for the reaction (Table 1, entries 15 and 16, respectively). Thus, the optimum reaction conditions were determined with 2.0 mol % $NiCl_2{\cdot}6H_2O$ as the catalyst and 4.0 mol % ^{t}BuOK as the activator in THF at −30 °C within 1 h.

With the optimal conditions in hand, we examined the scope of this anti-Markovnikov hydrosilylation of terminal olefins and various secondary silanes **3** were obtained in good yields with excellent selectivity. The hydrosilylation of alkyl and aryl alkenes (Scheme 2, **1a**−**1d**, **1f**, and **1g**) proceeded with complete substrate conversion and afforded products in >90% isolated yields. In the case of dienes, **1h** and **1i** gave the selective hydrosilylation products of the terminal alkenes in 87% and 91% yields, respectively, and the internal alkene and 1,1-disubstituted alkene moieties remained unaffected. To our delight, the hydrosilylation of olefins bearing a C−X bond (X = halide, oxygen, sulfur, or nitrogen) proceeded smoothly, allyl ethers (**1j**−**1p**) and halogenated substrates (**1v** and **1w**) being completely converted into the corresponding secondary silanes in good yields ranging from 82% to 92%. These phenomena strongly support the idea that this reaction proceeds through an electrophilic Si−H bond activation process; in traditional

Scheme 2. Scope of Substrates in the Hydrosilylation Reaction[a]



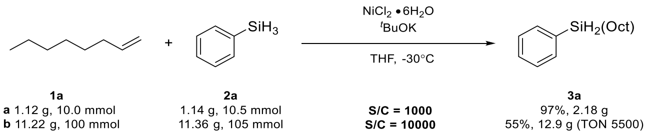
[a] General reaction conditions: olefin (**1**, 2.0 mmol), silane (**2**, 2.4 mmol), $NiCl_2·6H_2O$ (9.5 mg, 0.04 mmol, 2.0 mol %), ^tBuOK (9.0 mg, 0.08 mmol, 4.0 mol %), THF (3.0 mL), −30 °C, 1 h. The yields are isolated yields. [b] The reaction time was extended to 4 h. [c] $PhSiH_3$ (489 mg, 4.4 mmol, 2.2 equiv) was used. [d] The reaction temperature was set to −40 °C.

metal hydride-catalyzed reactions, retention of the internal alkenes and C−X bonds is difficult.[18] A variety of functional groups are well-tolerated to generate the corresponding products bearing pyridine (**1q**), furan (**1r**), thiophene (**1s**), indole (**1t**), benzotriazole (**1u**), epoxy (**1x** and **1y**), cyano (**1z**), acetal (**1bb**), ester (**1cc**), and amide (**1dd**) moieties in good yields (83−93%). Hydrosilylation of a strained imide substrate (**1ee**) proceeded in 71% yield, and the ketone substrate (**1aa**) was reduced to alcohol, as seen in our previous work.[19] The hydrosilylation of substrates containing N−H and O−H moieties ran along with intermolecular and intramolecular dehydrosilylation (Figure S1). In addition, styrene (**1e**) gave a mixture of linear and branched products in a 5:2 ratio and 94% yield.

The effect of hydrosilanes was also investigated. Alkyl silane **2ff** exhibited excellent reactivity to give **3ff** in 94% yield. An electron-donating aryl silane, such as a methoxyl group [p-$OMeC_6H_4SiH_3$ (**2hh**)], had no obvious impact on selectivity, and **3hh** was obtained in 95% yield; on the contrary, an electron-deficient aryl silane [p-$CF_3C_6H_4SiH_3$ (**2gg**)] gave its corresponding product in a comparatively lower yield because of the double hydrosilylation. With a further decrease in the reaction temperature to −40 °C, **3gg** was obtained in 92% yield. Conversely, secondary and tertiary silanes are not amenable to this protocol (Table S7).

