Catalysis Science & Technology

COMMUNICATION

View Article Online
View Journal | View Issue

(Salicylaldiminato)Ni(II)-catalysts for hydrosilylation of olefins†

Venu Srinivas, Yumiko Nakajima,* Wataru Ando, Kazuhiko Sato and Shigeru Shimada*

Cite this: *Catal. Sci. Technol.*, 2015, 5, 2081

Received 24th February 2015,
Accepted 26th February 2015

DOI: 10.1039/c5cy00270b

www.rsc.org/catalysis

A series of (salicylaldiminato)methylnickel complexes efficiently catalyse hydrosilylation of various olefins. The complexes are highly active for secondary hydrosilanes and exhibit excellent selectivity for monohydrosilylation. A possible mechanism, which includes a silylnickel complex as a key active species, is proposed.

Transition metal catalysed hydrosilylation of olefins is an excellent tool for synthesis of various organosilicon compounds and for cross-linking of silicone polymers in industry.[1] To date, hydrosilylation has depended on precious metal catalysts, particularly platinum.[1] Due to the high cost of these metals, there is an increasing demand for the development of non-precious metal catalysts. Thus far, first-row transition metal complexes containing Fe,[2] Co,[3] Ni,[4] *etc.* have attracted much attention due to their potential applicability as low-cost alternatives. However, examples of well-defined first-row transition metal catalyst systems still remain scarce because of the difficulty in controlling their complicated reactivity, which sometimes leads to an unwanted product mixture.

In this study, we found out that (salicylaldiminato)methylnickel complexes **1a–e** (Fig. 1), which have been so far intensively studied as olefin polymerization catalysts,[5] act as good hydrosilylation precatalysts of various olefins with excellent product selectivity and diverse substrate scope.

Ni(II) complexes **1a–e** were prepared by the reaction of [Ni(CH$_3$)$_2$(tmeda)] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) with a respective salicylaldimine derivative and pyridine or DMAP (DMAP = 4-dimethylaminopyridine) in diethyl ether.[5] Complexes **1b–d** are new compounds and were fully characterized by ^{1}H and ^{13}C NMR spectroscopy as well as elemental analysis.

The catalytic performance of **1a–e** is summarized in Table 1. Hydrosilylation of 1-octene with Et$_2$SiH$_2$ in the presence of 0.5 mol% of **1a** smoothly proceeded in CH$_3$CN at room temperature for 1 h to give Et$_2$(*n*Oct)SiH (**2**, 93%, *n*Oct = CH$_3$(CH$_2$)$_7$) with high selectivity, along with a small amount of dioctyl product Et$_2$(*n*Oct)$_2$Si (**3**, 4%) (entry 1). The use of other solvents (benzene, toluene, hexane or THF) resulted in the formation of a complicated mixture containing **2**, **3**, Et(*n*Oct)SiH$_2$, Et(*n*Oct)$_2$SiH and Et$_2$(*n*Oct)$_2$Si probably *via* substituent redistribution on the Si atom. Hence the reaction was conducted in CH$_3$CN for further investigation. Complex **1b** exhibited a similar catalytic activity forming **2** and **3** in 90% and 2% yields, respectively (entry 2). Complexes **1c** and **1d** were slightly less active than **1a** and **1b**, and required longer reaction times (8 h and 2.5 h, respectively) to give **2** in high yields (entries 3 and 4). The rather low activities of **1c** and **1d** are likely due to the bulky aryl substituent on the imino-*N* atom in **1c** and the strongly coordinating DMAP in **1d** (*vide infra*). To our surprise, complex **1e**, which was reported to be more active towards ethylene polymerization than **1a**,[5b] was not active even at elevated temperature up to 100 °C (entry 5). It was confirmed that transformation of **1e** gradually proceeded upon treatment with 1-octene and Ph$_2$SiH$_2$ to give unidentified compounds including insoluble black precipitates.[6]

