Silanes

International Edition: DOI: 10.1002/anie.201507829
German Edition: DOI: 10.1002/ange.201507829

Chemoselective Alkene Hydrosilylation Catalyzed by Nickel Pincer Complexes

*Ivan Buslov, Jeanne Becouse, Simona Mazza, Mickael Montandon-Clerc, and Xile Hu**

Abstract: *Chemoselective hydrosilylation of functionalized alkenes is difficult to achieve using base-metal catalysts. Reported herein is that well-defined bis(amino)amide nickel pincer complexes are efficient catalysts for anti-Markovnikov hydrosilylation of terminal alkenes with turnover frequencies of up to 83000 per hour and turnover numbers of up to 10000. Alkenes containing amino, ester, amido, ketone, and formyl groups are selectively hydrosilylated. A slight modification of reaction conditions allows tandem isomerization/hydrosilylation reactions of internal alkenes using these nickel catalysts.*

Hydrosilylation of alkenes is widely used for the production of numerous consumer goods and fine chemicals.[1,2] Platinum catalysts, such as Speier's[3] catalyst and Karstedt's[4] complex, are most often used for this reaction because of their high activity and selectivity. However, the high cost and low abundance of platinum motivates the development of alternative catalysts based on more-abundant and economical metals. A number of iron and nickel catalysts have shown good efficiency and activity for alkene hydrosilylation.[1a,5] In pioneering work, Chirik and co-workers reported that bis(imino)pyridine (PDI) iron(0) bis(dinitrogen) complexes catalyzed anti-Markovnikov hydrosilylation of terminal alkenes.[6] Modification of the steric properties of the PDI ligands allows addition of tertiary silanes.[7a,b] Related terpyridine and bis(imino)pyridine iron(II) dialkyl complexes also served as catalysts for the hydrosilylation of alkenes and alkynes.[7c] These iron complexes exhibit high activity with turnover frequencies (TOFs) of up to 100000 h^{-1}, but they are not compatible with carbonyl groups, which compete favorably with alkenes for hydrosilylation. The limited stability of these complexes is another constraint. Several groups had then used stable iron(II) complexes as precatalysts and either $NaBHEt_3$ or an organometallic reagent as an activating reagent to generate active iron catalysts for anti-Markovnikov alkene hydrosilylation.[8–10] While this modification improved the stability of the catalysts, functional-group compatibility remains to be improved. In a notable example, Huang and co-workers developed phosphinite iminopyridine (PNN) iron(II) complexes, where the more-electron-rich character of the PNN ligand, relative to PDI, was exploited to decrease the oxophilicity of the catalysts and improve their tolerance towards carbonyl groups. Indeed, in combination with $NaBHEt_3$ as the activating agent, these complexes catalyzed anti-Markovnikov hydrosilylation of alkenes containing several important functional groups, including esters, tertiary amides, and ketones.[9] Notwithstanding, internal alkenes and terminal alkenes containing secondary amide groups could not be hydrosilylated.

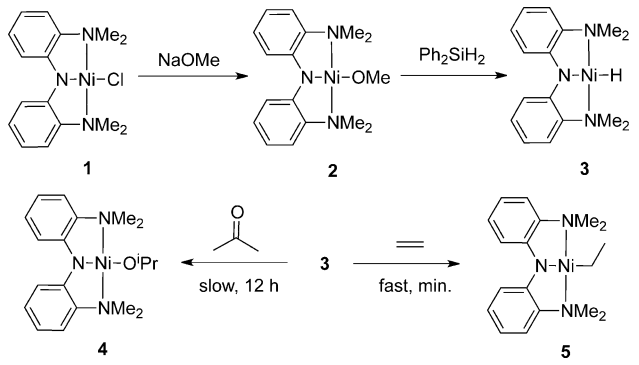
A number of nickel-based catalysts for regioselective hydrosilylation of alkenes have been reported recently. [Ni(R-Indenyl)(PPh_3)Cl] (R = Me, $SiMe_3$), activated by $NaBPh_4$, catalyzed hydrosilylation of styrene with $PhSiH_3$ to give the Markovnikov product.[11] Cationic allyl nickel complexes also catalyzed Markovnikov hydrosilylation of styrenes with phenylsilane.[12] In contrast, [$(PPh_3)_2NiBr_2$]-catalyzed anti-Markovnikov hydrosilylation of styrenes with Ph_2SiH_2.[13] A two-coordinate nickel bis(amido) complex also catalyzed anti-Markovnikov hydrosilylation of 1-octene with Ph_2SiH_2.[14] However, broad scope and functional group compatible hydrosilylation of alkenes has not been demonstrated by a nickel-based catalytic system. Herein, we report that nickel(II) bis(amino)amide (N_2N) pincer complexes catalyze chemoselective anti-Markovnikov hydrosilylation of alkenes. The catalysis has high activity and broad scope. Not only ester, keto, and NH_2 groups, but also formyl and secondary amide groups, previously only tolerated in precious metal catalysis, are compatible with this nickel catalysis. The nickel catalysts also catalyze tandem isomerization and anti-Markovnikov hydrosilylation of internal alkenes.

