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Ligand-Controlled Highly Stereoselective Syntheses of *E*- and *Z*-Allylsilanes from Dienes and Aldehydes Using Nickel Complex

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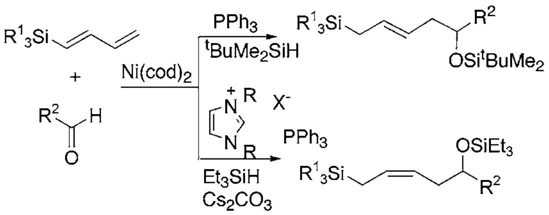
ABSTRACT



Synthetic methods of highly stereocontrolled *E*- and *Z*-allylsilanes were developed. When a toluene solution of diene having a silicon moiety and aldehyde was refluxed in the presence of silane using a catalytic amount of Ni(cod)$_2$ bearing PPh$_3$, *E*-allylsilane was obtained in high yield. On the other hand, when the reaction was carried out in THF upon heating in the presence of Ni(cod)$_2$, imidazolium salt, Cs$_2$CO$_3$, and PPh$_3$, *Z*-allylsilane was formed as a sole product.

Since the isolation and characterization of the first *N*-heterocyclic carbene (NHC) in 1991 by Arduengo,[1] much interest has been shown in this compound as a ligand of various metals, and many reactions using the transition metals such as palladium, nickel, ruthenium, and rhodium with these ligands were reported.[2] However, although the use of NHC as a ligand in a metal complex accelerates the reaction rate, ligand-controlled reactions by phosphine and NHC for the same reaction are scarcely known.[3] Here, we report the syntheses of highly stereocontrolled *E*- and *Z*-allylsilanes by coupling reactions of dienes having a silicon moiety and aldehyde in the presence of silane using a catalytic amount of nickel complex bearing PPh$_3$ or NHC. Our plan is shown in Scheme 1. If dienylsilane **1** can be reacted with aldehyde **2** in the presence of Ni(0), PPh$_3$, and hydrosilane, *E*-allylsilane *E*-**3** should be formed via a *syn*-π-allylnickelsilane complex **II** generated by nickel-catalyzed hydrosilylation of **1**.[4a,c] On the other hand, if a nickel complex having NHC **4** is used for this reaction, *Z*-allylsilane *Z*-**3** should be formed.[5]

Although the reaction pathway for formation of *Z*-olefin by the coupling reaction of a diene and an aldehyde in the presence of silane using Ni(NHC) is unclear,[5] one possible reaction course is shown in Scheme 2. Oxidative cyclization of the diene and the carbonyl group of the aldehyde gives

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[1] Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

[2] Recent reviews: (a) Jafarpour, L.; Nolan, S. P. *Adv. Organomet. Chem.* **2001**, *46*, 181. (b) Herrmann, W. A.; Weskamp, T.; Böhm, V. P. W. *Adv. Organomet. Chem.* **2002**, *48*, 1. (c) Hermann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

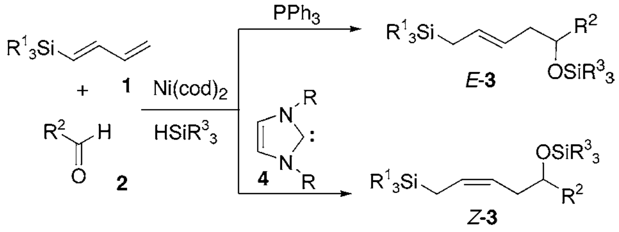
[3] In the ring-closing metathesis of enynes using a second-generation ruthenium−carbene complex bearing an NHC, the reaction proceeds via two pathways. Kitamura, T.; Sato, Y.; Mori, M. *Chem. Commun.* **2001**, 1258.

[4] Intramolecular coupling reactions of diene and aldehyde: (a) Sato, Y.; Takimoto, M.; Hayashi, K.; Katsuhara, T.; Takagi, K.; Mori, M. *J. Am. Chem. Soc.* **1994**, *116*, 9771. (b) Sato, Y.; Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2000**, *122*, 1624. Intermolecular coupling reactions: (c) Takimoto, M.; Hiraga, Y.; Sato, Y.; Mori, M. *Tetrahedron Lett.* **1998**, *39*, 4543. (d) Sato, Y.; Sawaki, R.; Saito, N.; Mori, M. *J. Org. Chem.* **2002**, *67*, 656. (e) Kimura, M.; Ezoe, A.; Shibata, K.; Tamaru, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4033. (f) Shibata, K.; Kimura, M.; Kojima, K.; Tanaka, S.; Tamaru, Y. *J. Organomet. Chem.* **2001**, *624*, 348.

