Hydrosilylation

International Edition: DOI: 10.1002/anie.201606832
German Edition: DOI: 10.1002/ange.201606832

An Easily Accessed Nickel Nanoparticle Catalyst for Alkene Hydrosilylation with Tertiary Silanes

*Ivan Buslov, Fang Song, and Xile Hu**

Abstract: *The first efficient and non-precious nanoparticle catalyst for alkene hydrosilylation with commercially relevant tertiary silanes has been developed. The nickel nanoparticle catalyst was prepared in situ from a simple nickel alkoxide precatalyst* $Ni(O^tBu)_2{\cdot}x\,KCl$. *The catalyst exhibits high activity for anti-Markovnikov hydrosilylation of unactivated terminal alkenes and isomerizing hydrosilylation of internal alkenes. The catalyst can be applied to synthesize a single terminal alkyl silane from a mixture of internal and terminal alkene isomers, and to remotely functionalize an internal alkene derived from a fatty acid.*

Hydrosilylation of alkenes is a main method to synthesize organosilicon compounds, which have broad applications in synthetic and material chemistry.[1] Platinum-based catalysts such as Karstedt's[2] and Speier's[3] catalysts are the most widely used in the industry owing to their stability, high activity, and broad scope. The high cost and low abundance of Pt have motivated the development of alternative catalysts based on Earth-abundant transition metals. While a number of systems based on Fe,[4] Co,[5] and Ni[6] complexes were shown to be efficient catalysts for hydrosilylation of alkenes, many of them are active only when using $PhSiH_3$ and Ph_2SiH_2 as hydrosilanes. The products of these reactions contain residual Si−H bonds, which leads to lower stability and utility of final products. Tertiary silanes are much more commercially relevant and are widely used to make silicones and silane coupling reagents. However, they are sterically demanding and less reactive. Chirik and co-workers showed that reducing the steric bulk of pyridine diimine (PDI) ligands enabled the first efficient iron-catalyzed alkene hydrosilylation using tertiary silanes.[7] This strategy proved successful in the development of several other Fe- and Co-based catalysts that hydrosilylated alkenes using tertiary silanes.[4c,8] Nevertheless, these catalysts employ designer ligands which can be expensive or difficult to make. Although Ni-based catalysts for alkene hydrosilylation are known,[6,9] only one system was shown to catalyze hydrosilylation of an unactivated alkene using a tertiary silane, and its scope was not reported.[10]

Compared to the significant progress of base metal-catalyzed homogeneous alkene hydrosilylation, the development of their heterogeneous counterparts falls much behind. Heterogeneous catalysts are potentially less costly and more amenable to immobilization and separation. Several heterogeneous Pt catalysts have been successfully used for alkene hydrosilylations.[11] Moreover, a recent study[11d] reopened the debates[12] on the nature of the active species, homogeneous or heterogeneous, formed upon activation of Karstedt's catalysts. However, to our knowledge, there is no prior report of non-precious metal nanoparticle catalysts capable of alkene hydrosilylation using tertiary silanes.[13] Herein we show that nickel nanoparticles catalyze hydrosilylation of unactivated alkenes with tertiary silanes. The nanoparticles can be easily accessed from in situ activation of a $Ni(O^tBu)_2{\cdot}x\,KCl$ precatalyst by the silane substrate. The precatalyst can be made in one step from stable and readily available reagents. Not only terminal alkenes are hydrosilylated with high anti-Markovnikov selectivity, but also internal alkenes are hydrosilylated through a tandem isomerization–hydrosilylation process to give terminal alkyl silanes. The catalytic system can be applied to synthesize a single terminal alkyl silane from a mixture of internal and terminal alkene isomers, and to remotely functionalize an internal alkene derived from a fatty acid.