Our group reported earlier that the bis(amino)amide nickel chloride complex [($^{Me}N_2N$)Ni-Cl] (**1**) was an excellent catalyst for cross-couplings of non-activated alkyl halides and direct C–H alkylation.[15] Reaction of **1** with NaOMe gave the methoxide complex [($^{Me}N_2N$)Ni-OMe] (**2**), which reacted with Ph_2SiH_2 to yield the hydride complex [($^{Me}N_2N$)Ni-H] (**3**; Scheme 1).[16] The complex **3** reacted with acetone and ethylene to give [($^{Me}N_2N$)Ni-O*i*Pr] (**4**) and [($^{Me}N_2N$)Ni-Et] (**5**), respectively. The reaction with acetone was slow and took 12 hours to complete. However, the reaction with ethylene was much faster and was complete within minutes. Thus, supported by the $^{Me}N_2N$ pincer ligand, the nickel(II) hydride species, the proposed intermediate in many nickel-catalyzed hydrosilylation reactions, reacts preferentially with the C=C bond over that of the carbonyl group. This result suggested that the N_2N pincer/Ni complexes might be potential catalysts for chemoselective hydrosilylation of alkenes containing carbonyl groups.

Indeed, in the presence of 1 equivalent of NaO*i*Pr, 10 mol% of **1** catalyzed hydrosilylation of 1-octene (**6a**)

[*] I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc, Prof. Dr. X. Hu
Laboratory of Inorganic Synthesis and Catalysis, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), ISCI-LSCI
BCH 3305, 1015 Lausanne (Switzerland)
E-mail: xile.hu@epfl.ch
Homepage: http://lsci.epfl.ch

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507829.



Scheme 1. Structure and transformations of N_2N pincer/Ni complexes.

with Ph_2SiH_2 at −70 °C to give octyldiphenylsilane (**7a**) in 93% yield. The NaO*i*Pr base was used to convert **1** into [($^{Me}N_2N$)Ni-O*i*Pr], which presumably activated the silane to give **3**. To conduct the reactions under base-free conditions, which may provide better group tolerance, the alkoxide complexes **2** and **4** were tested as catalysts. Both complexes catalyze the hydrosilylation of **6a** with Ph_2SiH_2 in high yields at room temperature. To estimate the activity, a solvent-free reaction of **6a** with Ph_2SiH_2 was performed at room temperature on a 10 mmol scale. Using 0.025 mol% of the catalyst [($^{Me}N_2N$)Ni-OMe], 98% conversion was reached within 2.5–3 minutes, thus giving an average TOF of about 83000 h^{-1}. The catalyst loading for this reaction could be lowered to 0.01 mol%, thus giving a TON of about 10000. This reactivity is among the highest for nonprecious metals in alkene hydrosilylation reactions.

