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# **Graphical abstract**



Bis(acetylacetonato)Ni(II)/NaBHEt<sub>3</sub>-catalyzed hydrosilylation of 1,3-dienes, alkenes and alkynes

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Abstract The utility of commercially available Ni(II) salts, Ni(acac)<sub>2</sub> (acac = acetylacetonato) (**1a**) and its derivatives bis(hexafluoroacetylacetonato)nickel(II) (**1b**) and bis(2,2,6,6-tetramethyl-3,5-heptanedionato)nickel(II) (**1c**) as versatile hydrosilylation catalyst precursors is described. Complexes **1a-c** catalyze 1,4-selective hydrosilylation of 1,3-dienes in the presence of NaBHEt<sub>3</sub> at ambient temperature. The reactions exhibit good regioselectivity to give the branched isomers as major products. The catalytic system also catalyzes hydrosilylation of alkenes including industriary important siloxy-, amino-, and epoxy-substituted ones as well as both terminal and internal alkynes.

#### Keywords

Hydrosilylation, Nickel, Olefin

#### **1. Introduction**

Hydrosilylation reaction of carbon-carbon multiple bonds is one of the most important processes for the production of orgaosilicon compounds and for the curing of

organosilicon materials [1]. For these reactions, precious metal complexes containing Pt, Rh, Ru etc., are widely used as catalysts. On the other hand, due to the low abundance and high cost of these metals [2], there is an emerging demand to develop inexpensive and environmentally benign earth-abundant metal catalysts. So far, several 3d metal catalysts containing Fe [3], Co [4] and Ni [5] have been revealed to be good candidates for non-precious metal surrogates. However, 3d metal complexes often exhibit diverse reactivity, and thus many side reactions simultaneously proceed during the catalytic reactions, leading to the formation of a complicated reaction mixture. In recent years, well-defined Fe catalysts with good selectivity have been developed. One notable example was reported by Chirik et al. using iron complexes bearing bis(imono)pyridine (PDI =  $2,6-(2,6-R_2C_6H_3N=CMe)_2C_5H_3N)$ , [Fe(PDI)(N<sub>2</sub>)<sub>2</sub>]  $(R = {}^{i}Pr)$  and  $[(PDI)Fe(N_2)]_2(\mu_2-N_2)$  (R = Et, Me), which exhibit higher reaction selectivity than platinum-based industrial catalysts [3c]. Another example is the bis(iminopyridine) Fe complex system, which demonstrated the first example of regio- and stereoselective hydrosilylation of 1,3-dienes [3a]. These examples successfully demonstrate the high capability of 3d metal complexes as a hydrosilylation catalyst although the systems still have room to be improved, such as high instability and complicated preparation method of the catalysts, etc.

The use of the commercially available Ni(II) salts, Ni(acac)<sub>2</sub> (acac = acetylacetonato) (**1a**) as a hydrosilylation catalyst has been reported in 1991 under rather harsh reaction conditions with low reaction selectivity [5d-f]. It is also reported that **1a** in conjunction with a proper reducing agent such as alkyl aluminum reagents AlR<sub>3</sub> [R<sub>3</sub> = Et<sub>3</sub>, Et<sub>2</sub>(OEt)], LiAlH<sub>4</sub>, and BuMgBr effectively catalyzes 1,4-selective hydrosilylation of 1,3-dienes at ambient temperature, while the system is not applicable to normal  $\alpha$ -alkene hydrosilylation reactions [5b,c]. Since simple and air

stable **1a** is a promising catalyst precursor, it is of great interest to further investigate the capability of **1a** as a hydrosilylation catalyst. In this study, we found that **1a** and its derivatives bis(hexafluoroacetylacetonato)nickel(II) (**1b**) and bis(2,2,6,6tetramethyl-3,5-heptandiono)nickel(II) (**1c**) (Figure 1), serve as a good hydrosilylation catalyst precursor in the presence of NaBHEt<sub>3</sub>.





Different from the previous systems, our system  $1/NaBHEt_3$  catalyzes hydrosilylation not only of 1,3-dienes but also of  $\alpha$ -alkenes at room temperature with a good selectivity. It was also revealed that the system catalyzed hydrosilylation of alkynes, furnishing monohydrosilylated products in moderate yields.