To demonstrate the practical utility of this Ni-catalyzed hydrosilylation reaction, the model reaction was conducted on a gram scale with a lower catalyst loading. The hydrosilylation of 1-octene (**1a**) and $PhSiH_3$ (**2a**) worked well and afforded the corresponding product in 97% isolated yield (99% NMR yield), as illustrated in Scheme 3. So far, the highest turnover number (TON) for the reaction on an 11 g scale is up to 5500 over 12 h with a 0.01 mol % loading of $NiCl_2·6H_2O$.

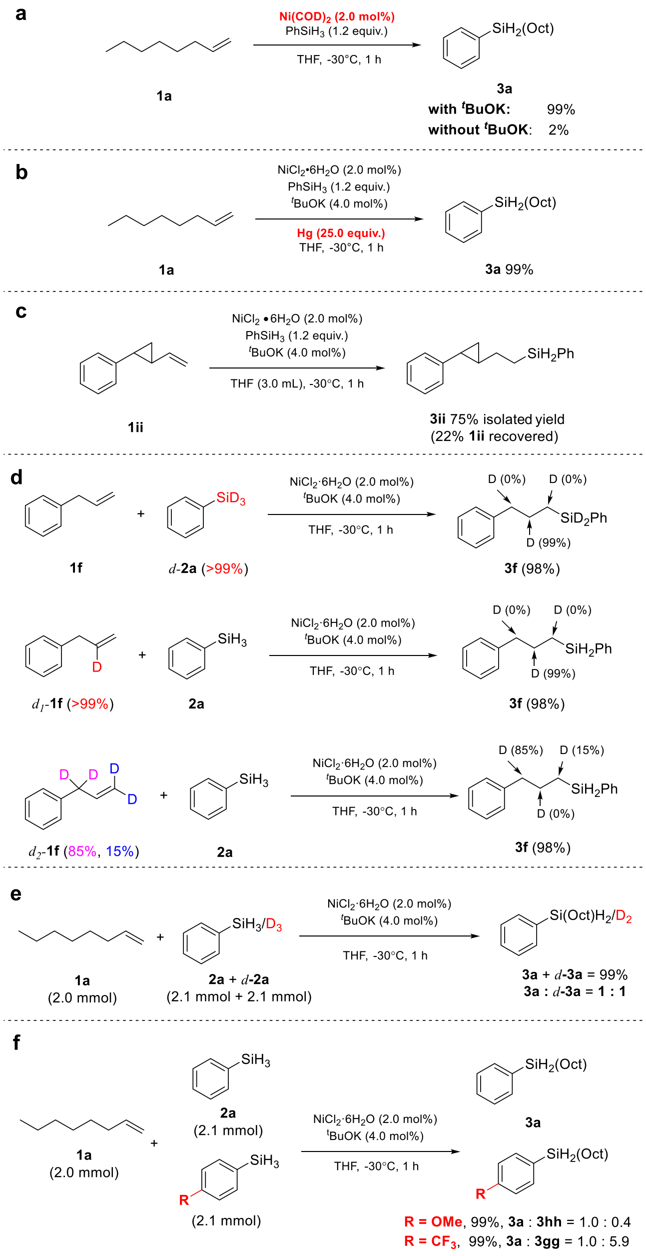
Scheme 3. Gram Scale Reaction and TON of the Hydrosilylation