The scope and tolerance of hydrosilylation were then explored using **2** as the catalyst (Table 1). For convenience of handling, the catalyst loading was 1 mol% on these lab-scale reactions (0.5 mmol). Secondary silanes worked best, while primary and tertiary silanes gave lower yields (about 30%).[17] A large number of functionalized alkenes were hydrosilylated with anti-Markovnikov selectivity. Not only terminal, but also cyclic alkenes (**7d**, **7q**) were reactive. The reaction was faster for a terminal alkene than for a cyclic alkene, so a substrate containing both groups was selectively hydrosilylated at the terminal alkene moiety (**7e**). Substitution at the β-position of the olefin was allowed (**7b**,**c**). Excellent functional-group tolerance was achieved. Epoxide (**7f**), aryl bromide (**7g**), alkyl bromide (**7h**), ester (**7i**, **7s**), and tertiary amine (**7m**) were readily tolerated. Moreover, primary amines (**7j–l**),[18] and NH-containing amides such as NH-$COCF_3$ (**7n**,**o**), carbamate NH-Boc (**7p**), and sulfonylamide NH-SO_2Me (**7r**), which were challenging for previous iron and nickel catalysts,[9] were compatible with the current method. Unfortunately, as for previous nonprecious catalysts, alcohols, carboxylic acids, and allylhalides remained incompatible. Interestingly, no hydrosilylation was obtained for the reactions of Ph_2SiH_2 with terminal (1-octyne and phenylacetylene) and internal (2-octyne) alkynes.

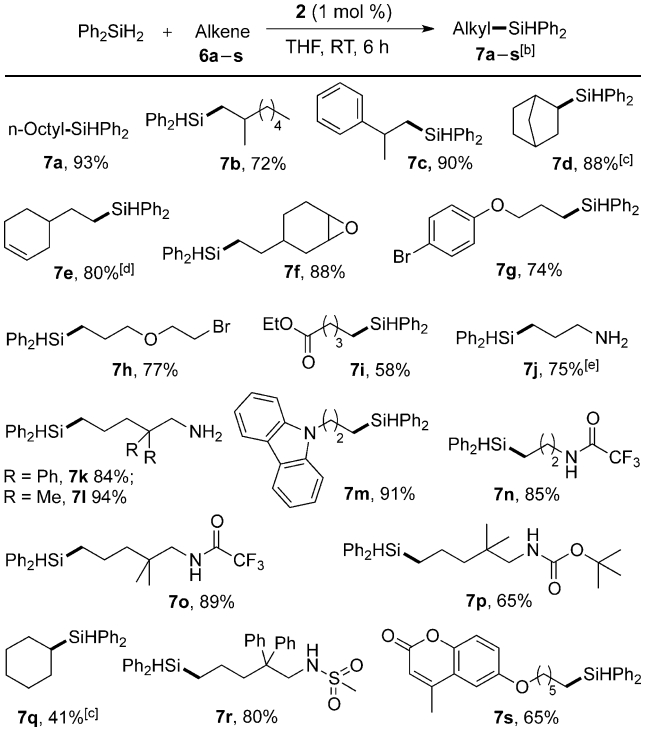
Nickel-catalyzed hydrosilylation of ketones and aldehydes is well established.[19] Therefore, selective hydrosilylation of alkenes in the presence of ketones and aldehydes is challenging. Using the protocol in Table 1, 5-hexen-2-one (**8a**) was hydrosilylated with Ph_2SiH_2, thus giving 6-(diphenylsilyl)hexan-2-one (**9a**) in 53% yield and 9:1 selectivity for alkene versus ketone hydrosilylation. Changing the solvent from THF to DMA improved the selectivity to as high as 15:1. The yields for carbonyl-containing alkenes were further increased using a loading of 2 mol%. Thus, both ketone and formyl groups were tolerated (**8a–d**; Scheme 2). To the best of our knowledge it is the first example of selective hydrosilylation of formyl-containing alkenes by a base-metal catalyst.

To illustrate the synthetic utility of the hydrosilylation products, two alkylsilanes (**7c** and **9b**) were oxidized using hydrogen peroxide, and the corresponding alcohols were obtained in good yields (Scheme 3).