#### 2. Results and discussion

**Hydrosilylation of 1,3-dienes.** It was revealed that the **1a**/NaBHEt<sub>3</sub> system exhibits similar catalytic performance as the previous system **1a**/AlEt<sub>3</sub> in hydrosilylation reactions of various 1,3-dines with (EtO)<sub>3</sub>SiH. The reaction was performed at room temperature in THF using each 1.0 mmol of substrates and 0.5 mol% of **1a**/NaBHEt<sub>3</sub>. Hydrosilylation of cyclohexadiene proceeded in a 1,4-fashion to form 3-triethoxysilylcyclohexene in 75% yield (Table 1, entry 1). Formation of (EtO)<sub>4</sub>Si (4%) was also observed, indicating the occurrence of substituent redistribution of (EtO)<sub>3</sub>SiH as a side reaction.[6] Isoprene hydrosilylation also proceeded in a 1,4-fashion, resulting in the formation of the corresponding hydrosilylated products as a mixture of two isomers, branched isomer, (*Z*)-2-methyl-1-triethoxysilyl-2-butene, and

linear isomer, 3-methyl-1-triethoxysilyl-2-butene, within 2 h in 79% total yield (Table 1, entry 2). In this reaction, the branched isomer was obtained predominantly (branched:linear = 79/21), accompanied by the slight formation of  $(EtO)_4Si$  (2%) and  $(EtO)_3SiOSi(OEt)_3$  (4%). In this system, the order of substrate addition is critical for the reaction selectivity. When **1a** and NaBHEt<sub>3</sub> were initially mixed and then  $(EtO)_3SiH$  and isoprene were successively added, substituent redistribution of the silane perferably proceeded to form a mixture of  $(EtO)_4Si$  (12%),  $(EtO)_3SiOSi(OEt)_3$  (6%), etc, as well as less amount of hydrosilylated products (61% total yield, branched:linear = 72/28). Superior results were obtained by the addition of silane and isoprene to the THF solution of **1a** and subsequent addition of NaBHEt<sub>3</sub>. Therefore, all the reactions in Table 1 were performed following the latter procedure.

Myrecene was also hydrosilylated with  $(EtO)_3SiH$  in 1 h, resulting in the formation of 1,4-adducts in 85% yields (branched:linear = 90/10) (Table 1, entry 3). In this reaction, various tertiary and secondary hydrosilanes were examined. The reactions proceeded under the same conditions, leading to the formation of 1,4-hydrosilylated products with good branched selectivity (Table 1, entries 3,4).

Different from above reactions, hydrosilylation of 1,3-pentadiene resulted in the formation of the linear isomer as a major product (93% total yield, branched:linear = 15/85) (Table 1, entry 5). Such a changeable regioselectivity was also reported in the 1,4-selective hydrosilylation of 1,3-dienes catalyzed by the previous **1a**/AlEt<sub>3</sub> system [5b]

Next, catalytic activities of **1b** and **1c** were similarly surveyed using isoprene and  $(EtO)_3SiH$  as standard substrates (Table 1, entry 2). The reactions also proceeded in a 1,4-fashion to predominantly give the branched product. Complex **1b** with electron withdrowing CF<sub>3</sub> groups exhibited slightly higher catalytic activity than **1a** to furnish

the hydrosilylated products mixture in 88% total yield within 1 h. On the other hand, the activity of **1c** with bulky *t*Bu groups was less; i.e. the reaction took 4 h to give the 1,4-hydrosilylated products in 76% total yield (Table 1, entry 2).

## Table 1





<sup>&</sup>lt;sup>a</sup>Reaction conditions: catalyst/NaBHEt<sub>3</sub> (0.005/0.005 mmol), alkene (1.0 mmol), silane (1.0 mmol), in THF (5 mL) at room temperature; <sup>b</sup>Isolated yield; <sup>c</sup>(EtO)<sub>4</sub>Si (2-4%) was isolated as a byproduct; <sup>d</sup>Ph<sub>3</sub>SiH (6%) was isolated as a byproduct.