We next investigated the substrate scope using the most effective precatalyst, **1a**. The results are summarized in Table 2. In the reaction of 1-octene with R$_2$SiH$_2$ (R = Ph, *n*Hex), selective monohydrosilylation also proceeded to give R$_2$(*n*Oct)SiH (**4** or **6**) (90–94% yield) as a major product accompanied by a small amount of R$_2$(*n*Oct)$_2$Si (entries 1 and 2). Complex **1a** catalysed hydrosilylation of 1-octene with primary silanes, PhSiH$_3$ and (*n*Oct)SiH$_3$, rather slowly to selectively give

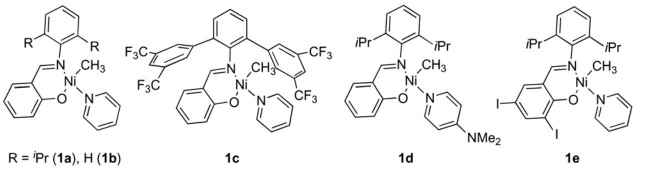


Fig. 1 (Salicylaldiminato)methylnickel complexes **1a–e**.

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.
E-mail: s-shimada@aist.go.jp

† Electronic supplementary information (ESI) available: Experimental details and compound characterization data. See DOI: 10.1039/c5cy00270b

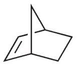
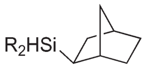
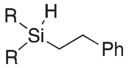
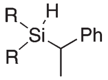
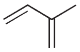
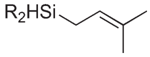
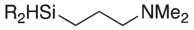
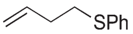
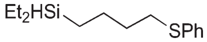
Table 1 Hydrosilylation of 1-octene with Et_2SiH_2 catalysed by **1**

$$Et_2SiH_2 + \text{1-octene} \xrightarrow[CH_3CN,\ 25\ ^\circ C]{\text{precatalyst (0.5 mol\%)}} \underset{\mathbf{2}}{Et_2(nOct)SiH} + \underset{\mathbf{3}}{Et_2(nOct)_2Si}$$

Entry	Precatalyst (0.5 mol%)	t/h	Product [yield/%][a] 2	3
1	**1a**	1	93	4
2	**1b**	1.3	90	2
3	**1c**	8	88	5
4	**1d**	2.5	92	4
5[b]	**1e**	24	0	0

[a] GC yield. [b] Starting materials were fully recovered.

Table 2 Reaction of various olefins with hydrosilanes catalysed by **1a**[a]

Entry	Silane	Olefin	t/h	Products; yield/%[b]
1	Ph_2SiH_2	1-Octene	1	$Ph_2(nOct)SiH$ (**4**); 90(91) $Ph_2(nOct)_2Si$ (**5**); 8(9)
2	$(nHex)_2SiH_2$	1-Octene	2	$(nHex)_2(nOct)SiH$ (**6**); 94(−) $(nHex)_2(nOct)_2Si$ (**7**); 3(−)
3	$RSiH_3$	1-Octene	24[c]	$(nOct)(R)SiH_2$ R = Ph (**8**); 15(20) = nOct (**9**); 20(24)
4	R_3SiH (R = Et, OEt)	1-Octene	48	No reaction
5	R_2SiH_2		1	 R = Et (**10**); 90(94) = Ph (**11**); 94(99)
6	Et_2SiH_2	2-Octene	12[d]	$Et_2(nOct)SiH$ (**2**); 85(90)
7	R_2SiH_2		10–36	 R = Et (**12a**); −(9) = Ph (**13a**); 55(−)  R = Et (**12b**); 85(90) Ph (**13b**); 40(−)
8	R_2SiH_2		0.5	 R = Et (**14**); 92(−) = Ph (**15**); 65(−)
9	R_2SiH_2		1	 R = Et (**16**); 96(−) = Ph (**17**); 98(−)
10	Et_2SiH_2		36[d]	 (**18**); 34(−)