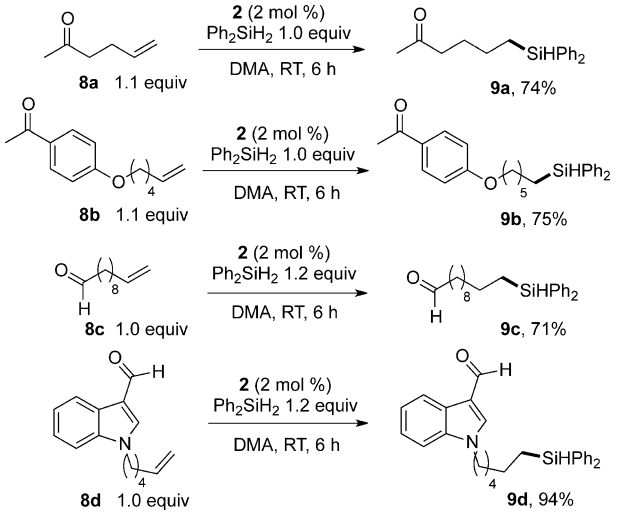
When internal alkenes such as 2-pentene, 2-octene, or 1-ethylcyclohexene were used as substrates, certain platinum- and rhodium-based catalysts can catalyze tandem isomerization and hydrosilylation to give terminal alkylsilanes.[3a,20] Recently, analogous tandem isomerization/hydroboration of internal alkenes was developed.[21] Related dehydrogenative silylation of internal olefins to yield allylsilanes was also reported.[22] However, there are few prior reports of base-metal-catalyzed isomerization/hydrosilylation reactions.[6]

It was found that in the presence of 10 mol% of **2**, 2-octene reacted with Ph_2SiH_2 to give octyldiphenylsilane (**7a**) in 77% yield (Table 2). The reaction is proposed to occur by the isomerization of 2-octene to 1-octene followed by anti-

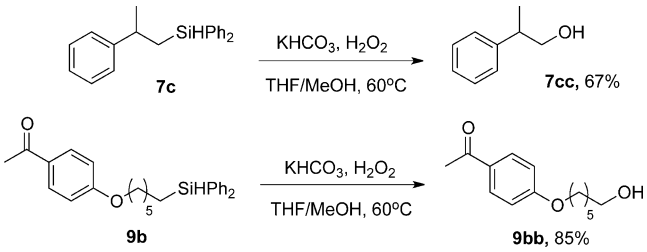
Table 1: Nickel-catalyzed hydrosilylation of terminal and cyclic alkenes.[a]



[a] Reaction conditions: alkene (0.5 mmol), Ph_2SiH_2 (1.2 equiv), [($^{Me}N_2N$)Ni-OMe] (1 mol%), THF (1 mL), 6 h, RT. [b] Yields of isolated products are reported. [c] 5% of [($^{Me}N_2N$)Ni-OMe] and 24 h. [d] Alkene (0.55 mmol), Ph_2SiH_2 (0.5 mmol). [e] 2 mmol scale, 8% of 2-(diphenylsilyl)propanamine was also produced. THF = tetrahydrofuran.



Scheme 2. Nickel-catalyzed hydrosilylation of ketone- and formyl-containing alkenes. Yields of the isolated products are reported. DMA = dimethylacetamide.



Scheme 3. Oxidation of alkylsilanes to alcohols.

Markovnikov hydrosilylation. The tandem isomerization and hydrosilylation also occurred with other such alkenes, having various functional groups (**13a–d**), with good selectivity for the formation of terminal alkylsilanes. For a cyclic substrate, such as 1-methylcyclohex-1-ene, the yield of the isomerization/hydrosilylation was low. For similar reactions of 3- and 4-octenes, a modification of reaction conditions was beneficial. Thus, **1** was used as the precatalyst, 1 equivalent of NaO*t*Bu was used as the base, and the reactions were conducted at −70 °C (Method B). Under these reaction conditions, 3- and 4-octenes were isomerized and hydrosilylated to give **7a** in good yields. It is noted that these tandem reactions are slower than hydrosilylation reactions of terminal alkenes, thus suggesting that the slow step is the isomerization.