Hydrosilylation of alkenes. It was reported that selective hydrosilylation of  $\alpha$ alkenes is not successful by using **1a** with or without any additives as a catalyst in the previous attempts.[5b, 5f] On the other hand, it was found that **1a** and **1b** catalyzed alkene hydrosilylation reactions in the presence of NaBHEt<sub>3</sub> although the reaction proceeded at slower rate compared with the 1,3-diene hydrosilylation reactions. Hydrosilylation of 1-octene took place at 50 °C in the presence of 1a (0.5 mol%) and NaBHEt<sub>3</sub> (0.5 mol%) to selectively form *anti*-Markovnikov product (*n*Oct)(EtO)<sub>3</sub>Si in 85% isolated yield (Table 2, entry 1). Small amounts of (EtO)<sub>4</sub>Si (5%) and internal alkenes (< 5%) were also formed. Styrene and norbornene were also hydrosilylated at higher catalyst loading (1.0 mol%) of 1b, resulting in the formation of the corresponding hydrosilylated products in moderate yields (Table 2, entries 2, 3). It is interesting that, unlike a previously reported **1a**-catalyzed reaction of styrene with (EtO)<sub>3</sub>SiH, which selectively formed dehydrosilylated product, (EtO)<sub>3</sub>SiCH=CHPh[5g], the present catalyst system gave the *hydrosilylated* product selectively.

The system was also utilized for hydrosilylation of industrially important alkenes with various functional groups, such as epoxy[3d,5k,7,9], amino[5k,7,8] and siloxy[7] groups (entries 4-6). It is to be noted that 1,2-epoxy-4-vinylcyclohexane, which often undergoes ring-opening polymerization in the hydrosilylation reaction catalyzed by Pt catalysts [10], was selectively hydrosilylated with Ph<sub>2</sub>SiH<sub>2</sub> to give 1,2-epoxy-4-(2-diphenylsilylethyl)cyclohexane in 83% yield.

## Table 2

1a-1b/NaBHEt<sub>3</sub>-catalyzed hydrosilylation of alkenes<sup>a</sup>

	NaBEt <sub>3</sub> H (x mol%) R <sub>3</sub> Si							
$R_3SiH + P R$ THF, time, T °C								
entry	Cat (mol%)	R <sub>3</sub> SiH	<i>∕ R</i> ′	time (h)/ T (°C)	Product Yield (%) <sup>b</sup>			
1	<b>1a</b> (0.5)	(EtO) <sub>3</sub> SiH	<i>n</i> C <sub>6</sub> H <sub>13</sub>	10/50	(EtO) <sub>3</sub> SinC <sub>6</sub> H <sub>13</sub> 85% <sup>°</sup>			
2	<b>1b</b> (1.0)	(EtO) <sub>3</sub> SiH	Ph	72/50	$(EtO)_3Si_{42\%^d}$ Ph			
3	<b>1b</b> (1.0)	(EtO) <sub>3</sub> SiH		96/50	(EtO) <sub>3</sub> Si 52% <sup>d</sup>			
4	<b>1a</b> (0.5)	Ph <sub>2</sub> SiH <sub>2</sub>		4/ RT <sup>e</sup>	Ph <sub>2</sub> HSi 0 83% <sup>f</sup>			
5	<b>1a</b> (0.5)	Ph <sub>2</sub> SiH <sub>2</sub>	NMe <sub>2</sub>	1/ RT <sup>e</sup>	$Ph_2HSi_{88\%}^{f}$ NMe <sub>2</sub>			
6	<b>1a</b> (0.5)	Ph <sub>2</sub> SiH <sub>2</sub>	SiMe(OMe) <sub>2</sub>	14/RT <sup>e</sup>	Ph <sub>2</sub> HSi SiMe(OMe) <sub>2</sub> 72% <sup>f</sup>			

1 (x mol%)

<sup>a</sup>Reaction conditions: catalyst/NaBHEt<sub>3</sub> (0.005/0.005 mmol), alkene (1.0 mmol), silane (1.0 mmol), in THF (5 mL) ; <sup>b</sup>Isolated yield; <sup>c</sup>(EtO)<sub>4</sub>Si (5%) was isolated; <sup>d</sup>(EtO)<sub>4</sub>Si (10%) and (EtO)<sub>3</sub>OSi(OEt)<sub>3</sub> (5%) were also isolated. Unreacted styrene or 2-norbornene were recovered; <sup>e</sup>Room Temperature; <sup>f</sup>Ph<sub>3</sub>SiH (2-3%) was also isolated