We previously reported nickel pincer complexes as active alkene hydrosilylation catalysts.[6e] However, they were not efficient when using tertiary silanes. To develop catalysts for alkene hydrosilylation using tertiary silanes, we screened a large number of nickel alkoxide complexes with reduced steric bulk for the reaction of 1-decene with trimethoxysilane $(MeO)_3SiH$. Certain nickel complexes appeared to lose the ligands and decompose into black residues during the reaction; nevertheless, the desired hydrosilylation product was formed using these complexes. We hypothesized that these complexes were converted into nickel nanoparticles upon reaction with silane, which were responsible for the hydrosilylation activity. We then searched for simpler precursors of the presumed nickel nanoparticles which contained no designer ligands. A number of nickel salts including $Ni(OAc)_2$ (OAc = acetate), $Ni(OTf)_2$ (OTf = trifluoromethanesulfonate), $Ni(acac)_2$ (acac = acetylacetonate), and $Ni(OH)_2$ were tested, but the best yield, obtained using $Ni(acac)_2$, was only 23% (Supporting Information, Table S1). A Ni^0 source, $Ni(COD)_2$, was also ineffective, giving a yield of 5%. The use of Ni alkoxides, however, led to much higher yields. While a method employing anhydrous $NiCl_2$ was reported for the synthesis of $Ni(O^tBu)_2$,[14] we chose to prepare it by reaction of a soluble nickel source, $Ni(TMEDA)Cl_2$ (TMEDA = tetramethylethylenediamine)

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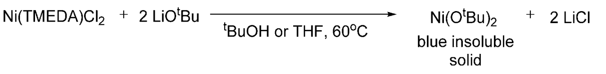
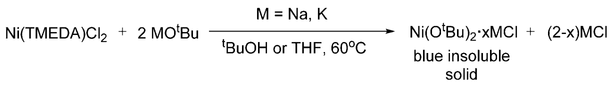
Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201606832.

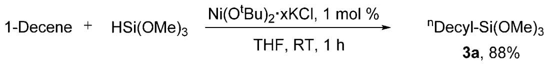
with MO^{t}Bu (M = Li, Na, K) in ^{t}BuOH or THF [Eq. (1), (2)]. The as-synthesized samples of Ni(O^{t}Bu)$_2$ are blue insoluble solids. The sample prepared using KO^{t}Bu was most active, giving a yield of 88 % at a loading of 1 mol % for the anti-Markovnikov hydrosilylation of 1-decene with (MeO)$_3$SiH [Eq. (3)]. Further experiments showed that the TON of this catalyst is higher than 850 and the TOF is about 1700 per hour for this reaction (see the Supporting Information). The samples prepared using NaO^{t}Bu and LiO^{t}Bu gave yields of 79 % and 28 %, respectively, under the same conditions. Infrared spectroscopy, power X-ray diffraction, elemental analysis, and transition electron microscopy (TEM) measurements indicated that Ni(O^{t}Bu)$_2$ in all samples were amorphous, and the samples prepared using NaO^{t}Bu and KO^{t}Bu contained additionally NaCl and KCl, respectively (Supporting Information, Figures S1–S8). For convenience, these two samples are labeled Ni(O^{t}Bu)$_2$·xNaCl ($x \approx 1.6$) and Ni(O^{t}Bu)$_2$·xKCl ($x \approx 1.4$).



$$\mathrm{Ni(TMEDA)Cl_2} + 2\,\mathrm{LiO^tBu} \xrightarrow[\mathrm{^tBuOH\ or\ THF,\ 60^oC}]{} \underset{\text{blue insoluble solid}}{\mathrm{Ni(O^tBu)_2}} + 2\,\mathrm{LiCl} \quad (1)$$



$$\mathrm{Ni(TMEDA)Cl_2} + 2\,\mathrm{MO^tBu} \xrightarrow[\mathrm{^tBuOH\ or\ THF,\ 60^oC}]{\mathrm{M = Na,\ K}} \underset{\text{blue insoluble solid}}{\mathrm{Ni(O^tBu)_2{\cdot}xMCl}} + (2\text{-}x)\mathrm{MCl} \quad (2)$$



$$\text{1-Decene} + \mathrm{HSi(OMe)_3} \xrightarrow[\text{THF, RT, 1 h}]{\mathrm{Ni(O^tBu)_2{\cdot}xKCl,\ 1\ mol\ \%}} \underset{\textbf{3a}\text{, 88\%}}{\mathrm{^nDecyl\text{-}Si(OMe)_3}} \quad (3)$$