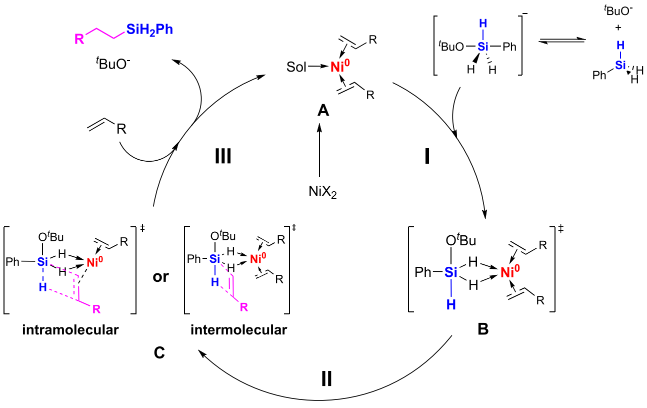
We next turned our attention to mechanistic investigations. The model reaction proceeded normally with $Ni(COD)_2$ instead of $NiCl_2·6H_2O$ under the standard conditions (Scheme 4a), but the reaction rate decreased significantly in the absence of ^tBuOK (Scheme 4b), suggesting that Ni(0) is the real catalytic species and the activator is crucial for the catalytic cycle. Although the reactions described previously provide a reasonable insight into the electrophilic Si−H bond activation (Table 1 and Scheme 2), detailed experiments were still needed. First, this system was confirmed to be homogeneous because the presence of Hg did not result in any deleterious effects on the model reaction (Scheme 4c). Next, a radical clock experiment with (2-vinylcyclopropyl)benzene (**1ii**) afforded normal addition product **3ii** in 75% yield with none of the ring-opened product being detected (Scheme 4d), showing that a radical process is not possible. Additionally, standard reactions with deuterated materials, d-**2a** and d-**1f**, were carried out independently, and no scrambling or dissociation of the deuterium was detected in the corresponding product **3f** (Scheme 4e); conversely, scrambling and dissociation of the deuterium caused by β-H elimination or allyl metallization are commonly observed in metal hydride-catalyzed reactions.[20] These results indicate that metal hydrides are not likely involved in this reaction.

Furthermore, we measured the kinetic data of the model reaction by ReactIR (Table S7). The reaction is first-order with regard to the catalyst [Ni] and silane [$PhSiH_3$], meaning that the Ni catalyst and silane are involved in the rate-determining step (RDS) as reactants. Meanwhile, the reaction is zero-order with respect to 1-octene concentration, meaning that olefin is not involved during the RDS and the addition between the Si−H bond and olefin is not the RDS. It was also confirmed by the kinetic isotope effect (KIE) experiments that the value of KIE in the hydrosilylation reaction with $PhSiH_3$/$PhSiD_3$ was determined to be 1.0 (Scheme 4e). Additionally, the electronic effect of the Si−H bond exhibited an obvious effect on the reaction rate (Scheme 4f). The electron-deficient silane (**2gg**) is more active to react than electron-donating silane p-$OMeC_6H_4SiH_3$ (**2hh**). Hence, we speculated that the electrophilic activation of the Si−H bond is probably the RDS.

Scheme 4. Mechanistic Studies



Scheme 5. Proposed Mechanism



On the basis of the evidence presented above, we have proposed a feasible reaction mechanism based on electrophilic Si−H bond activation, as illustrated in Scheme 5. The reaction begins with the reduction of nickel(II) to nickel(0) by the primary silane. To avoid deposition, the nickel(0) species are wrapped in complexes composed of alkene substrates and solvent molecules at low temperatures.[15a] It explains why coordinating solvents are beneficial for the reaction (Table S4). The activator, ^{t}BuOK, and silane are combined into an energetic pentacoordinate silicate. The RDS is the step **I** in which the Si−H bonds of the pentacoordinate silicate displace the weakly coordinated solvent molecule to form the active η^2-(Si-H)Ni(0) complex. This process completes the electrophilic activation of the Si−H bond, which can be observed by ^{1}H NMR (Figure S12).[21] Next, electrophilically intermolecular or intramolecular attack from the Si−H bond to alkene occurs and directly completes the addition. Then the secondary silane product and activator are released. In summary, this protocol undergoes an unconventional electrophilically activated hydrosilylation, differing from reported first-row metal-catalyzed hydrosilylation with primary silanes using Fe,[16a,21a,22] Co,[20a,23] Ni,[7b,24] Cu,[25] and Mn[26] catalysts.

In conclusion, a Ni-catalyzed selective anti-Markovnikov hydrosilylation of terminal alkenes in the absence of extra ligands has been developed. This protocol is economical and operationally simple. A new electrophilic hydrosilylation mechanism, rather than oxidative addition and radical mechanisms, has been proposed in which the C=C bond is attacked directly by an electrophilic Si−H bond with the assistance of a Ni(0) species and activator. Due to this unconventional mechanism, this reaction exhibits exclusive anti-Markovnikov selectivity for alkyl alkenes with a high TON (up to 5500) and broad tolerance for functionalized alkenes bearing sensitive groups, such as allyl ethers, halides, esters, amides, and various heterocycles, in good yields (71−94%). This electrophilic activation mode can be extended to a range of types of silanes with potential application for the synthesis of multifunctional silanes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00111.