#### 2.1 Alkyne hydrosilylation

The catalytic activity towards alkyne hydrosilylation was also surveyed. The results are summarized in Table 3. The 1a/NaBHEt<sub>3</sub> system exhibits a similar reactivity towards a terminal alkyne hydrosilylation reaction as 1a/AlEt<sub>3</sub>, which produces 1,3butadienylsilane derivatives via successive alkyne coupling and hydrosilylation [5b]. Thus, the reaction of 1-pentyne with (EtO)<sub>3</sub>SiH proceeded at room temperature to form  $CH_2=C(nPr)C(nPr)=CH[Si(OEt)_3]$  in 20% yield in the presence of 1a/NaBHEt<sub>3</sub> (1 mol% each) (Table 3, entry 1). On the other hand, our catalyst system proved to be effective for the hydrosilylation of internal alkynes, which did not proceed with the previous 1a/AlEt<sub>3</sub> system [5b]. Thus, hydrosilylation of diphenylacetylene with (EtO)<sub>3</sub>SiH proceeded at room temperature in the presence of 1a (1.0 mol%) and NaBHEt<sub>3</sub> (1.0)mol%) give monohydrosilylated product ((E)-1,2to diphenylvinyl)triethoxysilane (63%) (entry 2). Analogously, dihydrosilanes, Ph<sub>2</sub>SiH<sub>2</sub> and Et<sub>2</sub>SiH<sub>2</sub>, were also utilized in this reaction to form the corresponding monohydrosilylated products in 58% and 64% yields, respectively (entries 3,4). The reaction of an unsymmetrical alkyne, 1-phenyl-1-propyne, with (EtO)<sub>3</sub>SiH also proceeded to give a mixture of (E)-triethoxy(1-phenylprop-1-en-2-yl)silane and (E)triethoxy(1-phenylprop-1-en-1-yl)silane (47%) in 7:3 ratio (entry 5). In this reaction, formation of [2+2+2] cycloadduct, 2',4',6'-trimethyl-5'-phenyl-1,1':3',1"-terphenyl, was also observed in 8% yield.

The difference of the catalytic activity between our **1a**/NaBHEt<sub>3</sub> and previous **1a**/AlEt<sub>3</sub> systems would suggest the presence of different catalytically active species.

In the previous systems, Ni(0) is proposed as an active species [5b]. In contrast, we confirmed that Ni(cod)<sub>2</sub> (cod = cyclooctadiene) did not catalyze the hydrosilylation reaction of diphenylacetylene with (EtO)<sub>3</sub>SiH. One possible reaction pathway for **1a**/NaBHEt<sub>3</sub> system is the mechanism initiated by the formation of a nickel hydride species. However, preliminary experiments could not confirm the formation of the active hydride species during the reaction [11]. Based on the experimental results that other hydride reagents such as LiAlH<sub>4</sub> and NaBH<sub>4</sub> could not be utilized in our system, it is likely that not a nickel(II)hydride but a nickel(II) complex adducted with a triethylborohydride anion through B–H  $\sigma$ -coordination plays a key role in the catalytic cycle. The attempts to elucidate the reaction mechanism are not successful at this moment and further studies will be performed.

#### Table 3

R₂SiH + Ph────R			1a (1.0 mol%) NaBEt₃H (1.0 mol%)		
				HF, RT	
		3	Ph H	$= \begin{pmatrix} R & + & Ph \\ SiR_3 & R_3Si & H \end{pmatrix}$	
Entry	R <sub>3</sub> SiH	Alkyne	<i>t</i> (h)	Product Yield (%) <sup>b</sup>	
1	(EtO) <sub>3</sub> SiH	nPr— <del>—</del>	14	$n \Pr$ $n \Pr$ $Si(OEt)_3$ $20\%^{\circ}$	
2	(EtO) <sub>3</sub> SiH	Ph- <u></u> Ph	36	$ \begin{array}{c} Ph \qquad Ph \\ {\longrightarrow} \qquad \overset{Ph}{\longrightarrow} \\ H \qquad Si(OEt)_{3} \\ 63\%^{d} \end{array} $	

