Organometallics **1998,** *17,* 5233−5235

Nickel-Catalyzed Silaborative Dimerization of Alkynes

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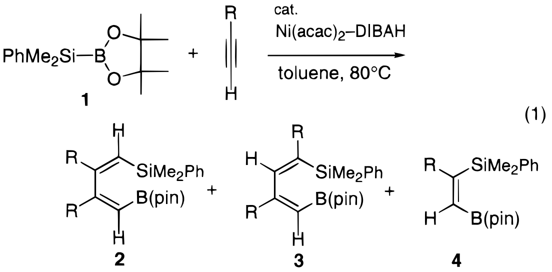
Received August 27, 1998

Summary: Double insertion of alkynes into the Si−B bond of (dimethylphenylsilyl)pinacolborane proceeded in the presence of nickel(0) catalysts to give cis,cis-1-silyl-4-boryl-1,3-butadiene derivatives in a regio- and stereoselective manner. Involvement of (silyl)(2-boryl-1-alkylvinyl)nickel(II) intermediates in the silaborative dimerization reaction was suggested by the regiochemical preference as well as on the basis of reactions of the corresponding germylborane with alkynes in the presence of Ni, Pd, and Pt catalysts.

Catalytic activation of σ-bonds between metallic elements such as boron, silicon, germanium, and tin has gained much attention, leading to development of new synthetic methods for organometallic compounds containing boron and group 14 elements.[1−4] It has been reported that palladium and platinum complex catalysts are effective for the activation of the interelement bonds, enabling the addition reactions across carbon−carbon multiple bonds as well as σ-bond metathesis reactions.[1] In contrast, nickel catalysts have hardly achieved the successful σ-bond activation except for the Si−Si bonds with neighboring participating groups[5] and those in the highly strained small rings.[6] Recently, we reported that regioselective addition of a silicon−boron bond of silylborane across carbon−carbon triple bonds was catalyzed by palladium complex catalysts in a highly regio- and stereoselective manner.[7] Furthermore, platinum complex catalysts were effective for the activation of the silicon−boron bond, promoting regioselective silaboration of alkenes[8] and silaborative coupling of dienes to aldehydes.[9] The appropriate choice of the metal as well as the ligands was crucially important for attaining not only the high yields but also the high regio- and stereoselectivities. Herein, we describe new dimerization reactions of alkynes with formation of a B−C bond as well as a Si−C bond through the activation of the silicon−boron bond by nickel(0) catalysts.[10]

Reaction of silylborane **1** with 2.5 molar equiv of 1-hexyne was carried out at 80 °C in the presence of a catalyst prepared from 5 mol % of $Ni(acac)_2$ with diisobutylaluminum hydride (DIBAH) as a reductant (Ni/Al = 1:2) (eq 1).[11,12] The reaction afforded silaborative dimerization products **2a** and **3a** in 50% yield as a 3:1 mixture along with a minor amount of silaboration product **4a** (Table 1; entry 1). NOE experiments revealed that the *Z*,*Z*-isomer **2a** was formed as a major isomer with head-to-head dimerization of alkyne, while the *Z*,*Z*-isomer **3a** was formed as a minor isomer with head-to-tail dimerization. No products derived from tail-to-tail or tail-to-head[13] dimerization nor those with trans C═C bonds were formed in the reaction. Moreover, the minor silaboration product **4a** was obtained as a single isomer, which was identical to that obtained in the palladium-catalyzed silaboration of 1-hexyne.[7]



(1)

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[1] For Si−Si bonds, see: (a) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351−1374. (b) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317−1350. (c) Suginome, M.; Ito, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 1925−1934.

[2] For B−B bonds, see: (a) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018−11019. (b) Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713−720. (c) Baker, R. T.; Nguyen, P.; Marder, T. B.; Westcott, S. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1336−1337. (d) Ishiyama, T.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1998**, *39*, 2357−2360, and references therein.

[3] For Si−Sn bonds, see: (a) Mitchell, T. N.; Killing, H.; Dicke, R.; Wickenkamp, R. *J. Chem. Soc., Chem. Commun.* **1985**, 354−355. (b) Chenard, B. L.; Zyl, C. M. V. *J. Org. Chem.* **1986**, *51*, 3561−3566. (c) Tsuji, Y.; Obora, Y. *J. Am. Chem. Soc.* **1991**, *113*, 9368−9369. (d) Murakami, M.; Amii, H.; Takizawa, N.; Ito, Y. *Organometallics* **1993**, *12*, 4223−4227, and references therein.

