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Alkoxy Hydrosilanes As Surrogates of Gaseous Silanes for Hydrosilylation of Alkenes

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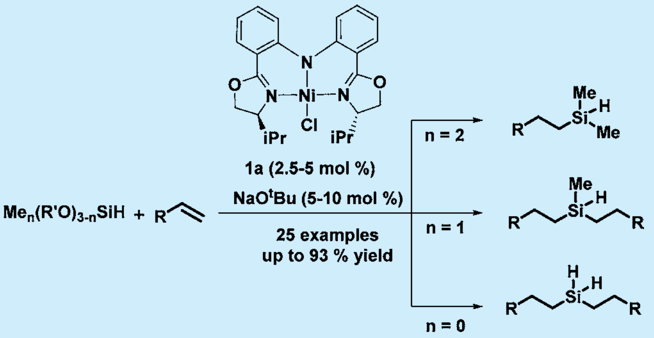
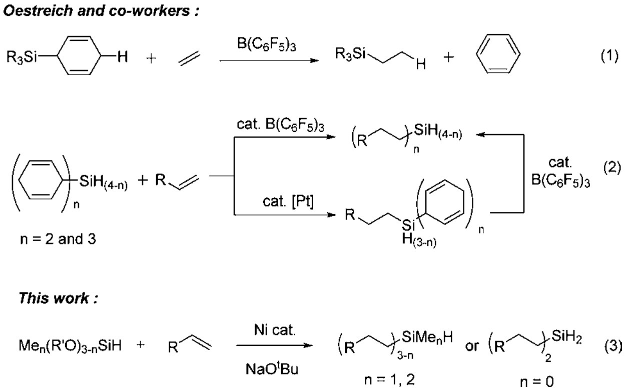
S Supporting Information

ABSTRACT: Me_2SiH_2, $MeSiH_3$, and SiH_4 are gaseous and flammable silanes that are inconvenient to use in chemical reactions. Catalytic amounts of a nickel pincer complex and NaO^tBu are reported to allow the synthesis of alkyl hydrosilanes from alkenes and alkoxy hydrosilanes, leading to the replacement of Me_2SiH_2, $MeSiH_3$, and SiH_4 by $Me_2(MeO)SiH$, $Me(EtO)_2SiH$, and $(MeO)_3SiH$ in hydrosilylation reactions of alkenes. The scope and mechanism of the reactions are also described.

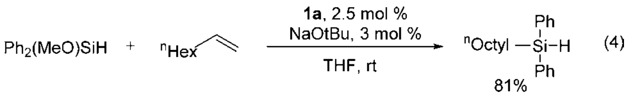


Silanes such as Me_2SiH_2, $MeSiH_3$, and SiH_4 (boiling points of −20, −57, and −112 °C, respectively) are flammable gases at room temperature and are inconvenient to handle on a laboratory scale.[1a] Moreover, SiH_4 is pyrophoric and causes severe safety concerns.[1b] As a result, these silanes are rarely applied in the hydrosilylation of alkenes,[2] which is one of the most important methods to produce silicon coupling reagents, silicon polymers, and organosilicon compounds for fine chemical synthesis.[3] 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).[4] 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_2SiH_2, $MeSiH_3$, and SiH_4 in Ni-catalyzed hydrosilylation of alkenes (eq 3, Scheme 1), yielding alkyl hydrosilanes otherwise difficult to access. A broad scope and good functional group compatibility have been achieved.

Scheme 1. Development of Surrogates of Gaseous Silanes



While studying Ni-catalyzed hydrosilylation of alkenes,[5] 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, $[iPr_2\text{-}(S,S)\text{-Bopa}]NiCl$ (**1a**) as precatalyst and NaO^tBu as base, $Ph_2(Octyl)SiH$ was isolated in an 81% yield (relative to 1-octene, eq 4). The conventional hydrosilylation product, $Ph_2(Octyl)(OMe)Si$, 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).[6] In tetrahydrofuran (THF) and at room temperature, $(Decyl)(Me)_2SiH$ 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^tBu 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, $[Ph_2\text{-}(R,R)\text{-Bopa}]NiCl$ (**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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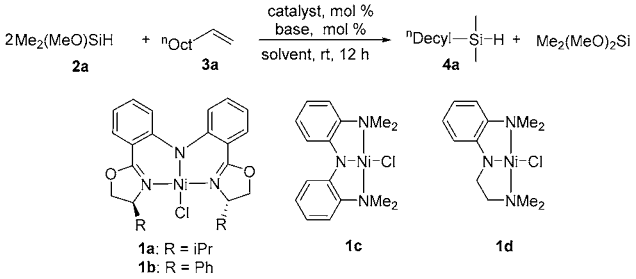
Table 1. Optimization of Reaction Conditions[a]