In summary, we have developed an efficient protocol for nickel-catalyzed anti-Markovnikov hydrosilylation of functionalized alkenes. While several nickel bis(amino)amide pincer complexes are competent catalysts, the methoxide complex [(^{Me}N$_2$N)Ni-OMe] (**2**) is a highly active and selective catalyst under base-fee conditions. Ester, amido, sulfonylamido, amino, ketone, and even formyl groups were tolerated. Furthermore, the nickel pincer complexes catalyze isomerization/hydrosilylation of internal functionalized alkenes.

Table 2: Nickel-catalyzed tandem isomerization/hydrosilylation of alkenes.

Entry	Method[a]	Substrate	Product	Yield [%][b]
1	A		*n*Octyl–SiHPh$_2$ **7a**	77[c]
2	A	**13a**	**14a**	63[c]
3	A	**13b**	**14b**	64[c]
4	A	**13c**	**14c**	92
5	A	**13d**	**14d**	42[c]
6	A	**13e**	**14e**	24[d]
7	B		*n*Octyl–SiHPh$_2$ **7a**	65
8	B		*n*Octyl–SiHPh$_2$ **7a**	59

[a] Method A: alkene (0.5 mmol), Ph_2SiH_2 (2.0 equiv), [(^{Me}N$_2$N)Ni-OMe] (10 mol%), THF (3 mL), 24 h, RT. Method B: alkene (0.5 mmol), Ph_2SiH_2 (2.0 equiv), NaO*t*Bu (1.0 equiv), [(^{Me}N$_2$N)Ni-Cl] (10 mol%), THF (3 mL), 24 h, −70 °C. [b] Yields of isolated products are reported. [c] 6–9% of internal hydrosilylation product was also obtained. [d] 1-Methylcyclohexene was used as the solvent, and GC-MS yield reported.

Acknowledgements

This work is supported by the EPFL and the Swiss National Science Foundation.

Keywords: alkenes · chemoselectivity · nickel · pincer ligands · silanes

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 14523–14526
Angew. Chem. **2015**, *127*, 14731–14734

[1] a) B. Marciniec, *Hydrosilylation*: *A Comprehensive Review on Recent Advances*, Springer, Berlin, **2009**; b) L. N. Lewis, J. Stein, Y. Gao, R. E. Colborn, G. Hutchins, *Platinum Met. Rev.* **1997**, *41*, 66; c) R. M. Hill, *In Silicone*, *Surfactants Science Series*, *Vol. 86* (Ed.: R. M. Hill), Marcel Dekker, New York, **1999**, p. 1.

[2] a) K. Tamao, N. Ishida, T. Tanaka, M. Kumada, *Organometallics* **1983**, *2*, 1694; b) I. Fleming, R. Henning, H. J. Plaut, *Chem. Soc. Chem. Commun.* **1984**, 29.

[3] a) J. L. Speier, J. A. Webster, G. H. Barnes, *J. Am. Chem. Soc.* **1957**, *79*, 974; b) J. L. Speier, *Adv. Organomet. Chem.* **1979**, *17*, 407.

[4] P. B. Hitchcock, M. F. Lappert, N. J. W. Warhurst, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 438; *Angew. Chem.* **1991**, *103*, 439.

[5] a) B. Marciniec, J. Gulinski, W. Urbaniac, Z. W. Kornetka, *Comprehensive Handbook on Hydrosilylation*, Pergamon, Oxford, **1992**; b) B. Marciniec, J. Gulinski, *J. Organomet. Chem.* **1993**, *446*, 15; c) B. Marciniec, *Coord. Chem. Rev.* **2005**, *249*, 2374; d) A. K. Roy, *Adv. Organomet. Chem.* **2008**, *55*, 1;

