

# Alkoxy Hydrosilanes As Surrogates of Gaseous Silanes for Hydrosilylation of Alkenes

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**Supporting Information** 

**ABSTRACT:** Me<sub>2</sub>SiH<sub>2</sub>, MeSiH<sub>3</sub>, and SiH<sub>4</sub> are gaseous and flammable silanes that are inconvenient to use in chemical reactions. Catalytic amounts of a nickel pincer complex and NaO<sup>t</sup>Bu are reported to allow the synthesis of alkyl hydrosilanes from alkenes and alkoxy hydrosilanes, leading to the replacement of Me<sub>2</sub>SiH<sub>2</sub>, MeSiH<sub>3</sub>, and SiH<sub>4</sub> by Me<sub>2</sub>(MeO)SiH, Me(EtO)<sub>2</sub>SiH, and (MeO)<sub>3</sub>SiH in hydrosilylation reactions of alkenes. The scope and mechanism of the reactions are also described.

 $\frac{1}{1}$   $\frac{1}{25 \text{ examples}}$   $\frac{1}{1}$   $\frac{1}{25 \text{ examples}}$   $\frac{1}{1}$   $\frac{1}{1}$ 

 $\mathbf{C}$  ilanes such as Me<sub>2</sub>SiH<sub>2</sub>, MeSiH<sub>3</sub>, and SiH<sub>4</sub> (boiling points  $\bigcirc$  of -20, -57, and -112 °C, respectively) are flammable gases at room temperature and are inconvenient to handle on a laboratory scale.<sup>1a</sup> Moreover, SiH<sub>4</sub> is pyrophoric and causes severe safety concerns.<sup>1b</sup> As a result, these silanes are rarely applied in the hydrosilylation of alkenes,<sup>2</sup> which is one of the most important methods to produce silicon coupling reagents, silicon polymers, and organosilicon compounds for fine chemical synthesis.<sup>3</sup> Oestreich and co-workers recently developed an elegant approach using 3-silylated cyclohexa-1,4-dienes, activated by  $B(C_6F_5)_3$ , as precursors for gaseous hydrosilanes (eqs 1-2, Scheme 1).<sup>4</sup> However, the scope and tolerance of this method remain modest due to the reactive  $B(C_6F_5)_3$  catalyst. Herein we report that readily available alkoxy hydrosilanes can be used as surrogates of Me<sub>2</sub>SiH<sub>2</sub>, MeSiH<sub>3</sub>, and SiH<sub>4</sub> in Ni-catalyzed hydrosilylation of alkenes (eq 3, Scheme 1), yielding alkyl hydrosilanes otherwise difficult to

# Scheme 1. Development of Surrogates of Gaseous Silanes



access. A broad scope and good functional group compatibility have been achieved.

While studying Ni-catalyzed hydrosilylation of alkenes,<sup>5</sup> we tested different nickel complexes for hydrosilylation using tertiary silanes. Unexpectedly, in the reaction of 1-octene with  $Ph_2(OMe)SiH$  using the nickel amido(bisoxazoline) complex, [iPr<sub>2</sub>-(*S*,*S*)-Bopa]NiCl (**1a**) as precatalyst and NaO<sup>t</sup>Bu as base,  $Ph_2(Octyl)SiH$  was isolated in an 81% yield (relative to 1-octene, eq 4). The conventional hydrosilylation product,

$$\begin{array}{cccc} \text{1a, 2.5 mol \%} & \text{Ph} \\ \text{NaOtBu, 3 mol \%} & \xrightarrow{\text{nOctyl} - \overset{\text{Si}-H}{\overset{\text{Si}-H}}} & (4) \\ \hline & \text{THF, rt} & \overset{\text{Ph}}{\overset{\text{NaOtBu, 3 mol \%}}} \end{array}$$

 $Ph_2(Octyl)(OMe)Si$ , was not formed. Recognizing that this unusual transformation might allow the replacement of certain silanes by alkoxy hydrosilanes in hydrosilylation reactions, we decided to further explore it.