Detailed experimental procedures, mechanistic studies, and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the financial support provided by the National Natural Science Foundation of China.

■ REFERENCES

(1) Rappoport, Z.; Apeloig, Y. *The Chemistry of Organic Silicon Compounds*; Wiley, 2001; Vol. 3.

(2) Obligacion, J. V.; Chirik, P. J. Earth-abundant transition metal catalysts for alkene hydrosilylation and hydroboration. *Nat. Rev. Chem.* **2018**, *2*, 15−34.

(3) Marciniec, B. *Hydrosilylation: A Comprehensive Review on Recent Advances*; Springer, 2009.

(4) (a) Troegel, D.; Stohrer, J. Recent advances and actual challenges in late transition metal catalyzed hydrosilylation of olefins from an industrial point of view. *Coord. Chem. Rev.* **2011**, *255*, 1440−1459. (b) Nakajima, Y.; Shimada, S. Hydrosilylation reaction of olefins: recent advances and perspectives. *RSC Adv.* **2015**, *5*, 20603−20616.

(5) (a) Sanagawa, A.; Nagashima, H. Cobalt(0) and Iron(0) Isocyanides as Catalysts for Alkene Hydrosilylation with Hydrosiloxanes. *Organometallics* **2018**, *37*, 2859−2871. (b) Noda, D.; Tahara, A.; Sunada, Y.; Nagashima, H. Non-Precious-Metal Catalytic Systems Involving Iron or Cobalt Carboxylates and Alkyl Isocyanides for Hydrosilylation of Alkenes with Hydrosiloxanes. *J. Am. Chem. Soc.* **2016**, *138*, 2480−2483. (c) Du, X.; Huang, Z. Advances in Base-Metal-Catalyzed Alkene Hydrosilylation. *ACS Catal.* **2017**, *7*, 1227−1243. (d) Sun, J.; Deng, L. Cobalt Complex-Catalyzed Hydrosilylation of Alkenes and Alkynes. *ACS Catal.* **2016**, *6*, 290−300. (e) Zaranek, M.; Pawluc, P. Markovnikov Hydrosilylation of Alkenes: How an Oddity Becomes the Goal. *ACS Catal.* **2018**, *8*, 9865−9876. (f) Buslov, I.; Keller, S. C.; Hu, X. Alkoxy Hydrosilanes As Surrogates of Gaseous Silanes for Hydrosilylation of Alkenes. *Org. Lett.* **2016**, *18*, 1928−1931. (g) Buslov, I.; Becouse, J.; Mazza, S.; Montandon-Clerc, M.; Hu, X. Chemoselective Alkene Hydrosilylation Catalyzed by Nickel Pincer Complexes. *Angew. Chem., Int. Ed.* **2015**, *54*, 14523−14526.

(6) (a) Galeandro-Diamant, T.; Suleimanov, I.; Veyre, L.; Bousquié, M.; Meille, V.; Thieuleux, C. Alkene hydrosilylation with supported and unsupported Ni nanoparticles: strong influence of the Ni environment on activity and selectivity. *Catal. Sci. Technol.* **2019**, *9*, 1555−1558. (b) Mitsudome, T.; Fujita, S.; Sheng, M.; Yamasaki, J.; Kobayashi, K.; Yoshida, T.; Maeno, Z.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. Air-stable and reusable cobalt ion-doped titanium oxide catalyst for alkene hydrosilylation. *Green Chem.* **2019**, *21*, 4566−4570. (c) Cao, L.; Lin, Z.; Peng, F.; Wang, W.; Huang, R.; Wang, C.; Yan, J.; Liang, J.; Zhang, Z.; Zhang, T.; Long, L.; Sun, J.; Lin, W. Self-Supporting Metal−Organic Layers as Single-Site Solid Catalysts. *Angew. Chem., Int. Ed.* **2016**, *55*, 4962−4966. (d) Jakoobi, M.; Dardun, V.; Veyre, L.; Meille, V.; Camp, C.; Thieuleux, C. Developing a Highly Active Catalytic System Based on Cobalt Nanoparticles for Terminal and Internal Alkene Hydrosilylation. *J. Org. Chem.* **2020**, *85*, 11732−11740. (e) Buslov, I.; Song, F.; Hu, X. An Easily Accessed Nickel Nanoparticle Catalyst for Alkene Hydrosilylation with Tertiary Silanes. *Angew. Chem., Int. Ed.* **2016**, *55*, 12295−12299.