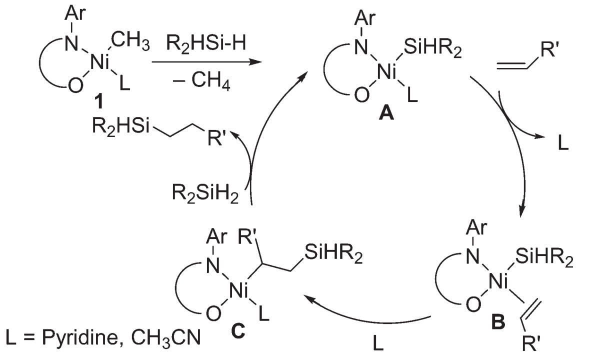
[a] **1a** (0.0025 mmol), silane (0.5 mmol), olefin (0.6 mmol) in CH_3CN (2 mL) at 25 °C. [b] Isolated yield (GC yield). [c] Toluene (2 mL) was used as a solvent. [d] Reaction at 50 °C.

monohydrosilylated products $Ph(nOct)SiH_2$ (**8**) and $(nOct)_2SiH_2$ (**9**) in 15% and 20% yields, respectively (entry 3). In these cases, large amounts of the starting materials were recovered from the resulting reaction mixture. Notably, even though a small excess of olefin was employed, the reactions did not form isomerized internal olefins, which are normally the major by-products in olefin hydrosilylation reactions catalysed by conventional platinum catalysts.[7] Tertiary silanes such as Et_3SiH and $(EtO)_3SiH$ were not applicable in this system probably due to the steric bulkiness of the silanes (entry 4).

Hydrosilylation of 2-norbornene with Et_2SiH_2 or Ph_2SiH_2 smoothly took place to selectively provide *exo*-**10** (90%) or *exo*-**11** (94%), respectively (entry 5). Interestingly, hydrosilylation of an unstrained internal olefin, 2-octene, also efficiently proceeded at 50 °C, selectively giving terminally silylated product **2** in a good yield (entry 6), likely *via* successive olefin isomerization and hydrosilylation. Styrene was also hydrosilylated with Et_2SiH_2 or Ph_2SiH_2 to yield α- and β-hydrosilylated products (entry 7). While in the case of Et_2SiH_2, α-silylated (Markovnikov addition) product **12b** (85%) was predominantly obtained, and a nonselective mixture of α- and β-silylated products (**13b**, 40%, and **13a**, 55%, respectively) was formed in the case of Ph_2SiH_2. Perfect 1,4-selectivity was observed in the hydrosilylation of isoprene with Et_2SiH_2 and Ph_2SiH_2 to form allylsilanes **14** (92%) and **15** (65%), respectively (entry 8), which are useful precursors for the construction of a plethora of carbo- and heterocyclic systems.[8] Hydrosilylation of *N*,*N*-dimethylallylamine with Et_2SiH_2 and Ph_2SiH_2 quantitatively took place to furnish silylpropylamines **16** and **17** in 1 h at 25 °C (96–98%, entry 9). But-3-en-1-yl(phenyl)sulfane also underwent hydrosilylation with Et_2SiH_2 at 50 °C to produce **18**, albeit in a low yield (entry 10). Despite their industrial importance, examples of hydrosilylation of functionalized olefins are still limited,[2d,e,9] since they sometimes poison the conventional platinum catalysts.[10] The above results observed for the olefins having nitrogen and sulfur functionalities strongly indicate potential compatibility of **1a** towards important functionalized substrates.

To obtain information on the reaction mechanism, reactions of **1a** with a stoichiometric amount of 1-octene or Ph_2SiH_2 were performed in CD_3CN followed by ^{1}H NMR spectroscopy. Complex **1a** did not react with 1-octene at room temperature. On the other hand, **1a** was completely consumed by the treatment with Ph_2SiH_2 after 15 min and a new Si*H* signal appeared at δ 5.85 ppm, whereas no signal assignable to Ni*H* was observed in the hydride region (δ 0 to −30 ppm). In addition, formation of CH_4 (δ 0.24 ppm) was detected. The non-decoupled ^{29}Si NMR spectrum exhibited one doublet at −19.0 ppm ($^1J_{SiH}$ = 219 Hz). The correlation between the two signals, δ_H 5.85 ppm and δ_{Si} −19.0 ppm, was confirmed by two dimensional NMR (Si–H HSQC) spectroscopy. Thus, formation of an intermediary silyl complex was strongly indicated, although full identification is still underway.[11] Subsequent addition of 1-octene (1.0 equiv.) and Ph_2SiH_2 (1.0 equiv.) to the reaction mixture resulted in the formation of the corresponding hydrosilylation products **4** and **5**. In this reaction, broadening of the coordinated pyridine signal was detected, indicating the rapid dissociation equilibrium of pyridine during the reaction. It was also confirmed that **1a** did not react with Et_3SiH, suggesting that the reaction is significantly influenced by the steric bulkiness of hydrosilanes. These observations successfully explain the lower activity of **1c** and **1d**, which have the bulky aryl group-substituted imino group and the strongly coordinating DMAP ligand, respectively.

