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Stereoselective 1,4-Silaboration of 1,3-Dienes Catalyzed by Nickel Complexes

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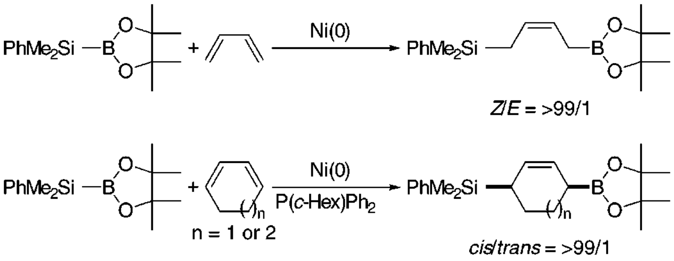
ABSTRACT



The silicon–boron bond of (dimethylphenylsilyl)pinacolborane was stereoselectively added to acyclic 1,3-dienes in a 1,4-fashion to give (*Z*)-4-boryl-1-silyl-2-alkene derivatives in the presence of a Ni(0) catalyst generated from Ni(acac)$_2$ and diisobutylaluminum hydride. 1,4-Silaboration of cyclic 1,3-dienes required the use of cyclohexyldiphenylphosphine with the Ni(0) catalyst to afford *cis*-4-boryl-1-silyl-2-cycloalkene derivatives in high yields with high stereoselectivities.

Transition-metal catalyzed insertion reactions of carbon−carbon multiple bonds to inter-element σ-bonds such as Si−Si,[1] Si−Sn,[2] and B−B[3] have provided powerful methods for the preparation of organometallic compounds containing multiple metallic elements in regio- and stereodefined fashions. The synthetic applications of these organometallic compounds have been extensively explored.[4,5]

We have reported regioselective additions of the silicon−boron bond of silylboranes to alkynes[6] and alkenes,[7] which are catalyzed by palladium and platinum complexes. Moreover, silaboration of 1,3-dienes was found to be catalyzed by a platinum complex, giving 1,4-conjugate adducts as a 1:1 mixture of the corresponding *Z*- and *E*-isomers.[8] Re-

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(1) (a) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317. (b) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (c) Suginome, M.; Ito, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 1925.

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(5) For examples of the use of bis-silylation for stereoselective organic synthesis, see: (a) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487. (b) Suginome, M.; Yamamoto, Y.; Fujii, K.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9608. (c) Suginome, M.; Iwanami, T.; Ito, Y. *J. Org. Chem.* **1998**, *63*, 6096.

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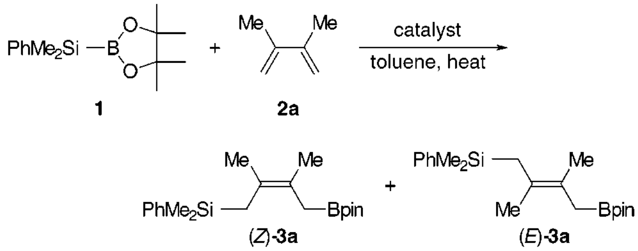
cently, we found that nickel complexes were also able to activate the silicon−boron bond, promoting a silaborative dimerization of alkynes.[9] This finding opened up new possibilities in bismetalation chemistry, since nickel catalysts have scarcely been employed for activation of inter-element σ-bonds.[10] Herein, we wish to report that nickel complexes catalyzed the stereoselective 1,4-addition of the silicon−boron bond of silylborane to acyclic as well as cyclic 1,3-dienes effectively. The 1,4-silaboration produced stereodefined 4-boryl-1-silyl-2-alkene derivatives having both allylsilane and allylborane moieties, which were utilized in selective allylation of aldehydes and ketones.

Reactions of 2,3-dimethyl-1,3-butadiene (**2a**) with (dimethylphenylsilyl)pinacolborane (**1**) were carried out in the presence of a catalytic amount of group 10 metal (Ni, Pd, and Pt) complexes (Table 1).

Table 1. Reaction of Silylborane **1** with 2,3-Dimethyl-1,3-butadiene (**2a**) in the Presence of Nickel, Palladium, and Platinum Complexes[a]



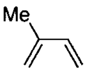
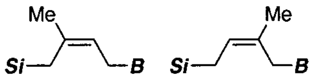
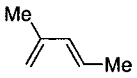
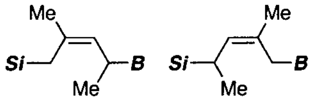
entry	catalyst[b]	temp/°C	yield/%[c]	Z/E[d]
1	$Ni(acac)_2$−DIBAH	80	90	>99/1
2	$Pd(OAc)_2$−*t*-OcNC	110	0	
3	$Pt(CH_2{=}CH_2)(PPh_3)_2$	110	95	48/52

[a] Silylborane **1** (1 equiv) and **2a** (2 equiv) were heated in the presence of Ni (0.05 equiv), Pd (0.02 equiv), or Pt (0.02 equiv) catalyst in toluene for 24 h. [b] Ni/DIBAH = 1/2; Pd/isocyanide = 1/15. [c] Isolated yield by bulb-to-bulb distillation. [d] Determined by ^{1}H NMR.