(7) (a) Yang, X.; Wang, C. Diverse Fates of β-Silyl Radical under Manganese Catalysis: Hydrosilylation and Dehydrogenative Silylation of Alkenes. *Chin. J. Chem.* **2018**, *36*, 1047−1051. (b) Vijaykumar, G.; Pariyar, A.; Ahmed, J.; Shaw, B. K.; Adhikari, D.; Mandal, S. K. Tuning the redox non-innocence of a phenalenyl ligand toward efficient nickel-assisted catalytic hydrosilylation. *Chem. Sci.* **2018**, *9*, 2817−2825. (c) Dong, J.; Yuan, X.-A.; Yan, Z.; Mu, L.; Ma, J.; Zhu, C.; Xie, J. Manganese-catalysed divergent silylation of alkenes. *Nat. Chem.* **2020**, DOI: 10.1038/s41557-020-00589-8.

(8) (a) Matthews, S. L.; Pons, V.; Heinekey, D. M. Silane Complexes of Electrophilic Metal Centers. *Inorg. Chem.* **2006**, *45*, 6453−6459. (b) Lipke, M. C.; Liberman-Martin, A. L.; Tilley, T. D. Electrophilic Activation of Silicon-Hydrogen Bonds in Catalytic Hydrosilations. *Angew. Chem., Int. Ed.* **2017**, *56*, 2260−2294.

(9) (a) Power, P. P. Main-group elements as transition metals. *Nature* **2010**, *463*, 171−177. (b) Oestreich, M.; Hermeke, J.; Mohr, J. A unified survey of Si−H and H−H bond activation catalysed by electron-deficient boranes. *Chem. Soc. Rev.* **2015**, *44*, 2202−2220.

(10) (a) Lipke, M. C.; Poradowski, M.-N.; Raynaud, C.; Eisenstein, O.; Tilley, T. D. Catalytic Olefin Hydrosilations Mediated by Ruthenium η^3-H_2Si σ Complexes of Primary and Secondary Silanes. *ACS Catal.* **2018**, *8*, 11513−11523. (b) Fasulo, M. E.; Lipke, M. C.; Tilley, T. D. Structural and mechanistic investigation of a cationic hydrogen-substituted ruthenium silylene catalyst for alkene hydrosilation. *Chem. Sci.* **2013**, *4*, 3882−3887. (c) Calimano, E.; Tilley, T. D. Alkene Hydrosilation by a Cationic Hydrogen-Substituted Iridium Silylene Complex. *J. Am. Chem. Soc.* **2008**, *130*, 9226−9227.

(11) (a) Schubert, U. η^2 Coordination of Si−H σ Bonds to Transition Metals. *Adv. Organomet. Chem.* **1990**, *30*, 151−187. (b) Nikonov, G. I. New types of non-classical interligand interactions involving silicon based ligands. *J. Organomet. Chem.* **2001**, *635*, 24−36. (c) Lin, Z. Structural and bonding characteristics in transition metal−silane complexes. *Chem. Soc. Rev.* **2002**, *31*, 239−245. (d) Crabtree, R. H. Transition Metal Complexation of σ Bonds. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789−805.