[4] For Sn−B bonds, see: Onozawa, S.-y.; Hatanaka, Y.; Sakakura, T.; Shimada, S.; Tanaka, M. *Organometallics* **1996**, *15*, 5450−5452.

[5] For hydrodisilanes, see: Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263−9264. For vinyldisilanes, see: Ishikawa, M.; Nishimura, Y.; Sakamoto, H.; Ono, T.; Ohshita, J. *Organometallics* **1992**, *11*, 483−484.

[6] Ishikawa, M.; Naka, A. *Synlett* **1995**, 794−802.

[7] Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777−2778.

[8] Suginome, M.; Nakamura, H.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2516−2518.

[9] Suginome, M.; Nakamura, H.; Matsuda, T.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4248−4249.

[10] Nickel-catalyzed hydrosilative dimerization of terminal alkynes was reported, see: (a) Lappert, M. F.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1972**, 1272. (b) Lappert, M. F.; Nile, T. A.; Takahashi, S. *J. Organomet. Chem.* **1973**, *72*, 425−439. For an application to diynes, see: (c) Tamao, K.; Kobayashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 6478−6480.

[11] Typical procedure for the Ni-catalyzed silaborative dimerization of alkynes: To a mixture of $Ni(acac)_2$ (7.7 mg, 0.030 mmol) and alkyne (2.5−6.0 equiv based on **1** employed) in toluene (0.15 mL) was added DIBAH (11 μL, 0.060 mmol) at 0 °C.; the mixture was stirred for 30 min at 0 °C. To the mixture was then added **1** (158 mg, 0.60 mmol) at room temperature under nitrogen; the mixture was stirred at 80 °C for 48 h. The mixture was diluted with hexane and stirred under air for 6 h at room temperature. Filtration of the mixture and evaporation of the volatile material followed by column chromatography on silica gel or preparative GPC gave the products.

[12] Use of *n*-BuLi or MeMgBr as a reductant gave results identical to that with DIBAH.

[13] The tail-to-head silaborative dimerization would give the diene product with a boryl group at the substituted alkyne carbon.

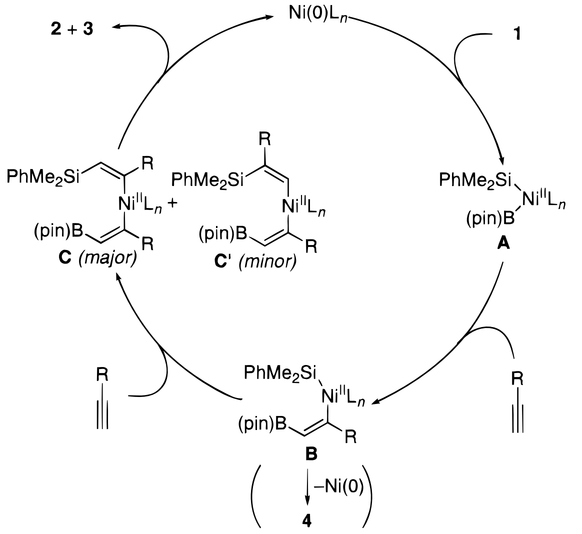
10.1021/om9807250 CCC: $15.00

Table 1. Reactions of Silylborane 1 with Terminal Alkynes in the Presence of Nickel Catalysts[a]

entry	alkyne R (equiv)	additive	selectivity[b,c] (**2** + **3**)/**4**	yield/%[d] of **2** + **3**	regio[b] **2**/**3**
1	Bu (2.5)	none	94/6	50	76/24
2	Bu (4.0)	none	92/8	64	74/26
3	Bu (6.0)	none	96/4	78	75/25
4[e]	Bu (4.0)	none	93/7	52	75/25
5	Bu (4.0)	PBu_3	96/4	68	75/25
6	*c*-Pen (4.0)	none	87/13	39	59/41

[a] Ni(acac)$_2$ (5 mol %) and DIBAH (10 mol %) were used unless otherwise noted. [b] Determined by ^{1}H NMR of the reaction mixtures. [c] Isolated yields. [d] In all cases, the compounds **4** were obtained as single isomers. [e] Ni(acac)$_2$ (2 mol %) and DIBAH (4 mol %) were used.

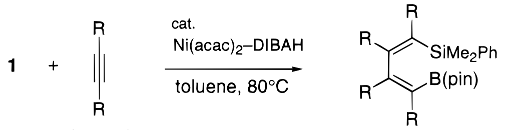
Scheme 1. Possible Mechanism for Nickel-Catalyzed Silaborative Dimerization of Alkynes



The regiochemical outcome revealed that the boryl groups were exclusively introduced to the terminal alkynyl carbon of 1-hexyne for all the products.