During the hydrosilylation reaction, when (MeO)$_3$SiH was added to the reaction mixture containing the insoluble Ni(O^{t}Bu)$_2$·xKCl precatalyst, the latter solid immediately reacted and a dark brown solution was formed. We suspected that the Ni^{II} precatalyst was converted into colloidal nickel nanoparticles in this process, which is the active catalyst. When the reaction of 1-decene with (MeO)$_3$SiH was conducted in the presence of an excess of Hg (200 equiv relative to Ni), the yield of **3a** was only 20 %. This significant drop of yield is consistent with nickel nanoparticles being the catalyst. To confirm the formation of nickel nanoparticles, the colloidal solution was subjected to TEM measurements. Indeed, ultra-small nanocrystals were observed (Figure 1 a). The bright field image (Supporting Information, Figure S9) and corresponding high-angle annular dark field (HAADF) image (Figure 1 b) indicate that the nickel nanocrystals are regular over a large area. The size distribution of the nanocrystals is fairly narrow (Figure 1 c). The average size is about 3.5 nm. Lattice fringes were observed in high-resolution TEM images (Figure 1 d). The inter-planar distances of about 0.20 nm and about 0.18 nm correspond to the (111) and (020) planes of nickel metal (space group: $Fm\bar{3}m$, JCPDS No. 01-1258). This assignment was confirmed by the corresponding fast Fourier transformation (FFT) image (inset in Figure 1 d). The elemental mapping analysis showed that the nanocrystals were mainly made of Ni (Supporting Information, Figure S10).

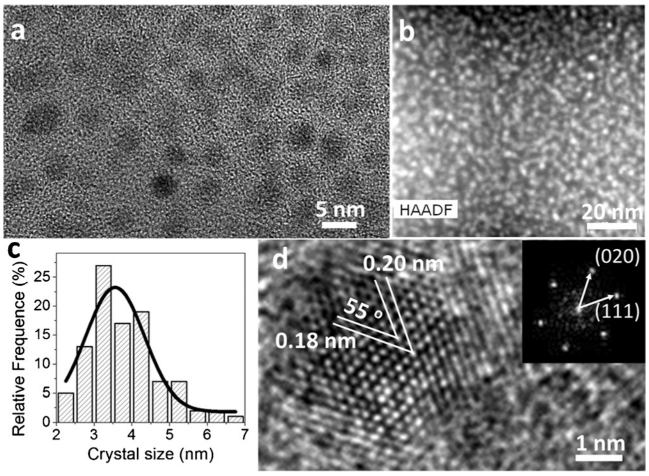


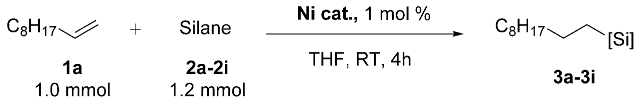
Figure 1. a) TEM image of nickel nanocrystals. b) HAADF image of nickel nanocrystals in large-area view. White dots in the HAADF image are nickel nanocrystals. c) Crystal size distribution. d) High-resolution TEM image of a nanocrystal. Inset: corresponding FFT image.

While the conversion of Ni(O^{t}Bu)$_2$·xKCl and Ni(O^{t}Bu)$_2$·xNaCl to nickel nanoparticles was observed instantaneously, the conversion of Ni(O^{t}Bu)$_2$ was slow and after 15 minutes, a large portion of Ni(O^{t}Bu)$_2$ was still observed by TEM (Supporting Information, Figure S11). To compare the stability of the nickel nanoparticles prepared from Ni(O^{t}Bu)$_2$·xKCl and Ni(O^{t}Bu)$_2$, aliquots of reaction mixture after 6 hours were analyzed by TEM (Supporting Information, Figure S12). The nanoparticles made from Ni(O^{t}Bu)$_2$·xKCl remained well-dispersed, while those from Ni(O^{t}Bu)$_2$ already aggregated. Thus, the lower efficiency of Ni(O^{t}Bu)$_2$ is attributed to its inefficiency to generate nickel nanoparticles, and maybe additionally the lower stability of the resulting nanoparticles. The presence of well-dispersed K$^+$ and Na$^+$ ions (Supporting Information, Figure S7) might influence the growth of nanoparticles via electrostatic interactions, as suggested for cation-dependent formation of nickel phosphate nanotubes in a recent report.[15] The Cl$^-$ anion might stabilize the nanoparticles against aggregation.