entry	complex, mol %	base, mol %	solvent	yield, %[b]
1	**1a**, 2.5	NaO^{t}Bu, 5	THF	**91**
2	**1a**, 2.5	CsF, 5	THF	<1
3	**1a**, 2.5	NaO^{t}Bu, 5	toluene	45
4	**1a**, 2.5	NaO^{t}Bu, 5	Et$_2$O	31
5	**1b**, 2.5	NaO^{t}Bu, 5	THF	59
6	**1c**, 2.5	NaO^{t}Bu, 5	THF	40
7	**1d**, 2.5	NaO^{t}Bu, 5	THF	48
8	NiCl$_2$(PPh$_3$)$_2$, 2.5	NaO^{t}Bu, 7.5	THF	41
9	**1a**, 1	NaO^{t}Bu, 2	THF	87
10	**1a**, 2.5	NaO^{t}Bu, 2.5	THF	0
11	**1a**, 2.5	KO^{t}Bu, 5	THF	90

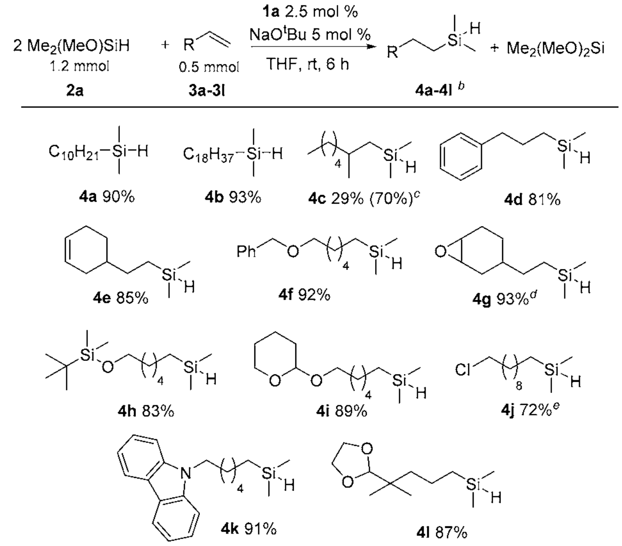
[a] Conditions: 1-decene (0.5 mmol), dimethylmethoxysilane (1.2 mmol), under N$_2$ in THF (4 mL), 12 h, rt. [b] GC-MS yields are reported, and *n*-dodecane was used as an internal standard. The yield is relative to **3a**.

below 50% (entries 6−7, Table 1). A soluble Ni(II) complex, NiCl$_2$(PPh$_3$)$_2$, 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^{t}Bu relative to **1a** was added, no (Decyl)(Me)$_2$SiH was formed (entry 10, Table 1). When NaO^{t}Bu was replaced by KO^{t}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 *β*-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.[7,8]

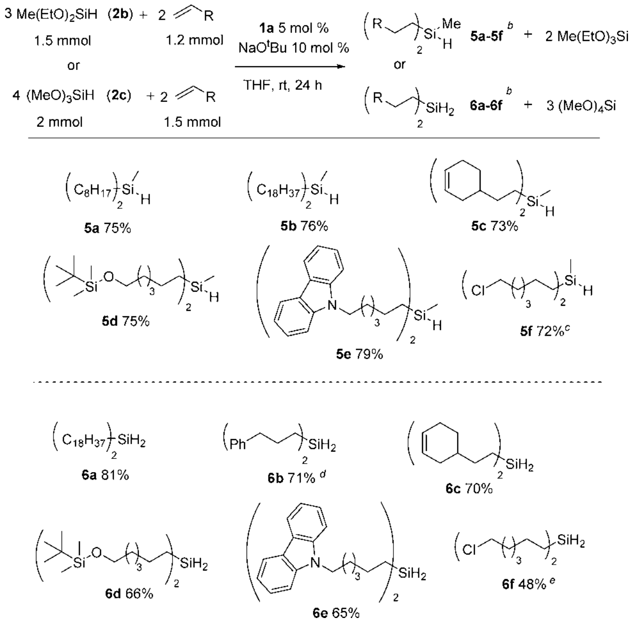
Next, the reactions of alkenes with Me(EtO)$_2$SiH and (MeO)$_3$SiH were investigated. To our delight, the reactions gave various functionalized hydrosilanes in good yields (**5a**−**6f**, Scheme 3). An increase of the loading of the catalyst to 5 mol % was necessary. For the reactions of alkenes with Me(EtO)$_2$SiH, (Alkyl)$_2$(Me)SiH was formed, in which the two alkyl groups came from the alkene. Interestingly, for the reactions of alkenes with (MeO)$_3$SiH, (Alkyl)$_2$SiH$_2$ was obtained as the major product, and only less than 3% of (Alkyl)$_3$SiH 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)$_3$SiH did not exceed 6%.