The nickel catalyst, generated in situ by mixing $Ni(acac)_2$ with diisobutylaluminum hydride (DIBAH), was most effective for the stereoselective silaboration of **2a**, affording 1,4-silaboration product **3a** with *Z*-stereochemistry as the sole product in 90% yield (entry 1).[11] Neither the 1,2-addition product[3d] nor the silaborative dimerization product[12] was detected in the reaction mixture. As previously reported,[8] the platinum−phosphine complex also promoted the 1,4-conjugate addition with low stereoselectivity (entry 3). The palladium−1,1,3,3-tetramethylbutyl isocyanide (*t*-OcNC) complex, which was most effective for the silaboration of alkynes, did not give any adducts (entry 2).[13] The yield for the 1,4-silaboration adducts depended markedly upon the substituents on the boron atom of the silylborane. For example, the reaction of bis(diethylamino)(dimethylphenylsilyl)borane with **2a** was sluggish in the presence of either the nickel or platinum catalyst.[14]

The nickel-catalyzed 1,4-silaborations of some 1,3-dienes **2b**−**d** are summarized in Table 2.[15] Isoprene (**2b**) reacted with **1** to give **3b** and **4b** in 92% combined yield with high stereoselectivity but only moderate regioselectivity (**3b**/**4b** = 72/28). 2-Methyl-1,3-pentadiene (**2c**) afforded **3c** (56%) and **4c** (28%) with slightly lower regioselectivity than that of **2b**. Silaboration of gaseous 1,3-butadiene (**2d**) also proceeded under atmospheric pressure to give **3d** in high yield. Almost no reactions were detected with 1,1- and 1,4-disubstituted 1,3-dienes such as 4-methyl-1,3-pentadiene and 2,4-hexadiene, respectively, under the same reaction conditions.

Table 2. Nickel-Catalyzed 1,4-Silaboration of 1,3-Dienes **2b**−**d**[a]

Entry	Diene 2	yield/%	product(s) 3,4[b]
1	 **2b**	92	 **3b**/**4b** = 72/28
2	 **2c**	84	 **3c**/**4c** = 67/33
3[c]	 **2d**	90	 **3d**

[a] Silylborane **1** (1 equiv) and **2b**−**d** (2 equiv) were reacted in the presence of $Ni(acac)_2$ (0.05 equiv) and DIBAH (0.10 equiv) in toluene at 80 °C for 24 h unless otherwise noted. [b] Ratios of **3** and **4** were determined by ^{1}H NMR. [c] The reaction was carried out under 1 atm of 1,3-butadiene.

Compounds **3a** and **3d** thus obtained were reacted with benzaldehyde to give **5a** and **5d** stereoselectively (Scheme

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[8] Suginome, M.; Nakamura, H.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4248.

[9] Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **1998**, *17*, 5233.

[10] (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (b) Jzang, T. T.; Liu, C.-S. *Main Group Met. Chem.* **1987**, *10*, 373. (c) Ishikawa, M.; Nishihara, Y.; Sakamoto, H.; Ono, T.; Oshita, J. *Organometallics* **1992**, *11*, 483.

[11] **Typical Procedure for the Nickel-Catalyzed 1,4-Silaboration of 1,3-Dienes.** To a mixture of $Ni(acac)_2$ (25.7 mg, 0.10 mmol) and 1,3-diene (2 equiv based on **1**) in a Schlenk tube was added DIBAH (0.2 M solution in toluene, 1.0 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C. To the mixture was added **1** (521 mg, 2.0 mmol); the mixture was heated at 80 °C for 24 h. Evaporation of volatile materials followed by bulb-to-bulb distillation afforded the products.

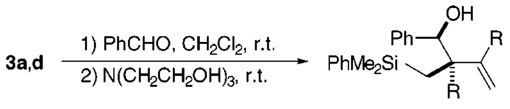
[12] For transition-metal catalyzed bismetalative dimerization of 1,3-dienes, see: (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *Chem. Lett.* **1975**, 887. (b) Obora, Y.; Tsuji, Y.; Kawamura, T. *Organometallics* **1993**, *12*, 2853. (c) Obora, Y.; Tsuji, Y.; Kakehi, T.; Kobayashi, M.; Shinkai, Y.; Ebihara, M.; Kawamura, T. *J. Chem. Soc., Perkin Trans. 1* **1995**, 599 and references therein. See also ref 3c.

[13] Palladium−phosphine and palladium−phosphite complexes were also ineffective for the reaction.

[14] The reaction of 1,3-dienes with a stannylborane having nitrogen groups on the boron atom is effectively catalyzed by a palladium−phosphine complex. See: Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Tetrahedron Lett.* **1998**, *39*, 9043.