**1a**/NaBHEt<sub>3</sub>-catalyzed hydrosilylation of alkynes<sup>a</sup>



<sup>a</sup>Reaction conditions: catalyst/NaBHEt<sub>3</sub> (0.01 mmol), alkyne (1.0 mmol), silane (1.0 mmol), in THF (5 mL); <sup>b</sup>Isolated yield; <sup>c</sup>(EtO)<sub>4</sub>Si (8%) and (EtO)<sub>3</sub>SiOSi(OEt)<sub>3</sub> (2%) were also isolated; <sup>d</sup>(EtO)<sub>4</sub>Si (11%) and (EtO)<sub>3</sub>SiOSi(OEt)<sub>3</sub> (6%) were isolated; <sup>e</sup>Ph<sub>3</sub>SiH (10%) was also isolated; <sup>f</sup>Unreacted Et<sub>2</sub>SiH<sub>2</sub> (ca. 20%) was recovered; <sup>g</sup>(EtO)<sub>4</sub>Si (8%) and (EtO)<sub>3</sub>SiOSi(OEt)<sub>3</sub> (7%) were also isolated; <sup>h</sup>[2+2+2] cycloadduct [2',4',6'-trimethyl-5'-phenyl-1,1':3',1"-terphenyl] of 1-phenyl-1-propyne was also isolated (8%).

#### Conclusion

In conclusion, hydrosilylation reaction was efficiently accomplished under mild reaction conditions by using the commercially available nickel(II) salts **1a-c** combined with NaBHEt<sub>3</sub> as a co-catalyst. The hydrosilylation of 1,3-dienes proceeded with good 1,4-regioselectivity. The catalyst system is also applicable to alkenes with various substituents and both terminal and internal alkynes to selectively afford the corresponding hydrosilylated products in good to excellent yields. These studies revealed that our **1a-c**/NaBHEt<sub>3</sub> systems exhibit a wider applicability in comparison with the previous **1a**-catalyzed systems especially in alkene and alkyne hydrosilylation reactions.

Although significant progress has been recently made in the development of 3d metal hydrosilylation catalyst systems, most cases still suffer from several problems, such as low selectivity, limited substrates scope, difficulty in handling due to the low stability of the catalysts, etc. Thus, this study, which demonstrated the

utility of commercially available and cheap Ni(II) salts **1a-c** as a versatile hydrosilylation catalyst precursor, would expand the scope of 3d metal species in this field. For the further improvement of the catalytic systems, precise design of the system based on understanding of the mechanism is indispensable. Further detailed study including mechanistic investigations is currently underway, and the results will be reported in due course

#### 3. Experimental

#### General considerations.

Unless otherwise noted, all manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glove box. Toluene, benzene, hexane, CH<sub>2</sub>Cl<sub>2</sub> and THF were purified by a solvent purification system (MBraun SPS-800/Glass Contour Ultimate Solvent System). Other solvents (benzene-*d*<sub>6</sub>, toluene-*d*<sub>8</sub>, and THF-*d*<sub>8</sub>) were dried over sodium benzophenone ketyl and distilled. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra (<sup>1</sup>H, 600 MHz; <sup>13</sup>C, 150 MHz; <sup>29</sup>Si, 119 MHz) were recorded using a Bruker AVANCE 600 spectrometer. Chemical shifts are reported in  $\delta$  (ppm) and are referenced to the residual solvent signals for <sup>1</sup>H and to tetramethylsilane (0.0 ppm) for <sup>13</sup>C and <sup>29</sup>Si. GLC analysis was performed on a Shimadzu GC-14B instrument (FID; CBP-1, 25 m × 0.25 mm). Elemental analyses were carried out on a Thermo Scientific FLASH2000 CHNS analyzer.

Catalytic hydrosilylations. A typical procedure (Table 2, entry 1) is as follows. To a stirred solution of Ni(acac)<sub>2</sub> (1a) (1.3 mg, 0.005 mmol) in THF (5 mL) was added 1octene (112 mg, 1.0 mmol) and (EtO)<sub>3</sub>SiH (164 mg, 1.0 mmol) at room temperature. After the mixture was stirred for 1 min, NaBHEt<sub>3</sub> (1.0 M in THF, 5 µL, 0.005 mmol) was added and the resulting mixture was heated at 50 °C. The solution was stirred at the same temperature, and the progress of the reaction was monitored by GLC. After completion of the reaction, mesitylene (60 mg, 0.50 mmol) was added as an internal standard to the reaction mixture. The GLC analysis of the resulting solution revealed the formation of (EtO)<sub>3</sub>(*n*Oct)Si (0.90 mmol, 90%) and (EtO)<sub>4</sub>Si (0.05 mmol, 5%). The solution was concentrated under vacuum, and the residue was purified by gel permeation chromatography (GPC) using toluene as an eluent to give (EtO)<sub>3</sub>(nOct)Si (234 mg, 0.85 mmol, 85%). The  ${}^{1}H$ ,  ${}^{13}C{}^{1}H$  and  ${}^{29}Si{}^{1}H$  NMR spectra of the isolated compound are consistent with the reported data. A similar procedure was employed for the hydrosilylation using other silanes and 1,3-diene/alkenes/alkynes. These reactions were carried out at room temperature except for the reactions, Table 2, entries 2-3. The  ${}^{1}\text{H}/{}^{13}\text{C}$  NMR spectroscopic data for the new compounds are given in the supplementary data.