Based on these observations, one possible mechanism for the complex **1**-catalysed hydrosilylation is proposed (Scheme 1). Precatalyst **1** initially reacts with a hydrosilane to give silyl intermediate **A** *via* elimination of CH_4. Intermediate **A** further undergoes olefin insertion, possibly *via* olefin-coordinated intermediate **B**, to give **C**. Reaction of **C** with hydrosilane regenerates **A** accompanied by the formation of the hydrosilylated product. Through the reaction cycle, ligand exchange between pyridine and 1-octene/acetonitrile could occur.



Scheme 1 Proposed mechanism of complex **1**-catalysed olefin hydrosilylation.

As mentioned above, complex **1a** did not catalyse the hydrosilylation reaction of tertiary hydrosilanes, Et_3SiH and $(EtO)_3SiH$, with 1-octene. Thus, the observed formation of **3** in the hydrosilylation of 1-octene with Et_2SiH_2 is not likely by double hydrosilylation of silanes *via* the intermediate tertiary hydrosilane $Et_2(nOct)SiH$ (**2**). Actually, it was indicated that **3** was formed *via* disproportionation of **2**; *i.e.* octyl group disproportionation of **2** proceeded in the presence of **1a** (1 mol%) and Et_2SiH_2 (10 mol%) to furnish **3** in 15% yield after 24 h. In this reaction, Et_2SiH_2 was necessary to generate catalytically active species.

In conclusion, well-defined (salicylaldiminato)Ni(II)-precatalysts for hydrosilylation of olefins have been established. In this system, selective tertiary hydrosilane formation was achieved *via* predominant monohydrosilylation of secondary hydrosilanes with a variety of olefins. The precatalyst is also applicable for the hydrosilylation of amino- and sulfur-functionalized olefins, showing its good functional group tolerance.

Although several Ni complexes were thus far employed as hydrosilylation catalysts, it was reported that the previous systems suffer from limited substrate scope and improper reaction selectivity.[4] It is therefore worth noting that this study successfully presents the high potential of nickel complexes as hydrosilylation catalysts. Further modification to expand the scope of our Ni system is now underway and will be reported in due course.

Acknowledgements

This work was supported by the "Development of Innovative Catalytic Processes for Organosilicon Functional Materials" project (PL: K. Sato) from the Ministry of Economy, Trade and Industry, Japan (METI), and the New Energy and Industrial Technology Development Organization (NEDO).

Notes and references

1 (*a*) B. Marciniec, J. Gulinski, W. Urbaniak and Z. W. Kornetka, *Comprehensive Handbook on Hydrosilylation*, Pergamon, Oxford, UK, 1992; (*b*) B. Marciniec, *Hydrosilylation: A Comprehensive*

Review on Recent Advances, Springer, Berlin, 2009; (*c*) D. Troegel and J. Stohrer, *Coord. Chem. Rev.*, 2011, **255**, 1440; (*d*) L. N. Lewis, J. Stein, Y. Gao, R. E. Colborn and G. Hutchins, *Platinum Met. Rev.*, 1997, **41**, 66.

2 (*a*) J. Y. Wu, B. N. Stanzl and T. Ritter, *J. Am. Chem. Soc.*, 2010, **132**, 13214; (*b*) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis and P. J. Chirik, *Science*, 2012, **335**, 567; (*c*) K. Kamata, A. Suzuki, Y. Nakai and H. Nakazawa, *Organometallics*, 2012, **31**, 3825; (*d*) D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter and Z. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 19154; (*e*) M. D. Greenhalgh, D. J. Frank and S. P. Thomas, *Adv. Synth. Catal.*, 2014, **356**, 584.