(12) (a) Tanabe, M.; Kamono, M.; Tanaka, K.; Osakada, K. Triangular Triplatinum Complex with Four Bridging Si Ligands: Dynamic Behavior of the Molecule and Catalysis. *Organometallics* **2017**, *36*, 1929−1935. (b) Tanabe, M.; Yumoto, R.; Osakada, K. Reaction of an alkyne with dinickel-diphenylsilyl complexes. An emissive disilane formed via the consecutive Si−C and Si−Si bond-making processes. *Chem. Commun.* **2012**, *48*, 2125−2127. (c) Beck, R.; Johnson, S. A. Structural Similarities in Dinuclear, Tetranuclear, and Pentanuclear Nickel Silyl and Silylene Complexes Obtained via Si−H and Si−C Activation. *Organometallics* **2012**, *31*, 3599−3609.

(13) (a) Wu, S.; Li, X.; Xiong, Z.; Xu, W.; Lu, Y.; Sun, H. Synthesis and Reactivity of Silyl Iron, Cobalt, and Nickel Complexes Bearing a [PSiP]-Pincer Ligand via Si−H Bond Activation. *Organometallics*

2013, *32*, 3227−3237. (b) Takaya, J.; Iwasawa, N. Reaction of bis(o-phosphinophenyl)silane with M(PPh_3)$_4$ (M = Ni, Pd, Pt): synthesis and structural analysis of η^2-(Si−H) metal(0) and pentacoordinate silyl metal(ii) hydride complexes of the Ni triad bearing a PSiP-pincer ligand. *Dalton Trans.* **2011**, *40*, 8814−8821.

(14) (a) Corey, J. Y. Reactions of Hydrosilanes with Transition Metal Complexes. *Chem. Rev.* **2016**, *116*, 11291−11435. (b) Corey, J. Y.; Braddock-Wilking, J. Reactions of Hydrosilanes with Transition-Metal Complexes: Formation of Stable Transition-Metal Silyl Compounds. *Chem. Rev.* **1999**, *99*, 175−292.

(15) (a) Nattmann, L.; Saeb, R.; Nöthling, N.; Cornella, J. An air-stable binary Ni(0)−olefin catalyst. *Nat. Catal.* **2020**, *3*, 6−13. (b) Tran, V. T.; Li, Z. Q.; Apolinar, O.; Derosa, J.; Joannou, M. V.; Wisniewski, S. R.; Eastgate, M. D.; Engle, K. M. Ni(COD)(DQ): An Air-Stable 18-Electron Nickel(0)-Olefin Precatalyst. *Angew. Chem., Int. Ed.* **2020**, *59*, 7409−7413.

(16) (a) Docherty, J. H.; Peng, J.; Dominey, A. P.; Thomas, S. P. Activation and discovery of earth-abundant metal catalysts using sodium tert-butoxide. *Nat. Chem.* **2017**, *9*, 595. (b) Asgari, P.; Hua, Y.; Bokka, A.; Thiamsiri, C.; Prasitwatcharakorn, W.; Karedath, A.; Chen, X.; Sardar, S.; Yum, K.; Leem, G.; Pierce, B. S.; Nam, K.; Gao, J.; Jeon, J. Catalytic hydrogen atom transfer from hydrosilanes to vinylarenes for hydrosilylation and polymerization. *Nat. Catal.* **2019**, *2*, 164−173. (c) Toutov, A. A.; Liu, W.-B.; Betz, K. N.; Fedorov, A.; Stoltz, B. M.; Grubbs, R. H. Silylation of C-H bonds in aromatic heterocycles by an Earth-abundant metal catalyst. *Nature* **2015**, *518*, 80−84.