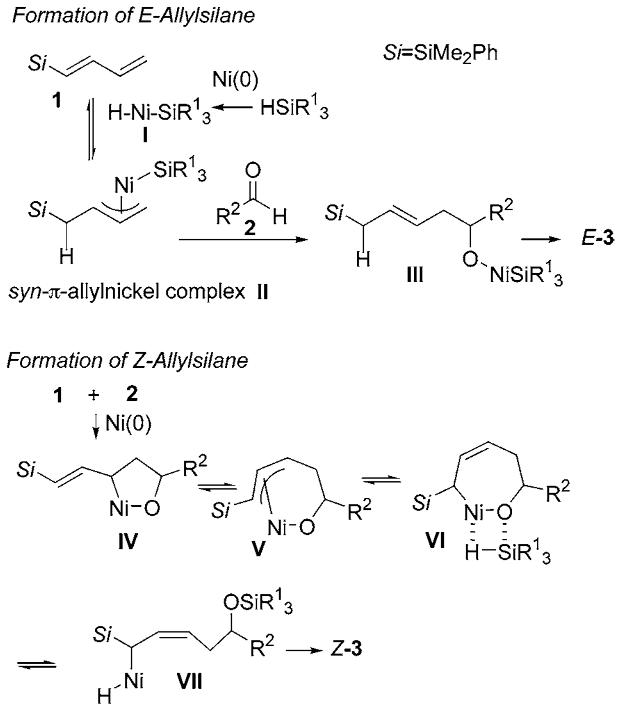
[5] Sato, Y.; Sawaki, R.; Mori, M. *Organometallics* **2001**, *20*, 5510.

10.1021/ol049908a CCC: $27.50

Scheme 1. Plan for Syntheses of *E*- and *Z*-Allylsilanes



Scheme 2. Possible Reaction Pathways

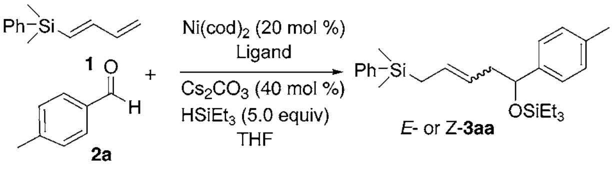


oxanickelacycle **IV**,[6] which is in equilibrium with π-allylnickel complex **V** and oxanickelacycle **VI**. σ-Bond metathesis between **VI** and hydrosilane[7] gives *Z*-allylnickel hydride complex **VII**, from which *Z*-**3** should be formed (Scheme 2).

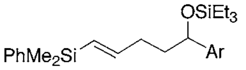
When Et_3SiH (5.0 equiv) was added to a THF solution of $Ni(cod)_2$ (20 mol %) and PPh_3 (40 mol %) at 0 °C and then diene (1.0 equiv) and *p*-tolulaldehyde (1.0 equiv) were added and the solution was stirred at 50 °C for 6 h, *E*-allylsilane *E*-**3aa** was obtained in 56% yield along with vinylsilane **5** and the hydrosilylation product **6** of **1** in 21% and 17% yields, respectively, after the usual workup (Table 1, entry 1).

On the other hand, when imidazolium salt **7a** (20 mol %) and Cs_2CO_3[8] (40 mol %) were used to generate the NHC as a ligand in situ instead of PPh_3 under similar reaction conditions, *Z*-allylsilane *Z*-**3aa** was obtained in 38% yield along with *E*-allylsilane *E*-**3aa** in 13% yield (entry 2). These results clearly indicate that the use of PPh_3 gave *E*-**3aa** as a major product but that *Z*-**3aa** was obtained using NHC as a ligand.