Following the hydrosilylation reaction of 1-octene with  $(EtO)_3SiH$  catalyzed by 1a/NaBHEt<sub>3</sub>. To an NMR tube equipped with a Teflon valve were added Ni(acac)<sub>2</sub> (13.0 mg, 0.05 mmol), 1-octene (11.3 mg, 0.1 mmol), (EtO)<sub>3</sub>SiH (16.0 mg, 0.1 mmol), and THF-d<sub>8</sub> (0.5 mL). After the addition of NaBHEt<sub>3</sub> (1.0 M in THF, 50 µL, 0.05 mmol) to this solution at room temperature, the reaction was followed by <sup>1</sup>H NMR. After 2 h, the reaction did not proceed and only the signals assignable to the starting materials [1-octene and (EtO)<sub>3</sub>SiH] were detected by <sup>1</sup>H NMR. The reaction was

further followed at 50 °C for 14 h, and formation of  $(EtO)_3(nOct)Si$  (54%) as well as  $(EtO)_4Si$  (8%) and  $(EtO)_3SiOSi(OEt)_3$  (7%) was observed. During the reaction, no hydride signals were detected in the high field region ( $\delta 0 - 30$  ppm).

Attempted hydrosilylation of isoprene with  $(EtO)_3SiH$  catalyzed by  $[Ni(\eta-4-cycloocte-1-yl)(CF_3C(O)CHCOCF_3)]$ . An NMR tube equipped with a Teflon valve was charged with a THF- $d_8$  solution (0.5 mL) containing  $[Ni(\eta-4-cycloocte-1-yl)(CF_3C(O)CHCOCF_3)]$  (19 mg, 0.05 mmol), isoprene (1.0 mmol), and  $(EtO)_3SiH$  (164 mg, 1.0 mmol). No significant changes were detected by <sup>1</sup>H NMR at room temperature for 24 h. However, formation of a small amount of the corresponding hydrosilylated product (5%) was confirmed by <sup>1</sup>H NMR at 50 °C after 24 h. In the reaction solution, insoluble black precipitates were also formed.

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#### 4. References

[1] (a) B. Marciniec, Hydrosilylation: A Comprehensive Review on Recent Advances, Springer, Berlin, 2009; (b) D. Troegel, J. Stohrer, Coord. Chem. Rev. 255 (2011) 1440; (c) M. Pagliaro, R. Ciriminna, V. Pandarus, F. Béland, Eur. J. Org. Chem. (2013) 6227; (d) Y. Nakajima, S. Shimada, RSC adv. (2015) 20603.

- [2] I. E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J.-P. Declercq, Science 298 (2002) 204.
- [3] For Fe-catalyzed alkene hydrosilylation see: (a) J. Y. Wu, B. N. Stanzl, T. Ritter, J. Am. Chem. Soc. 132 (2010) 13214; (b) K. Kamata, A. Suzuki, Y. Nakai, H. Nakazawa, Organometallics 31 (2012) 3825; (c) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, Science 335 (2012) 567; (d) A. M. Tondreau, C. C. H. Atienza, J. M. Darmon, C. Milsmann, H. M. Hoyt, K. J. Weller, S. A. Nye, K. M. Lewis, J. Boyer, J. G. P. Delis, E. Lobkovsky, P. J. Chirik, Organometallics 31 (2012) 4886; (e) D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter, Z. Huang, J. Am. Chem. Soc. 135 (2013) 19154; (f) M. D. Greenhalgh, D. J. Frank, S. P. Thomas, Adv. Synth. Catal. 356 (2014) 584; (g) Y. Sunada, D. Noda, H. Soejima, H. Tsutsumi, H. Nagashima, Organometallics 34 (2015) 2896; (h) B. Marciniec, A. Kownacka, I. Kownacki, M. Hoffmann, R. Taylor, J. Organomet. Chem. 791 (2015) 58.
- [4] For Co-catalyzed alkene hydrosilylation see: (a) F. Seitz, M. S. Wrighton, Angew. Chem., Int. Ed. Engl. 27 (1988) 289; (b) M. Brookhart, B. E. Grant, J. Am. Chem. Soc. 115 (1993) 2151; (c) C. C. H. Atienza, T. Diao, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, J. L. Boyer, A. K. Roy, P. J. Chirik, J. Am. Chem. Soc. 136 (2014) 12108; (d) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, J. Am. Chem. Soc., 137 (2015) 13244 and references therein.
- [5] For Ni-catalyzed alkene hydrosilylation see: (a) Y. Kiso, M. Kumada, K. Tamao, M. Umeno, J. Organomet. Chem. 50 (1973) 297; (b) M. F. Lappert, T. A. Nile, S. Takahashi J. Organomet. Chem. 72 (1974) 425; (c) A. J. Cornish,