The yields of the dimerization products were improved by use of a large excess of the alkyne (entries 2 and 3); 78% yield was attained by use of 6 molar equiv of 1-hexyne. The reaction also proceeded with a catalyst loading as low as 2 mol % of Ni complex but in slightly lower yield (entry 4). Although additives such as PPh_3 and $P(OEt)_3$ resulted in significant retardation of the reaction, P(n-Bu)$_3$ on the nickel catalyst resulted in slight improvement of the yield for the dimerization products (entry 5). The dimerization of a terminal alkyne with the bulkier cyclopentyl group (R = *cyclo*-Pen) required higher temperature (110 °C) to give dienes **2b** and **3b** in 39% yield with lower regioselectivity (entry 6).

Internal alkynes also afforded the silaborative dimerization products in higher yields. Thus, 3-hexyne and 5-decyne (2.5 equiv) furnished (*Z*,*Z*)-dimerization products **5a** and **5b** in 90% and 88% yields, respectively, in the presence of the nickel catalyst (eq 2).[14] Moreover,

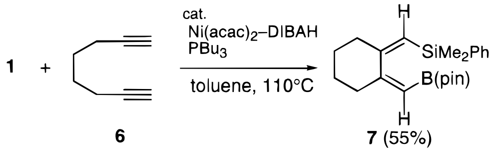


(2)

5a (R = Et; 92%)
5b (R = Bu; 88%)
5c (R = TBSO(CH$_2$)$_3$; 78%)

1,8-bis(*tert*-butyldimethylsilyloxy)-4-octyne afforded the corresponding diene **5c** in good yield. It is remarked that diphenylacetylene, one of the most reactive internal alkynes in the palladium-catalyzed silaboration,[7] was inert under the identical conditions.

The silaborative dimerization was applicable to intramolecular cyclization of diyne **6**, leading to dimethylenecyclohexane derivative **7** in 55% yield (eq 3).[15,16]



(3)

6

7 (55%)

A possible mechanism for the Ni-catalyzed silaborative dimerization of alkynes is illustrated in Scheme 1. The (silyl)(boryl)Ni(II) intermediate **A**, which may be formed by oxidative addition of the Si–B bond onto the Ni(0) complex, undergoes cis-insertion of a terminal alkyne into the B–Ni bond with highly regioselective Ni–C bond formation at the internal alkynyl carbon to give (silyl)(2-boryl-1-alkylvinyl)nickel(II) intermediate **B**. The following insertion of alkyne into the Si–Ni bond of **B** takes place with the moderate regiochemical preference for the Ni–C bond formation at the internal alkynyl carbon to give **C** and **C′**, whose reductive elimination furnishes silaborative dimerization products **2** and **3**, respectively. Another possibility for the second insertion, in which the alkyne inserts into the Ni–C bond of **B** to form (silyl)(dienyl)Ni(II) species, may be excluded, since the resultant (silyl)(dienyl)Ni(II) species should be susceptible to further insertion of alkynes into the Ni–C bond to give silaborative trimerization products, which were not indeed detected in the reaction mixture.[17] The insertion of alkyne into the Si–Ni bond of **B** may be much faster than the insertion into the B–Ni bond of **A**, since the single-insertion product **4** was obtained only in low yield. Moreover, attempted silaborative cross-dimerization of 1-hexyne and diphenylacetylene afforded **5d** in moderate yield together with the homodimerization products **2a** and **3a** in 22% total yield without formation of any other cross-dimerization products (eq 4). Thus, diphenylacetylene, which is a stronger ligand for nickel(0) than 1-hexyne but is reluctant to insert into the Ni–B bond of **A**, may be selectively inserted into the Ni–Si bond of **B**.

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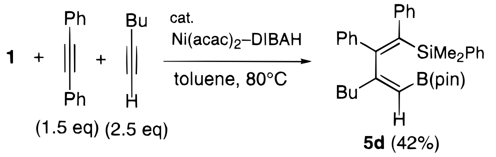
[14] Single-insertion products corresponding to **4** were also formed in 5–8% yields.

[15] In the absence of PBu_3, **7** was obtained in 33% yield under otherwise identical conditions.