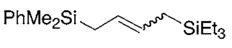
Table 1. Coupling Reactions of 1-Silyl-1,3-dienes with Aldehyde



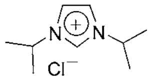
entry	ligand (mol %)	temp. (°C)	time (h)	yields (%)	
				Z-**3aa**	*E*-**3aa**
1	PPh_3 (40)[a]	50	6	-	56[b]
2	**7a** (20)	50	19	38	13
3	**7b** (20)	50	29	47	-
4	**7b** (20)	reflux	25	53	-
5	**7b**+PPh_3 (20+20)	reflux	22	64	-



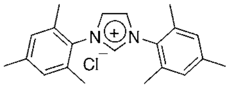
5



6



7a

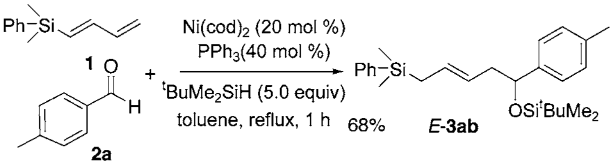


7b

[a] In the absence of Cs_2CO_3. [b] Vinylsilane **5** and allylsilane **6** were obtained in 21% yield and 17% yield, respectively.

To improve the yield of the desired *E*-allylsilane *E*-**3a**, the reactions were carried out using various silanes because *E*-allylsilane *E*-**3** should be obtained via π-allylnickelsilane complex **II**.[4a,4c] As a result, in the presence of Si^tBuMe_2H instead of Et_3SiH, *E*-**3ab** was obtained in 60% yield as a sole product. The use of toluene as a solvent allowed heating which increased the yield of *E*-**3ab** to 68% (Scheme 3).

Scheme 3. Reaction of Diene and Aldehyde Using Ni−PPh_3



Subsequently, to improve the yield and the selectivity of *Z*-allylsilane, optimization reactions were performed under the various conditions. The use of **7b** instead of **7a** as an imidazolium salt gave only *Z*-allylsilane *Z*-**3aa** in 47% yield

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[6] Although the reaction of **1** and aldehyde **2a** using Ni(0)−NHC should give four oxanickelacycles, two allylnickel complexes would be more stable than homoallylnickel complexes,[4d] and seven-membered oxanickelacycle **VI**, which is in a state of equilibrium with five-membered oxanickelacycle **IV**, would be more stable because of the effect of the silyl group. See: Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870.

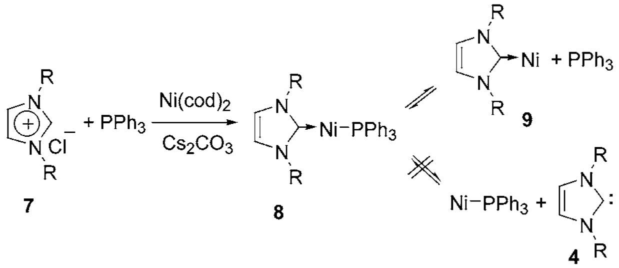
[7] Tang, X.-Q.; Montgomery, J. *J. Am. Chem. Soc.* **1999**, *121*, 6098. Sato, Y.; Saito, N.; Mori, M. *J. Am. Chem. Soc.* **2000**, *122*, 2371.

[8] Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804.

(Table 1, entry 3). A higher reaction temperature resulted in an increase in the yield of the desired compound *Z*-**3aa** (entry 4). It has been established in the coupling of dienes and aldehydes that optimum yields resulted from the use of Ni/NHC ratio of 1.[5] However, the nickel species (Ni/NHC ratio of 1) was unstable because the dark red color of Ni(0) changed to light red during a longer reaction time upon heating. It was thought that PPh_3 could act as a stabilizer of unstable Ni(NHC) since Ni(NHC)(PPh_3) should be in equilibrium with Ni(NHC) and PPh_3.[9] When a THF solution of **1** and **2a** was refluxed in the presence of $Ni(cod)_2$ (20 mol %), **7b** (20 mol %), PPh_3 (20 mol %), and Cs_2CO_3 (40 mol %), the color of Ni(0) remained unchanged during the reaction. Surprisingly, only *Z*-**3aa** was obtained as the sole product despite the presence of PPh_3 and the yield was increased to 64% (entry 5).

Probably, Ni(NHC)(PPh_3) **8** is formed from $Ni(cod)_2$, PPh_3, imidazolium salt **7b** and Cs_2CO_3, but Ni(NHC) **9b**, not Ni(PPh_3), acts as an active species since the *Z*-allylsilane was formed in this reaction (Scheme 4).