The UV/Vis spectrum of a colloidal solution containing the nickel nanoparticles is similar to the spectra of other reported colloidal nickel particles (Supporting Information, Figure S13).[16] This colloidal solution can be generated in the absence of an alkene, and can be then used as a catalyst for alkene hydrosilylation. For example, a catalyst solution was generated by reaction of Ni(O^{t}Bu)$_2$·xKCl with (MeO)$_3$SiH. When this solution was used as the catalyst (1 mol % loading) for the hydrosilylation of 1-decene with (EtO)$_3$SiH, a yield of 74 % was obtained. If nickel nanoparticles were removed from the solution after partial conversion by filtering through silica or celite, then the resulting solution was no longer catalytically active (see the Supporting Information). As mentioned above, other soluble nickel salts such as Ni(acac)$_2$ and Ni(COD)$_2$ were not suitable precatalysts for the hydrosilylation. When these complexes were used, no formation of nickel nanoparticles was observed.

The Ni(O^{t}Bu)$_2$·xKCl precatalyst was tested for hydrosilylation of 1-decene with other tertirary silanes at room

Table 1: Ni-catalyzed hydrosilylation of 1-decene with various silanes.[a]



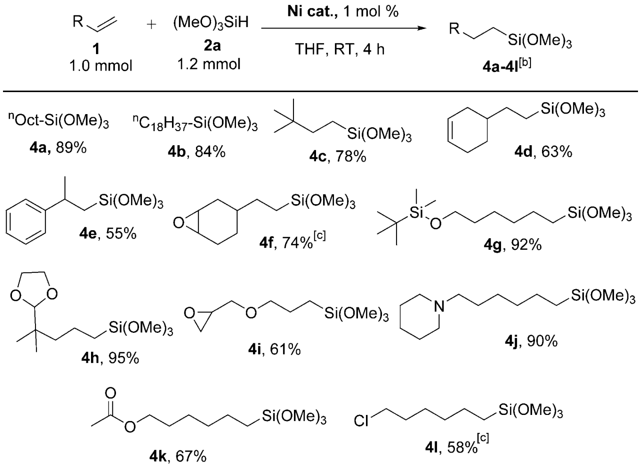
Entry	Silane	Yield [%][b]
1	$(MeO)_3SiH$	88 (86)
2	$(EtO)_3SiH$	91 (88)
3	$Me_2(MeO)SiH$	84 (83)
4	$Me(EtO)_2SiH$	81 (77)
5	PMDS	35
6	MD′M	14
7	Et_3SiH	6
8	Ph_3SiH	43 (44)
9	Ph_2SiH_2	82[c]
10	PMDS	55 (52)[d]
11	MD′M	24[d]

[a] Conditions: 1-decene (1 mmol), silane (1.2 mmol), Ni cat. (1 mol%), THF (2 mL), 4 h, RT. [b] Determined by GC-MS using dodecane as an internal standard. Numbers in parentheses are yields of isolated products. [c] 12% of didecyldiphenylsilane was formed. [d] Alkene 5 mmol, hydrosiloxane 6 mmol, Ni precat. 1 mol%, neat, 60 °C, 2 h. $(MeO)_3SiH$ 2 mol% was added as an activator.

temperature (Table 1). $(EtO)_3SiH$, $Me_2(MeO)SiH$, and $Me(EtO)_2SiH$ could be used, with yields of above 80% (**3b**–**3d**). For 1,1,3,3,3-pentamethyldisiloxane (PMDS) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD′M), the yields were lower, possibly due to the slow activation of the precatalyst (Table 1, entries 5 and 6). However, better conversion and yields were obtained with these silanes if a small amount of $(MeO)_3SiH$ was added to activate the precatalyst and if the temperature was increased to 60 °C (Table 1, entries 10 and 11). Trialkylsilane Et_3SiH was not applicable in this reaction (Table 1, entry 7). Interestingly, triphenylsilane, which was not capable of activating the bis(amino)amide nickel complex in our previous work,[6e] gave moderate yield of decyltriphenylsilane using new catalyst (Table 1, entry 8). According to GC-MS analysis, diphenylsilane formed $Ph_2(^nDec)SiH$ in 82% yield, contaminated with $Ph_2(^nDec)_2Si$ (Table 1, entry 9).