The reaction of 1-decene with  $Me_2(MeO)SiH$  was chosen as the test reaction for the optimization of conditions (Table 1).<sup>6</sup> In tetrahydrofuran (THF) and at room temperature, (Decyl)-(Me)<sub>2</sub>SiH was formed in a 91% yield using 2.5 mol % of 1a as catalyst and 5 mol % of NaOtBu as base (entry 1, Table 1).  $Me_2(MeO)_2Si$  was the byproduct. If NaO<sup>t</sup>Bu was replaced by CsF, the yield was less than 1% (entry 2, Table 1). The yields were lower when THF was replaced by toluene or diethyl ether (entries 3–4, Table 1). When 1a was replaced by its phenyl analogue, [Ph<sub>2</sub>-(*R*,*R*)-Bopa]NiCl (1b), the yield dropped to 59% (entry 5, Table 1). Two other Ni pincer complexes, 1c and 1d, were also tested as catalysts. However, the yields were

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# Table 1. Optimization of Reaction Conditions<sup>a</sup>



<sup>*a*</sup>Conditions: 1-decene (0.5 mmol), dimethylmethoxysilane (1.2 mmol), under N<sub>2</sub> in THF (4 mL), 12 h, rt. <sup>*b*</sup>GC-MS yields are reported, and *n*-dodecane was used as an internal standard. The yield is relative to 3a.

below 50% (entries 6–7, Table 1). A soluble Ni(II) complex, NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, was also tested as a catalyst, but again the yield was modest (entry 8, Table 1). These results confirmed the superior catalytic activity of 1a in this reaction. When the loading of 1a was reduced to 1 mol %, the yield was nearly the same (87%; entry 9, Table 1). When 1 equiv of NaO<sup>t</sup>Bu relative to 1a was added, no (Decyl)(Me)<sub>2</sub>SiH was formed (entry 10, Table 1). When NaO<sup>t</sup>Bu was replaced by KO<sup>t</sup>Bu, the yield was similar (entry 11, Table 1).

The optimized conditions were applied for the reactions of  $Me_2(MeO)SiH$  with various terminal alkenes (Scheme 2). 1-Decene and 1-octadecene were hydrosilylated with high yields (4a, 4b). 2-Methyl-2-heptene, which contained a methyl group at the  $\beta$ -position of the alkene, was also converted to the corresponding hydrosilane in a good yield (4c). The reaction was selective for the terminal C=C bond while leaving an internal C=C bond intact (4e). Functional groups such as ether (4f), epoxide (4g), tert-butyldimethylsilyl- (4h) and tetrahydropyran-protected alcohol (4i), alkyl halide (4j), amine (4k), and acetal (4l) were tolerated in the catalysis. Unfortunately alkenes bearing carbonyl, ester, amide, and imide groups were not suitable reaction partners, likely due to the high reducing power of silanes in the presence of a base.<sup>7,8</sup>

Next, the reactions of alkenes with  $Me(EtO)_2SiH$  and  $(MeO)_3SiH$  were investigated. To our delight, the reactions gave various functionalized hydrosilanes in good yields (**5a**–**6f**, **Scheme 3**). An increase of the loading of the catalyst to 5 mol % was necessary. For the reactions of alkenes with Me- $(EtO)_2SiH$ ,  $(Alkyl)_2(Me)SiH$  was formed, in which the two alkyl groups came from the alkene. Interestingly, for the reactions of alkenes with  $(MeO)_3SiH$ ,  $(Alkyl)_2SiH_2$  was obtained as the major product, and only less than 3% of  $(Alkyl)_3SiH$  was detected by GC-MS. Even when the alkene was in large excess (6 equiv) and the reaction time was increased to 36 h, the yield of  $(Alkyl)_3SiH$  did not exceed 6%.





<sup>*a*</sup>Conditions: alkene (0.5 mmol), dimethylmethoxysilane (1.2 mmol), **1a** (2.5 mol %), NaO<sup>t</sup>Bu (5 mol %), THF (3 mL), 6 h, rt. <sup>*b*</sup>Isolated yields relative to alkene are reported. <sup>*c*</sup>GC-MS yields using *n*-dodecane as an internal standard are reported in parentheses. <sup>*d*</sup>Alkene (0.5 mmol), dimethylmethoxysilane (2.5 mmol), 24 h. <sup>*e*</sup>Alkene (0.5 mmol), **2a** (2.0 mmol).