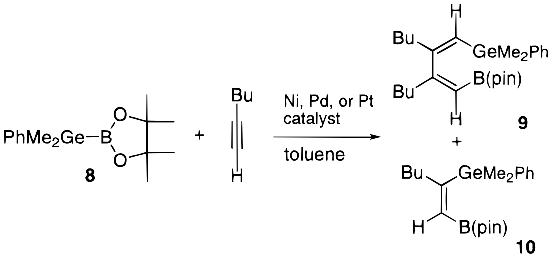
[16] Similar silaborative cyclization was reported in the reaction of **6** with a silylborane having an *N*,*N′*-dimethylethylenediamine ligand on the boron atom in the presence of a palladium catalyst. See: Onozawa, S.-y.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1997**, 1229–1230.

[17] For the hydrosilative dimerization, Lappert and Takahashi proposed a mechanism involving a first insertion of alkyne into the Ni–H bond of a (hydride)(silyl)Ni(II) intermediate followed by a second insertion into the newly formed Ni–C bond. See ref 10.



(4)

Related reactions of germylborane **8** with 1-hexyne, which were found to be catalyzed by not only nickel complex but also palladium and platinum complexes (eq 5, Table 2), may be relevant to the reaction mechanism.



(5)

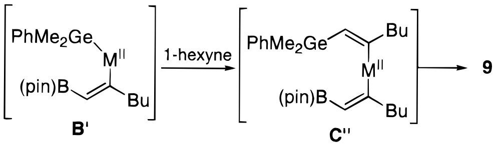
The nickel catalyst also promoted the germaborative dimerization of 1-hexyne, producing **9** selectively as a 3:1 mixture of regioisomers corresponding to **2** and **3** in moderate yield (entry 1). On the other hand, the palladium–isonitrile complex catalyst, which afforded only a single-insertion product **4** in the reaction of 1-hexyne with silylborane **1**, gave a 1:1 mixture of **9** and **10** in high total yield in the reaction with germylborane **8** (entry 2). However, the platinum–triphenylphosphine complex catalyzed the germaboration of 1-hexyne, producing **10** exclusively in high yield (entry 3).

The product selectivities in the germaboration reactions of 1-hexyne might be rationalized by a possible involvement of (germyl)(2-boryl-1-alkylvinyl)[M] complexes **B′** ([M] = Ni, Pd, Pt), which undergo either reductive elimination giving **10** or further insertion of 1-hexyne into the germyl–[M] bond followed by reductive elimination from the resultant bis(alkenyl)[M] intermediate **C″** leading to **9** (eq 6). The results summarized in Table 2 may suggest that the germyl–platinum bond of **B′** ([M] = Pt) is relatively less susceptible to the insertion of 1-hexyne leading to **9** than the corresponding germyl–palladium bond of **B′** ([M] = Pd), which is, in turn, less susceptible to undergoing the alkyne insertion than the corresponding germyl–nickel bond of **B′** ([M] = Ni).

Table 2. Reactions of Germylborane 8 with 1-Hexyne in the Presence of Nickel, Palladium, and Platinum Complexes

entry	catalyst	**9** yield/% (ratio)[d]	**10** yield/% (ratio)[e]	**9**/**10**[f]
1	$Ni(acac)_2$/DIBAH[a]	74 (74/26)	trace	96/4
2	$Pd(acac)_2$/*t*-OcNC[b]	39 (96/4)	46 (>99/1)	47/53
3	$Pt(CH_2{=}CH_2)(PPh_3)_2$[c]	0	87 (91/9)	<1/99

[a] $Ni(acac)_2$ (0.05 eq), DIBAH (0.10 eq), 1-hexyne (4.0 eq), and **8** were reacted at 80 °C. [b] $Pd(acac)_2$ (0.02 eq), 1,1,3,3-tetramethylbutyl isocyanide (0.08 eq), 1-octyne (2.5 eq), and **8** were reacted at 110 °C. [c] $Pt(CH_2{=}CH_2)(PPh_3)_2$ (0.02 eq), 1-octyne (1.5 eq), and **8** were reacted at 80 °C. [d] Regioisomeric ratios of head-to-head and head-to-tail dimers. [e] Regioisomeric ratios of 1-boryl and 2-boryl derivatives. [f] Determined by ^1H NMR of the crude reaction mixtures.



(6)

In summary, silaborative dimerization of 1-alkyne was achieved by nickel complex catalyst. We proposed a mechanism involving the (silyl)(boryl)nickel(II) complex intermediate, which is formed via oxidative addition of the silicon–boron bond and undergoes stepwise insertion of 1-alkyne into the boron–nickel bond and then the silicon–nickel bond.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, "The Chemistry of Inter-element Linkage" (09239226) from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Text giving detailed experimental procedures and characterization data for the new compounds (5 pages). Ordering information is given on any current masthead page.

OM9807250