The scope of alkenes was then examined for this catalytic system using $(MeO)_3SiH$ as the silane. The reactions were performed with 1 mol% of Ni precatalyst in THF at room temperature. A large number of unactivated terminal alkenes could be hydrosilylated (Table 2). When both internal and terminal C=C double bonds are present, hydrosilylation is selective for the terminal double bond (**4d**). Importantly, functional groups such as epoxide (**4f**), tert-butyldimethylsilyl-protected alcohol (**4g**), acetal (**4h**), amine (**4j**), ester (**4k**), and alkyl chloride (**4l**) were tolerated. Allyl glycidyl ether is an important substrate because the alkoxysilanes derived from this alkene find broad applications in coatings and as coupling agents for epoxy composites employed for electronic chip encapsulation.[17] However, hydrosilylation of allyl esters of this type using Pt catalysts are known to lead to side reactions.[18] To our delight, the present nickel system is efficient for hydrosilylation of allyl glycidyl ether, giving **4i** in a 61% yield. More sensitive functional groups such as ketone, aldehyde, and amide are unfortunately not tolerated.

Table 2: Ni-catalyzed hydrosilylation of functionalized alkenes with $(MeO)_3SiH$.[a]

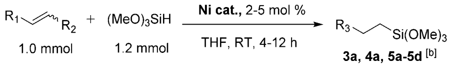


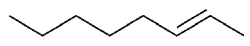
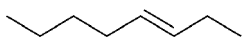
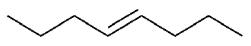
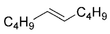
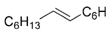
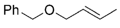
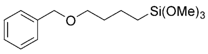
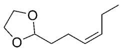
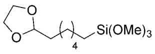
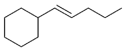
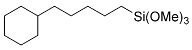
[a] Conditions : alkene (1.0 mmol), $(MeO)_3SiH$ (1.2 mmol), Ni cat. (1 mol%), THF (2 mL), 4 h, RT. [b] Yields of isolated products are reported. For **4d**, the conversion was 83%, and the amount of side-product silanes where the internal olefin was isomerized is less than 4%; for **4e**, the conversion was 60% and 2% cumene was obtained as a side product; for **4f**, the conversion was 75%; for **4k**, 24% isomerized internal alkenes and 6% of reduction product were also obtained. [c] $(MeO)_3SiH$ (1.5 mmol).

Internal alkenes are generally unsuitable substrates for alkene hydrosilylation. Only very recently a couple of Ni- and Co-based catalytic systems were shown to convert internal alkenes into terminal silanes through a tandem isomerization–hydrosilylation process.[8b,6e] In principle, this process can be used for the remote functionalization of alkenes, which has emerged as a desirable strategy in organic synthesis.[19] However, using the two reported catalytic systems, the tandem isomerization–hydrosilylation process remains sluggish. The scope is narrow and largely limited to simple 2-alkenes. The conversion is often incomplete. To our delight, the current system is very efficient for the tandem isomerization-hydrosilylation of various internal alkenes (Table 3). 2-, 3-, and 4-octenes were all selectively transformed to terminal trimethoxy(octyl)silane **4a** in high yields (Table 3, entries 1–3). Even 5-decene and 7-tetradecene were hydrosilylated in high yields and selectivities (Table 3, entries 4 and 5). It should be emphasized that for 7-tetradecene, the isomerization of alkene has to be repeated five times before being hydrosilylated. Not only simple and linear internal alkenes, but also those containing functional groups such as ether and acetal (Table 3, entries 6 and 7), as well as an alkene with a secondary alkyl substituent (Table 3, entry 8) could be used. Both *cis*- and *trans*-alkenes were selectively converted in high yields.