e) D. Troegel, J. Stohrer, *Coord. Chem. Rev.* **2011**, *255*, 1440; f) Y. Nakajima, S. Shimada, *RSC Adv.* **2015**, *5*, 20603.
[6] S. C. Bart, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2004**, *126*, 13794.
[7] a) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, *Science* **2012**, *335*, 567; b) C. C. H. Atienza, A. M. Tondreau, K. J. Weller, K. M. Lewis, R. W. Cruse, S. A. Nye, J. L. Boyer, J. G. P. Delis, P. Chirik, *J. ACS Catal.* **2012**, *2*, 2169; c) 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* **2012**, *31*, 4886.
[8] K. Kamata, A. Suzuki, Y. Nakai, H. Nakazawa, *Organometallics* **2012**, *31*, 3825.
[9] D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter, Z. Huang, *J. Am. Chem. Soc.* **2013**, *135*, 19154.
[10] M. D. Greenhalgh, D. J. Frank, S. P. Thomas, *Adv. Synth. Catal.* **2014**, *356*, 584.
[11] Y. Chen, C. Sui-Seng, S. Boucher, D. Zargarian, *Organometallics* **2005**, *24*, 149.
[12] a) I. Hyder, M. Jiménez-Tenorio, M. C. Puerta, P. Valerga, *Dalton Trans.* **2007**, 3000; b) L. B. Junquera, M. C. Puerta, P. Valerga, *Organometallics* **2012**, *31*, 2175.
[13] A. Kuznetsov, V. Gevorgyan, *Org. Lett.* **2012**, *14*, 914.
[14] M. I. Lipschutz, T. D. Tilley, *Chem. Commun.* **2012**, *48*, 7146.
[15] a) O. Vechorkin, X. L. Hu, *Angew. Chem. Int. Ed.* **2009**, *48*, 2937; *Angew. Chem.* **2009**, *121*, 2981; b) O. Vechorkin, V. Proust, X. L. Hu, *J. Am. Chem. Soc.* **2009**, *131*, 9756; c) O. Vechorkin, D. Barmaz, V. Proust, X. L. Hu, *J. Am. Chem. Soc.* **2009**, *131*, 12078; d) O. Vechorkin, V. Proust, X. L. Hu, *Angew. Chem. Int. Ed.* **2010**, *49*, 3061; *Angew. Chem.* **2010**, *122*, 3125; e) X. L. Hu, *Chem. Sci.* **2011**, *2*, 1867; f) O. Vechorkin, R. Scopelliti, X. L. Hu, *Angew. Chem. Int. Ed.* **2011**, *50*, 11777; *Angew. Chem.* **2011**, *123*, 11981.
[16] J. Breitenfeld, R. Scopelliti, X. L. Hu, *Organometallics* **2012**, *31*, 2128.
[17] For more details see the Supporting Information.
[18] N. Sabourault, G. R. Mignani, A. Wagner, C. Mioskowski, *Org. Lett.* **2002**, *4*, 2117.
[19] a) S. Chakraborty, H. R. Guan, *Dalton Trans.* **2010**, *39*, 7427; b) S. Chakraborty, J. A. Krause, H. Guan, *Organometallics* **2009**, *28*, 582; c) B. L. Tran, M. Pink, D. J. Mindiola, *Organometallics* **2009**, *28*, 2234.
[20] a) R. A. Benkeser, S. Dunny, G. S. Li, P. G. Nerlekar, S. D. Work, *J. Am. Chem. Soc.* **1968**, *90*, 1871; b) A. J. Chalk, J. F. Harrod, *J. Am. Chem. Soc.* **1965**, *87*, 16.
[21] a) S. Pereira, M. Srebnik, *J. Am. Chem. Soc.* **1996**, *118*, 909; b) Y. Yamamoto, R. Fujikawa, T. Umemoto, N. Miyaura, *Tetrahedron* **2004**, *60*, 10695; c) J. V. Obligacion, P. J. Chirik, *J. Am. Chem. Soc.* **2013**, *135*, 19107; d) X. Jia, L. Zhang, C. Qin, X. Leng, Z. Huang, *Chem. Commun.* **2014**, *50*, 11056; e) W. N. Palmer, T. Diao, I. Pappas, P. J. Chirik, *ACS Catal.* **2015**, *5*, 622.
[22] 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.* **2014**, *136*, 12108.

Received: August 21, 2015
Revised: September 14, 2015
Published online: October 2, 2015