(17) (a) Liu, W.-B.; Schuman, D. P.; Yang, Y.-F.; Toutov, A. A.; Liang, Y.; Klare, H. F. T.; Nesnas, N.; Oestreich, M.; Blackmond, D. G.; Virgil, S. C.; Banerjee, S.; Zare, R. N.; Grubbs, R. H.; Houk, K. N.; Stoltz, B. M. Potassium tert-Butoxide-Catalyzed Dehydrogenative C−H Silylation of Heteroaromatics: A Combined Experimental and Computational Mechanistic Study. *J. Am. Chem. Soc.* **2017**, *139*, 6867−6879. (b) Banerjee, S.; Yang, Y.-F.; Jenkins, I. D.; Liang, Y.; Toutov, A. A.; Liu, W.-B.; Schuman, D. P.; Grubbs, R. H.; Stoltz, B. M.; Krenske, E. H.; Houk, K. N.; Zare, R. N. Ionic and Neutral Mechanisms for C−H Bond Silylation of Aromatic Heterocycles Catalyzed by Potassium tert-Butoxide. *J. Am. Chem. Soc.* **2017**, *139*, 6880−6887.

(18) Rock, C. L.; Trovitch, R. J. Anti-Markovnikov terminal and gem-olefin hydrosilylation using a κ^4-diimine nickel catalyst: selectivity for alkene hydrosilylation over ether C−O bond cleavage. *Dalton Trans.* **2019**, *48*, 461−467.

(19) Ding, G.; Li, C.; Shen, Y.; Lu, B.; Zhang, Z.; Xie, X. Potassium Hydroxide-Catalyzed Chemoselective Reduction of Cyclic Imides with Hydrosilanes: Synthesis of ω-Hydroxylactams and Lactams. *Adv. Synth. Catal.* **2016**, *358*, 1241−1250.

(20) (a) Wang, C.; Teo, W. J.; Ge, S. Cobalt-Catalyzed Regiodivergent Hydrosilylation of Vinylarenes and Aliphatic Alkenes: Ligand- and Silane-Dependent Regioselectivities. *ACS Catal.* **2017**, *7*, 855−863. (b) Pappas, I.; Treacy, S.; Chirik, P. J. Alkene Hydrosilylation Using Tertiary Silanes with α-Diimine Nickel Catalysts. Redox-Active Ligands Promote a Distinct Mechanistic Pathway from Platinum Catalysts. *ACS Catal.* **2016**, *6*, 4105−4109.

(21) (a) Bart, S. C.; Lobkovsky, E.; Chirik, P. J. Preparation and Molecular and Electronic Structures of Iron(0) Dinitrogen and Silane Complexes and Their Application to Catalytic Hydrogenation and Hydrosilation. *J. Am. Chem. Soc.* **2004**, *126*, 13794−13807. (b) Ohki, Y.; Kojima, T.; Oshima, M.; Suzuki, H. $\{(\eta^5\text{-}C_5Me_5)Fe\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}H_2SitBu_2)$, a Versatile Precursor for Bimetallic Active Species. *Organometallics* **2001**, *20*, 2654−2656. (c) Thomas, C. M.; Peters, J. C. An η^3-H_2SiR_2 Adduct of $[\{PhB(CH_2P^iPr_2)_3\}Fe^{II}H]$. *Angew. Chem.* **2006**, *118*, 790−794.

(22) (a) Greenhalgh, M. D.; Frank, D. J.; Thomas, S. P. Iron-Catalysed Chemo-, Regio-, and Stereoselective Hydrosilylation of Alkenes and Alkynes using a Bench-Stable Iron(II) Pre-Catalyst. *Adv. Synth. Catal.* **2014**, *356*, 584−590. (b) Du, X.; Zhang, Y.; Peng, D.; Huang, Z. Base−Metal-Catalyzed Regiodivergent Alkene Hydrosilylations. *Angew. Chem., Int. Ed.* **2016**, *55*, 6671−6675. (c) Hayasaka, K.; Kamata, K.; Nakazawa, H. Highly Efficient Olefin Hydrosilylation Catalyzed by Iron Complexes with Iminobipyridine Ligand. *Bull. Chem. Soc. Jpn.* **2016**, *89*, 394−404. (d) Cheng, B.; Liu, W.; Lu, Z. Iron-Catalyzed Highly Enantioselective Hydrosilylation of Unactivated Terminal Alkenes. *J. Am. Chem. Soc.* **2018**, *140*, 5014−5017. (e) Toya, Y.; Hayasaka, K.; Nakazawa, H. Hydrosilylation of Olefins Catalyzed by Iron Complexes Bearing Ketimine-Type Iminobipyridine Ligands. *Organometallics* **2017**, *36*, 1727−1735. (f) Hu, M.-Y.; He, Q.; Fan, S.-J.; Wang, Z.-C.; Liu, L.-Y.; Mu, Y.-J.; Peng, Q.; Zhu, S.-F. Ligands with 1,10-phenanthroline scaffold for highly regioselective iron-catalyzed alkene hydrosilylation. *Nat. Commun.* **2018**, *9*, 221.