3 (*a*) F. Seitz and M. S. Wrighton, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 289; (*b*) M. Brookhart and B. E. Grant, *J. Am. Chem. Soc.*, 1993, **115**, 2151.

4 (*a*) Y. Kiso, M. Kumada, K. Tamao and M. Umeno, *J. Organomet. Chem.*, 1973, **50**, 297; (*b*) B. Marciniec, H. Maciejewski and I. Kownacki, *J. Mol. Catal. A: Chem.*, 1998, **135**, 223; (*c*) D. Gareau, C. Sui-Seng, L. F. Groux, F. Brisse and D. Zargarian, *Organometallics*, 2005, **24**, 4003; (*d*) I. Hyder, M. Jiménez-Tenorio, M. C. Puerta and P. Valerga, *Dalton Trans.*, 2007, 3000; (*e*) M. I. Lipschutz and T. D. Tilley, *Chem. Commun.*, 2012, **48**, 7146.

5 (*a*) A. Osichow, I. Göttker-Schnetmann and S. Mecking, *Organometallics*, 2013, **32**, 5239; (*b*) F. M. Bauers and S. Mecking, *Macromolecules*, 2001, **34**, 1165.

6 During the reaction, collapse of the salicylaldiminato ligand skeleton, which was not observed in the case of **1a–d**, was evidenced by ^{1}H and ^{13}C NMR spectroscopy, possibly indicating the occurrence of C–I bond cleavage.

7 (*a*) I. E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant and J.-P. Declercq, *Science*, 2002, **298**, 204; (*b*) I. E. Markó, S. Stérin, O. Buisine, G. Berthon, G. Michaud, B. Tinant and J.-P. Declercq, *Adv. Synth. Catal.*, 2004, **346**, 1429.

8 (*a*) C. E. Masse and J. S. Panek, *Chem. Rev.*, 1995, **95**, 1293; (*b*) M. D. Groaning, G. P. Brengel and A. I. Meyers, *J. Org. Chem.*, 1998, **63**, 5517; (*c*) H. J. Knolker, G. Baum, O. Schmitt and G. Wanzl, *Chem. Commun.*, 1999, 1737; (*d*) S. R. Angle and N. A. El-Said, *J. Am. Chem. Soc.*, 2002, **124**, 3608.

9 (*a*) G. A. Molander and P. J. Nichols, *J. Am. Chem. Soc.*, 1995, **117**, 4415; (*b*) H. Zhou, S. R. Venumbaka, J. W. Fitch and P. E. Cassidy, *Macromol. Symp.*, 2003, **192**, 115; (*c*) N. Sabourault, G. Mignani, A. Wagner and C. Mioskowski, *Org. Lett.*, 2002, **13**, 2117; (*d*) M. Igarashi, T. Matsumoto, T. Kobayashi, K. Sato, W. Ando, S. Shimada, M. Hara and H. Uchida, *J. Organomet. Chem.*, 2014, **749**, 421; (*e*) J. B. Perales and D. L. Van Vranken, *J. Org. Chem.*, 2001, **66**, 7270.

10 (*a*) J. Li, C. Niu, J. Peng, Y. Deng, G. Zhang, Y. Bai, C. Ma, W. Xiao and G. Lai, *Appl. Organomet. Chem.*, 2014, **28**, 454; (*b*) Y. Yoshikawa, K. Yamamoto and K. M. Tanaka, *EP Pat.* 0.604.104, 1994; (*c*) C. A. Hoag and S. W. Wilson, *US Pat.* 5346723, 1994.

11 Examples of silylnickel complexes: (*a*) D. Adhikari, M. Pink and D. J. Mindiola, *Organometallics*, 2009, **28**, 2072; (*b*) S. N. MacMillan, W. H. Harman and J. C. Peters, *Chem. Sci.*, 2014, **5**, 590; (*c*) W. Chen, S. Shimada, M. Tanaka, Y. Kobayashi and K. Saigo, *J. Am. Chem. Soc.*, 2004, **126**, 8072.