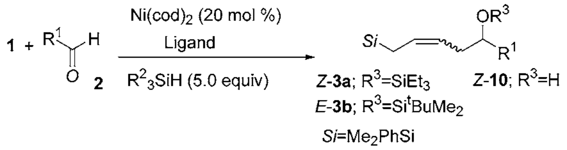
Scheme 4. Active Ni(0) Species in Ni(NHC)(PPh_3)

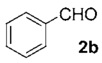
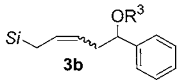
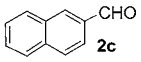
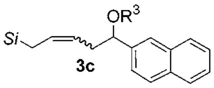
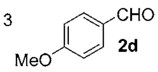
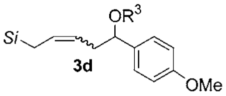
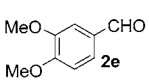
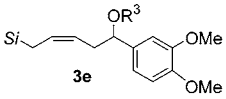
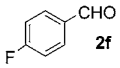
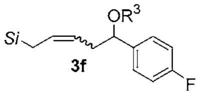
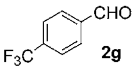
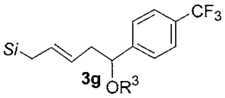
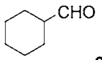
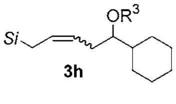


Since the role of PPh_3 is thought to stabilize a Ni(NHC) species, the yield of *Z*-**3aa** should be improved.

Various *E*- and *Z*-allylsilanes were synthesized from dienylsilane **1** and aldehydes **2** (Table 2). It was interesting that the use of Ni(NHC)(PPh_3) generated from $Ni(cod)_2$, PPh_3, **7b**, and Cs_2CO_3 (method A) gave only the desired *Z*-allylsilane *Z*-**3**, while the use of $Ni(PPh_3)_2$ generated from $Ni(cod)_2$ and PPh_3 (method B) gave *E*-allylsilane *E*-**3** as the sole product. The electron-donating group on the aromatic ring gave a high yield of the desired *Z*-allylsilane (entries 3 and 4), but *E*-olefins were obtained in high yield in the case of an aldehyde having an electron-withdrawing group on the aromatic ring (entries 5 and 6).

Table 2. Coupling Reactions of Diene and Various Aldehydes



entry	Substrate	product	time (h)	method[a]	yield (%) *Z*-**3**	yield (%) *E*-**3**
1	 **2b**	 **3b**	5	A	59[b]	—
			1	B	—	71
2	 **2c**	 **3c**	16	A	70[b]	—
			0.5	B	—	70
3	 **2d**	 **3d**	15	A[c]	70[b]	—
			0.5	B	—	55
4	 **2e**	 **3e**	13	A[c]	73[b]	—
			0.5	B	—	54
5	 **2f**	 **3f**	7	A	45[b]	—
			0.5	B	—	75
6	 **2g**	 **3g**	21	A	—	—
			0.5	B	—	76
7	 **2h**	 **3h**	18	A	38	—
			0.5	B	—	63

[a] Method A: ligand, **7b** (20 mol %) + PPh_3 (20 mol %); silane, Et_3SiH; THF reflux. Method B: ligand, PPh_3 (40 mol %); silane, ${}^tBuMe_2SiH$; toluene reflux. [b] Yields were obtained from gas chromatography because *Z*-**10** is unstable. 1.5 equiv of **2** was used in each case. *Z*-**3ba**/*Z*-**10b** = 4.4:1. *Z*-**3ca**/*Z*-**10c** = 1.8:1. *Z*-**3da**/*Z*-**10d** = 1:0. *Z*-**3ea**/*Z*-**10e** = 1:0. *Z*-**3fa**/*Z*-**10f** = 2.8:1. [b] Reaction temperature, 50 °C.

These results indicated that when the reaction was carried out using Ni(NHC) (ratio of Ni to NHC being 1:1), phosphine ligand can be added as a stabilizer of unstable Ni(NHC) because Ni(PPh_3) is not generated from Ni(NHC)(PPh_3). Furthermore, it is a novel example showing different reaction pathways in the same coupling reaction by phosphine and NHC ligands on Ni(0).

Further studies are now in progress.

Supporting Information Available: Information on experimental procedures and spectral data of *Z*-**3aa**, *E*-**3ab**, ***Z*-3ba-3ha**, *E*-**3bb-3-hb**, *Z*-**10b**, *Z*-**10c**, and *Z*-**10f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] Palladium complexes bearing NHC and phosphine have been reported. (a) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C.-P. Weskamp, T. *J. Organomet. Chem.* **2001**, *617*, 616. (b) Titcomb, L. R.; Caddick, S.; Cloke, F. G. N.; Wilson, D. J.; McKerrecher, D. *Chem. Commun.* **2001**, 1388.