(23) (a) Mo, Z.; Liu, Y.; Deng, L. Anchoring of Silyl Donors on a N-Heterocyclic Carbene through the Cobalt-Mediated Silylation of Benzylic C-H Bonds. *Angew. Chem., Int. Ed.* **2013**, *52*, 10845−10849. (b) Chen, C.; Hecht, M. B.; Kavara, A.; Brennessel, W. W.; Mercado, B. Q.; Weix, D. J.; Holland, P. L. Rapid, Regioconvergent, Solvent-Free Alkene Hydrosilylation with a Cobalt Catalyst. *J. Am. Chem. Soc.* **2015**, *137*, 13244−13247. (c) Gorczyński, A.; Zaranek, M.; Witomska, S.; Bocian, A.; Stefankiewicz, A. R.; Kubicki, M.; Patroniak, V.; Pawluć, P. The cobalt(II) complex of a new tridentate Schiff-base ligand as a catalyst for hydrosilylation of olefins. *Catal. Commun.* **2016**, *78*, 71−74. (d) Cheng, B.; Lu, P.; Zhang, H.; Cheng, X.; Lu, Z. Highly Enantioselective Cobalt-Catalyzed Hydrosilylation of Alkenes. *J. Am. Chem. Soc.* **2017**, *139*, 9439−9442. (e) Raya, B.; Jing, S.; Balasanthiran, V.; RajanBabu, T. V. Control of Selectivity through Synergy between Catalysts, Silanes, and Reaction Conditions in Cobalt-Catalyzed Hydrosilylation of Dienes and Terminal Alkenes. *ACS Catal.* **2017**, *7*, 2275−2283. (f) Gutiérrez-Tarriño, S.; Concepción, P.; Oña-Burgos, P. Cobalt Catalysts for Alkene Hydrosilylation under Aerobic Conditions without Dry Solvents or Additives. *Eur. J. Inorg. Chem.* **2018**, *2018*, 4867−4874.

(24) (a) Chen, Y.; Sui-Seng, C.; Boucher, S.; Zargarian, D. Influence of $SiMe_3$ Substituents on Structures and Hydrosilylation Activities of $((SiMe_3)_{1\text{ or }2}$-Indenyl)Ni($PPh_3$)Cl. *Organometallics* **2005**, *24*, 149−155. (b) Benítez Junquera, L.; Puerta, M. C.; Valerga, P. R-Allyl Nickel(II) Complexes with Chelating N-Heterocyclic Carbenes: Synthesis, Structural Characterization, and Catalytic Activity. *Organometallics* **2012**, *31*, 2175−2183. (c) Srinivas, V.; Nakajima, Y.; Ando, W.; Sato, K.; Shimada, S. (Salicylaldiminato)Ni(ii)-catalysts for hydrosilylation of olefins. *Catal. Sci. Technol.* **2015**, *5*, 2081−2084.

(25) Gribble, M. W.; Pirnot, M. T.; Bandar, J. S.; Liu, R. Y.; Buchwald, S. L. Asymmetric Copper Hydride-Catalyzed Markovnikov Hydrosilylation of Vinylarenes and Vinyl Heterocycles. *J. Am. Chem. Soc.* **2017**, *139*, 2192−2195.

(26) Carney, J. R.; Dillon, B. R.; Campbell, L.; Thomas, S. P. Manganese-Catalyzed Hydrofunctionalization of Alkenes. *Angew. Chem., Int. Ed.* **2018**, *57*, 10620−10624.