The unprecedented activity and selectivity of this nickel nanoparticle catalyst in the isomerization–hydrosilylation tandem process prompted us to further exploit its potential applications. Triethoxy(octyl)silane is widely used in coatings and is produced annually in a greater than 6000 ton scale.[1,8a] It might be economically advantageous to synthesize this silane from a mixture of octenes. To explore this possibility, an

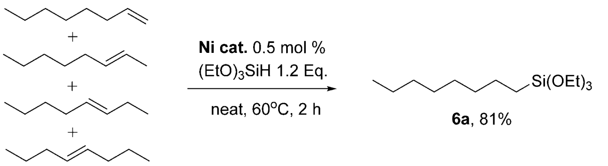
Table 3: Ni-catalyzed tandem isomerization-hydrosilylation of internal alkenes with (MeO)$_3$SiH.[a]



Entry	Substrate	Product		Yield[b] [%]
1		n-Octyl—Si(OMe)$_3$	**4a**	95[c]
2		n-Octyl—Si(OMe)$_3$	**4a**	97[c]
3		n-Octyl—Si(OMe)$_3$	**4a**	89
4		n-Decyl—Si(OMe)$_3$	**3a**	83
5		n-Tetradecyl—Si(OMe)$_3$	**5a**	71
6			**5b**	74[c]
7			**5c**	79
8			**5d**	69

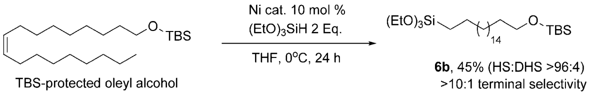
[a] Conditions: alkene (0.5 mmol), silane (1.2 equiv), Ni cat. (5 mol%), THF (3 mL), 12 h, RT. [b] Yields of isolated products are reported. [c] Ni cat. (2 mol%), 4 h.

equimolar mixture of 1-octene, 2-octene, 3-octene, and 4-octene was prepared and then subjected to the isomerization–hydrosilylation process using 0.5% of nickel catalyst and (EtO)$_3$SiH. After 2 hours at 60 °C, triethoxy(octyl)silane (**6a**) was obtained in a 81% yield with 96:4 HS/DHS selectivity [Eq. (4); HS = hydrosilylation; DHS = dehydrogenative silylation; triethoxy(oct-1-en-1-yl)silane was formed as the DHS by-product]. Thus, the current catalytic system is applicable for the synthesis of a single terminal alkyl silane from a mixture of different internal and terminal olefin isomers.



(4)

Unsaturated fatty acids from plant oils are easily available and are a unique class of chemical feedstock owing to their characteristic long-chain methylene sequences.[20] The generation of α,ω-difuntionalized compounds from plant oils while incorporating the entire length of fatty acids is attractive but challenging. We tested the current catalytic system for the isomerizing hydrosilylation of TBS-protected *cis*-9-octadecen-1-ol (oleyl alcohol, 85% purity; TBS = tert-butyldimethylsilyl). With 10 mol% of Ni precatalyst and using triethoxysilane at 0°C, the linear and saturated product, O-tert-butyldimethylsilyl 18-(triethoxysilyl)octadecan-1-ol (**6b**), was obtained in a 45% yield [Eq. (5); the conversion was 80%]. The reaction had good HS/DHS (> 94:6) and terminal selectivity (> 10:1). The isomerization propagated over 8 carbon–carbon bonds from the initial position of the double bond. It should be noted that the corresponding terminal olefin is not available from a mixture of monounsaturated fatty acids. Thus, the current catalyst system is potentially useful for the utilization of renewable feedstock materials.



(5)

In summary, a new nickel nanoparticle catalyst has been developed for the hydrosilylation of unactivated alkenes with tertiary silanes. The catalyst can be easily prepared in situ from a simple Ni(O^{t}Bu)$_2$·xKCl precatalyst. The catalyst catalyzes anti-Markovnikov hydrosilylation of terminal alkenes and isomerizing hydrosilylation of internal alkenes. The catalyst can be applied to synthesize single terminal alkyl silanes from a mixture of alkene isomers, and convert fatty acid-derived internal alkenes into α,ω-difuntionalized compounds.

Acknowledgements

This work is supported by the Swiss National Science Foundation (200020_162362).

Keywords: hydrosilylation · isomerization · nanoparticles · nickel · tertiary silanes

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 12295–12299
Angew. Chem. **2016**, *128*, 12483–12487

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Received: July 14, 2016