Scheme 2. Ni-Catalyzed Synthesis of Alkylhydrosilanes Using 2a and Alkenes[a]



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

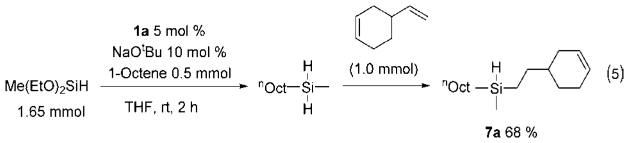
Scheme 3. Ni-Catalyzed Synthesis of Alkyl Hydrosilanes Using 2b−2c and Alkenes[a]



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

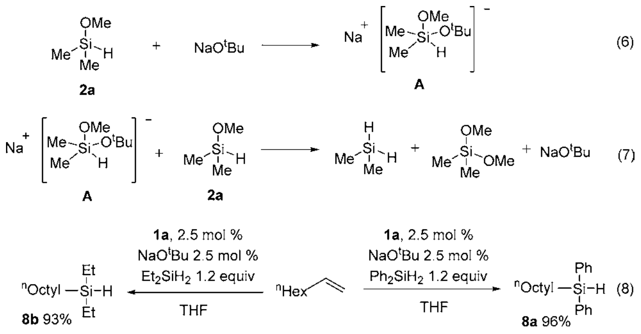
The reaction of isolated dioctadecylsilane (**6a**) with 1.2 equiv of 1-octadecene under the conditions of Scheme 3 was then monitored by ^1H NMR. (n-Octadecyl)$_2SiH_2$ (**6a**) was fully consumed in 1.5 h, and (n-octadecyl)$_3SiH$ was produced in a nearly quantitative yield. On the other hand, if 3 equiv of $(MeO)_4Si$ were added to the reaction mixture, the conversion of **6a** was less than 40% in 6 h. This result suggests that the $(MeO)_4Si$ byproduct inhibits the hydrosilylation of alkenes **6a**−**6f** with $(alkyl)_2SiH_2$, leading to selective formation of dialkylsilanes in the reaction of alkenes with $(MeO)_3SiH$.

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^{t}Bu to $Me_2(MeO)SiH$ led to a quick release of Me_2SiH_2, detected by ^1H NMR. Likewise, the addition of a catalytic amount of NaO^{t}Bu to $(MeO)_3SiH$ led to the formation of SiH_4, again detected by ^1H 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.

Scheme 4. Proposed Mechanism



Nucleophilic attack of an alkoxide anion on $Me_2(MeO)SiH$ gave the five-coordinate species (**A**), which reacted with another molecule of $Me_2(MeO)SiH$ to produce Me_2SiH_2 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.[9] The disproportionation of alkoxysilanes was followed by ^1H NMR. $Me_2(MeO)SiH$ was converted to Me_2SiH_2 and $Me_2(MeO)_2Si$ under 0.5 mol % of NaO^{t}Bu in THF-d8 in 50 min. An analogous reaction of $Me(EtO)_2SiH$ required 20 min to complete. The dispropotionation of trialkoxysilane $(MeO)_3SiH$ was even faster: in the presence of 0.1 mol % of NaO^{t}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^{t}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_2SiH_2, $MeSiH_3$, and SiH_4 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_4. When an actual reaction of 1-decene with $Me_2(MeO)SiH$ was monitored by ^1H NMR, a substoichiometric amount of Me_2SiH_2 was detected in the beginning, but it disappeared after 15 min. This result suggests that the generation of Me_2SiH_2 is faster than hydrosilylation, but hydrosilylation is sufficiently fast so that the intermediate is quickly consumed. In the reaction of 1-decene with $Me(EtO)_2SiH$, only $Me(Decyl)SiH_2$, but not $MeSiH_3$, was detected as an intermediate in the beginning of the reaction. This result suggests that hydrosilylation is faster than the generation of $MeSiH_3$. And in an actual reaction of 1-decene with $(MeO)_3SiH$, no SiH_4 was detected by ^1H NMR. The above-mentioned results suggest that the reactions of alkenes with $Me(EtO)_2SiH$ or $(MeO)_3SiH$ described here are potentially suitable for large scale applications because there was no significant buildup of flammable $MeSiH_3$ or pyrophoric SiH_4.[10] Even the reactions of alkenes with $Me_2(MeO)SiH$ might be suitable for large scale application given proper handling, because only a small amount of Me_2SiH_2 was formed as an intermediate in the beginning of the reaction. Me_2SiH_2 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 $Me_2(MeO)SiH$ 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.orglett.6b00792.

Experimental procedures and ^{1}H and ^{13}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.

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