# Scheme 3. Ni-Catalyzed Synthesis of Alkyl Hydrosilanes Using 2b–2c and Alkenes<sup>a</sup>



<sup>*a*</sup>Typical conditions: for reactions with **2b**, alkene (1.2 mmol), methyldiethoxysilane (1.5 mmol), **1a** (5 mol %), NaO<sup>t</sup>Bu (10 mol %), THF (4 mL), 24 h, rt; for reaction with **2c**, alkene (1.5 mmol), trimethoxysilane (2 mmol), **1a** (5 mol %), NaO<sup>t</sup>Bu (10 mol %), THF (4 mL), 24 h, rt. <sup>*b*</sup>Isolated yields relative to intermediate silanes are reported. The theoretical yield of **5a–6f** is 0.5 mmol. <sup>*c*</sup>Alkene (1.35 mmol) was used. <sup>*d*</sup>Alkene (1.8 mmol) was used.

The reaction of isolated dioctadecylsilane (6a) with 1.2 equiv of 1-octadecene under the conditions of Scheme 3 was then

monitored by <sup>1</sup>H NMR. (n-Octadecyl)<sub>2</sub>SiH<sub>2</sub> (**6a**) was fully consumed in 1.5 h, and (n-octadecyl)<sub>3</sub>SiH was produced in a nearly quantitative yield. On the other hand, if 3 equiv of  $(MeO)_4$ Si were added to the reaction mixture, the conversion of **6a** was less than 40% in 6 h. This result suggests that the  $(MeO)_4$ Si byproduct inhibits the hydrosilylation of alkenes **6a**–**6f** with  $(alkyl)_2$ SiH<sub>2</sub>, leading to selective formation of dialkylsilanes in the reaction of alkenes with  $(MeO)_3$ SiH.

The above reactions could be applied for the synthesis of alkyl hydrosilanes containing different alkyl groups. For example (2-(cyclohex-3-en-1-yl)ethyl)(methyl)(octyl)silane (7a) was obtained in a 68% yield by stepwise addition of 1-octene and 4-vinylcyclohex-1-ene (eq 5).



Several experiments were carried out to provide preliminary mechanistic insights into these reactions. The addition of a catalytic amount of NaO<sup>t</sup>Bu to Me<sub>2</sub>(MeO)SiH led to a quick release of Me<sub>2</sub>SiH<sub>2</sub>, detected by <sup>1</sup>H NMR. Likewise, the addition of a catalytic amount of NaO<sup>t</sup>Bu to (MeO)<sub>3</sub>SiH led to the formation of SiH<sub>4</sub>, again detected by <sup>1</sup>H NMR. Thus, the alkoxysilanes were proposed to react first with a base to give hydrosilanes in a sequence shown in eqs 6–7, Scheme 4.



Nucleophilic attack of an alkoxide anion on Me<sub>2</sub>(MeO)SiH gave the five-coordinate species (A), which reacted with another molecule of Me<sub>2</sub>(MeO)SiH to produce Me<sub>2</sub>SiH<sub>2</sub> and  $Me_2(MeO)_2Si$ , in a disproportionation manner. The base was also regenerated in this step. Similar base-catalyzed disproportionation reactions of alkoxysilanes were previously reported.<sup>9</sup> The disproportionation of alkoxysilanes was followed by <sup>1</sup>H NMR. Me<sub>2</sub>(MeO)SiH was converted to Me<sub>2</sub>SiH<sub>2</sub> and Me<sub>2</sub>(MeO)<sub>2</sub>Si under 0.5 mol % of NaO<sup>t</sup>Bu in THF-d8 in 50 min. An analogous reaction of Me(EtO)<sub>2</sub>SiH required 20 min to complete. The dispropotionation of trialkoxysilane (MeO)<sub>3</sub>SiH was even faster: in the presence of 0.1 mol % of NaO<sup>t</sup>Bu the conversion was completed after 5 min. Thus, the rate of disproportionation follows the order:  $(MeO)_3SiH > Me(EtO)_2SiH > Me_2(MeO)SiH$ . It was noted that the nickel complex did not accelerate the rate of disproportionation (see Supporting Information).

Complex 1a was found to be an efficient catalyst for the hydrosilylation of 1-octene by  $Ph_2SiH_2$  and  $Et_2SiH_2$  in the presence of 1 equiv of NaO<sup>t</sup>Bu (relative to 1a), giving the

respective hydrosilanes in good yields (eq 8, Scheme 4). Accordingly, we propose that the present reactions proceed first by base-catalyzed disproportionation of alkoxysilanes to give hydrosilanes; upon catalysis by 1a, hydrosilylated alkenes gave the alkylhydrosilanes.