[15] The regio- and stereochemical assignments were made by NOE experiments of the silaboration products or by transformation to homoallylic alcohols through reactions with benzaldehyde.

Scheme 1

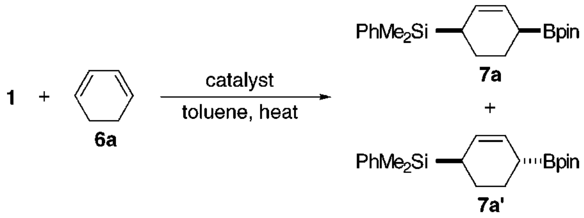


5a: R = Me; 87%
5d: R = H; 85%

1). On the basis of the stereochemistry of **5**, the *Z* geometry of **3** was confirmed unambiguously.[16]

Although various bismetalations of acyclic dienes have been reported so far, only a few examples have been known for cyclic dienes.[3e,10b,c] The nickel catalyst generated from Ni(acac)$_2$ and DIBAH did not promote the silaboration of 1,3-cyclohexadiene. However, it was found that the use of the appropriate phosphine ligand on nickel remarkably increased the catalytic activity as well as the stereoselectivity of the silaboration (Table 3).

Table 3. 1,4-Silaboration of 1,3-Cyclohexadiene (**6a**) with **1**[a]



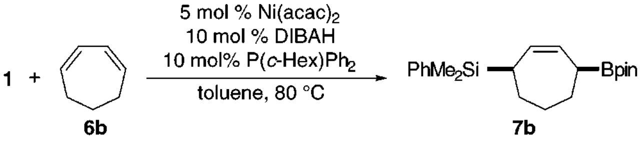
entry	phosphine	yield/%[b]	*cis*/*trans*[c]
1	none	0	
2	P(*n*-Bu)$_3$	39	94/6
3	PMe$_2$Ph	92[d]	60/40
4	PMePh$_2$	97	93/7
5	P(c-Hex)Ph$_2$	99	>99/1
6	PPh$_3$	0	
7	*e*	21	>99/1

[a] A mixture of **1** (1 equiv), **6a** (2 equiv), Ni(acac)$_2$ (0.05 equiv), DIBAH (0.10 equiv), and phosphine (0.10 equiv) was heated in toluene at 80 °C for 24 h unless otherwise noted. [b] Isolated yield. [c] Ratios of *cis*- and *trans*-isomers were determined by HPLC. [d] Contaminated with a small amount of byproducts. [e] Use of Pt(CH$_2$=CH$_2$)(PPh$_3$)$_2$ (0.02 equiv) instead of Ni catalysts.

The nickel catalyst bearing tributylphosphine induced the silaboration of 1,3-cyclohexadiene, but only in 39% yield (entry 2). *cis*-4-Boryl-1-silyl-2-cyclohexene **7a** was formed as the major product together with the corresponding *trans*-isomer **7a′** as the minor product. Although dimethylphenylphosphine also worked as a ligand to give the products in high yield, the stereoselectivity was exceptionally low (entry 3). The use of methyldiphenylphosphine gave the silaboration products in high yield with stereoselectivity similar to that with P(*n*-Bu)$_3$ (entry 4). Almost complete stereoselectivity with a quantitative yield was attained by using the more sterically congested cyclohexyldiphenylphosphine ligand (entry 5).[17] No reaction occurred when triphenylphosphine was used as the ligand (entry 6). It may be noted that a platinum−triphenylphosphine complex also catalyzed the reaction, affording **7a** stereoselectively in low yield (entry 7).

The reaction conditions were applicable to 1,3-cycloheptadiene (**6b**), providing **7b** in 93% yield with complete stereoselectivity (Scheme 2). However, cyclopentadiene and 1,3-cyclooctadiene were inert toward the reaction under identical reaction conditions.

Scheme 2



(93%, *cis*/*trans* = >99/1)

Although the mechanism for formation of the *trans*-isomer in the silaboration of cyclic 1,3-dienes is not clear at this moment, acceleration of the reductive elimination step by sterically bulky phosphine ligands such as P(c-Hex)Ph$_2$ may be the key for the observed high stereoselectivity.

In summary, the stereoselective addition of the silicon−boron bond of silylborane to 1,3-dienes was successfully catalyzed by nickel(0) catalysts. The silaboration of cyclic 1,3-dienes proceeded with perfect stereoselectivity with the appropriate choice of the phosphine ligand.

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Supporting Information Available: Experimental procedures and characterization data for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] (a) Hoffmann, R. W.; Zeiss, H.-J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 306. (b) Hoffmann, R. W.; Zeiss, H.-J. *J. Org. Chem.* **1981**, *46*, 1309.

[17] The reaction afforded **7a** in 80% yield in the presence of 2 mol % of the Ni catalyst.