M. F. Lappert, T. A. Nile, J. Organomet. Chem. 132 (1977) 133; (d) B.
Marciniec, H. Maciejewski, J, Mirecki, J. Organomet. Chem. 418 (1991) 61;
(e) B. Marciniec, H. Maciejewski, J. Organomet. Chem. 454 (1993) 45; (f) B.
Marciniec, H. Maciejewski, I. Kownacki, J. Mol. Catal. A: Chem. 135 (1998)
223; (g) H. Maciejewski, B. Marciniec, I. Kownacki, J. Organomet. Chem.
597 (2000) 175; (h) L. F. Groux, D. Zargarian, Organometallics 22 (2003)
4759; (i) L. B. Junquera, M. C. Puerta, P. Valerga, Organometallics 31 (2012)
2175; (j) V. Srinivas, Y. Nakajima, W. Ando, K. Sato, S. Shimada, Catal. Sci.
Technol. 5 (2015) 2081; (k) I. Buslov, J. Becouse, S. Mazza, M. Montandon-
Clerc, X. Hu, Angew. Chem. Int. Ed. 54 (2015) 14523.

- [6] It was confirmed that the substituent redistribution of (EtO)<sub>3</sub>SiH proceeded in the presence of 1.0 mol% of 1a/NaBHEt<sub>3</sub> to give (EtO)<sub>4</sub>Si (35%), and (EtO)<sub>3</sub>SiOSi(OEt)<sub>3</sub> (18%) in 8 h.
- [7] J. W. White in Progress in Organosilicon Chemistry (B. Marciniec, J. Chojnowski, eds.), Gordon & Breach, Basel (1995) p. 363.
- [8] (a) G. A. Molander, P. J. Nichols, J. Am. Chem. Soc. 117 (1995) 4415; (b) N. Sabourault, G. Mignani, A. Wagner, C. Mioskowski, Org. Lett. 13 (2002) 2117; (c) J. B. Perales, D. L. Van Vranken J. Org. Chem. 66 (2001) 7270; (d) M. Igarashi, T. Matsumoto, T. Kobayashi, K. Sato, W. Ando, S. Shimada, M. Hara, H. Uchida, J. Organomet. Chem. 749 (2014) 721.
- [9] I. E. Markó, S. Stérin, O. Buisine, G. Berthon, G. Michaud, B. Tinant, J.-P. Declercq, Adv. Synth. Catal. 346 (2004) 1429.
- [10] J. V. Crivello, M. Fan, J. Polym. Sci, Part A: Polym. Chem. 29 (1991) 1853.
- [11] Attempts to detect a nickel hydride species by following the reaction using <sup>1</sup>H NMR spectrum were not successful. It was also confirmed that  $[Ni(\eta-4-$

cycloocte-1-yl)(CF<sub>3</sub>C(O)CHCOCF<sub>3</sub>)], which was reported to be converted to a nickel hydride complex after the elimination of cyclooctadiene [12], did not catalyze the hydrosilylation of 1-octene with ( $EtO_{13}SiH$  at room temperature.

[12] (a) W. Keim, B. Hoffmann, R. Lodewick, M. Peuckert, G. Schmitt, J. Fleischhauer, U. Meier, J. Mol. Catal. 6 (1979) 79; (b) W. Keim, A. Behr, G. Kraus, J. Organomet. Chem. 251 (1983) 377.

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