Because Me<sub>2</sub>SiH<sub>2</sub>, MeSiH<sub>3</sub>, and SiH<sub>4</sub> were proposed as intermediates in the hydrosilylation reactions reported here, it is important to compare the rate of their generation and that of hydrosilylation. For large scale applications, the rate of hydrosilylation should be faster than the rate of disproportionation in order to avoid the buildup of flammable intermediates, especially the pyrophoric SiH<sub>4</sub>. When an actual reaction of 1-decene with Me<sub>2</sub>(MeO)SiH was monitored by <sup>1</sup>H NMR, a substoichiometric amount of Me<sub>2</sub>SiH<sub>2</sub> was detected in the beginning, but it disappeared after 15 min. This result suggests that the generation of Me<sub>2</sub>SiH<sub>2</sub> is faster than hydrosilylation, but hydrosilylation is sufficiently fast so that the intermediate is quickly consumed. In the reaction of 1decene with Me(EtO)2SiH, only Me(Decyl)SiH2, but not MeSiH<sub>3</sub>, was detected as an intermediate in the beginning of the reaction. This result suggests that hydrosilylation is faster than the generation of MeSiH<sub>3</sub>. And in an actual reaction of 1decene with (MeO)<sub>3</sub>SiH, no SiH<sub>4</sub> was detected by <sup>1</sup>H NMR. The above-mentioned results suggest that the reactions of alkenes with Me(EtO)<sub>2</sub>SiH or (MeO)<sub>3</sub>SiH described here are potentially suitable for large scale applications because there was no significant buildup of flammable MeSiH<sub>3</sub> or pyrophoric SiH<sub>4</sub>.<sup>10</sup> Even the reactions of alkenes with Me<sub>2</sub>(MeO)SiH might be suitable for large scale application given proper handling, because only a small amount of Me<sub>2</sub>SiH<sub>2</sub> was formed as an intermediate in the beginning of the reaction. Me<sub>2</sub>SiH<sub>2</sub> has good solubility in organic solvents and is not pyrophoric.

The superior activity of 1a compared to other nickel complexes (Table 1) is tentatively attributed to the former's inability to catalyze isomerization of alkenes under basic conditions, as well as its low efficiency for the hydrosilylation with alkoxysilanes. It was found that, under the reaction conditions of Table 1, various amounts of internal alkenes were formed using 1b-1d and  $NiCl_2(PPh_3)_2$  as catalysts. Only a minor amount of internal decenes were formed during the reaction (<5% by GCMS) when 1a was used as the catalyst. Moreover, less than 3% of conventional hydrosilylation product  $(Decyl)(Me)_2Si(OMe)$  was formed in the reaction of 1-decene with Me<sub>2</sub>(MeO)SiH using **1a** as precatalyst, while up to 19% of this compound was formed using other nickel catalysts in Table 1. Likewise, for the reactions with 2b and 2c (Scheme 3) using 1a as precatalyst, only 3-8% of conventional hydrosilylation products were formed.

In summary, we have developed a novel catalytic method allowing the use of alkoxy hydrosilanes as surrogates of gaseous silanes in hydrosilylation reactions of alkenes. While serving as a convenient and safer alternative to methods directly using  $Me_2SiH_2$ ,  $MeSiH_3$ , and  $SiH_4$ , the present approach actually facilitates the "formal" use of these underexplored reagents in chemical synthesis.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.6b00792.

Experimental procedures and  $^1\mathrm{H}$  and  $^{13}\mathrm{C}$  NMR spectra (PDF)

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#### Notes

The authors declare no competing financial interest.

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(6) *Caution*: As shown in the latter part of the paper, a small amount of  $Me_2SiH_2$  was formed as an intermediate in the beginning of the reaction, but it was quickly consumed during the reaction course.  $Me_2SiH_2$  is a flamable gas, so safety precautions should be made when opening the reaction vessel at the end of the reaction. No accident was encountered in our studies.

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(10) *Caution:* Even though we used this method without any incident and there was no buildup of  $MeSiH_3$  and  $SiH_4$  in the reactions, precautions are required to run these reactions in large scales due to the flammable nature of these intermediates.