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Nickel-Catalyzed Silaboration of Small-Ring Vinylcycloalkanes: Regio- and Stereoselective (*E*)-Allylsilane Formation via C−C Bond Cleavage

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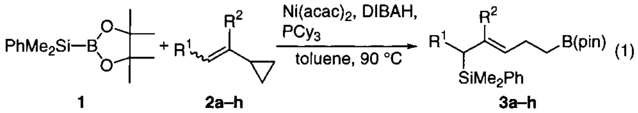
Summary: Vinylcyclopropanes and vinylcyclobutanes undergo regio- and stereoselective reaction with silylborane in the presence of nickel catalysts, giving (ω-borylalkyl)-substituted (E)-allylsilanes via cleavage of the carbon−carbon σ-bond in the rings.

The versatile utility of silylborane has recently been demonstrated in transition-metal-catalyzed additions,[1] C−C coupling,[2] and C−C cleavage reactions,[3] which lead to the synthesis of regio- and stereodefined organic compounds containing both silicon and boron.[4,5] In comparison with other bimetals such as disilanes,[1a,6] diborons,[7] and silylstannanes,[1a] the high but controllable reactivities in the presence of a variety of transition-metal catalysts including Ni, Pd, and Pt complexes are highly remarkable for the silylboranes. The silaboration products thus obtained are attractive as new tools in organic synthesis, since many methods have been developed for the selective functionalization not only at the silyl but also at the boryl moieties.[1c,8,9] Here, we report new nickel-catalyzed silaboration of vinylcyclopropanes (VCPs), which is accompanied by cleavage of C−C bonds in the cyclopropane ring. Although transition-metal-catalyzed cycloadditions of VCPs have gained much attention in synthetic organic chemistry,[10] little is known about their reactivity in transition-metal-catalyzed bis- or hydrometalations.[11] We also describe how the same protocol was applied to vinylcyclobutanes (VCBs). These reactions provided (ω-borylalkyl)-substituted allylsilanes in a highly regio- and stereoselective manner.

Table 1. Nickel-Catalyzed Reaction of VCPs 2 with 1[a]



entry	VCP (R^1, R^2)	equiv[b]	PCy_3/Ni[c]	product	% yield of **3**[d]
1	**2a** (H, Ph)	1.5	0	**3a**	15[e]
2	**2a**	1.5	1	**3a**	69
3	**2a**	1.5	2	**3a**	<30[e]
4	**2a**	3.0	1	**3a**	89
5	**2b** (H, *p*-FC_6H_4)	3.0	1	**3b**	81
6	**2c** (H, Me)	3.0	1	**3c**	74
7	**2d** (Ph, H)	1.5	1	**3d**	82
8	**2e** (*n*-Bu, H)	1.5	1	**3e**	84 (87)[f]
9	**2f** (Ph, Me)	1.5	1	**3f**	56
10	**2g** (Ph, Ph)	3.0	1	**3g**	44
11	**2h** (H, *c*-Pr)	1.5	1	**3h** + **4**[g]	38
12	**2h**	3.0	1	**3h** + **4**[h]	61

[a] Unless otherwise noted, reactions were carried out on a 0.8 mmol scale at 90 °C for 2−8 h in toluene in the presence of a nickel catalyst prepared from $Ni(acac)_2$ (5 mol %) and DIBAH (5 mol %) with or without PCy_3. [b] Molar equiv of **2** based on **1**. [c] Molar ratio of the added PCy_3 and $Ni(acac)_2$. [d] Isolated yield based on **1** unless otherwise noted. [e] NMR yield. [f] The value in parentheses indicates the yield obtained in a 4.0 mmol scale reaction. [g] **3h**:**4** = 76:24 (^{1}H NMR). [h] **3h**:**4** = 86:14 (^{1}H NMR).

Initially, VCP **2a** (R^1 = H, R^2 = Ph) was reacted with silylborane **1** in toluene at 90 °C in the presence of nickel catalysts generated from $Ni(acac)_2$ with diisobutylaluminum hydride (DIBAH) (eq 1; Table 1, entries 1−4). The reactions afforded silaboration product **3a** in varying yields, in which the proximal carbon−carbon bond in the cyclopropane ring was concomitantly cleaved. Whereas **3a** was formed only in low yield in the absence of phosphine ligand (entry 1), addition of PCy_3 (tricyclohexylphosphine, 1 equiv to Ni) improved the yield to 69% (entry 2).[12] Although further increase in the P/Ni ratio lowered the yield significantly (entry 3), use of

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(1) (a) Review: Suginome, M.; Ito, Y. *Chem. Rev.* **2000**, *100*, 3221. (b) Suginome, M.; Matsuda, T.; Yoshimoto, T.; Ito, Y. *Org. Lett.* **1999**, *1*, 1567. (c) Suginome, M.; Ohmori, Y.; Ito, Y. *J. Am. Chem. Soc.* **2001**, *123*, 4601.

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(5) For the convenient synthesis of (dimethylphenylsilyl)pinacolborane, see: Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647.

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(10) Wender, P. A.; Barzilay, C. M.; Dyckman, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 179, and references therein.

(11) For Rh-catalyzed hydrosilylation of VCPs, see: Bessmertnykh, A. G.; Blinov, K. A.; Grishin, Y. K.; Donskaya, N. A.; Beletskaya, I. P. *Tetrahedron Lett.* **1995**, *36*, 7901.

(12) PBu_3 was a little less effective than PCy_3, whereas reactions using PPh_3, $PCyPh_2$, $P(t\text{-}Bu)_3$, or PMe_2Ph resulted in lower yields (trace−10%) of **3a** than that in the *absence* of the phosphine ligands.

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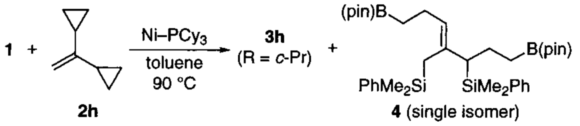
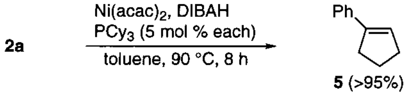
more equivalents of VCP **2a** gave **3a** in sufficiently high yield (entry 4). It is noteworthy that the silaboration of VCP proceeded with highly selective Si−C and B−C bond formations at the terminal vinyl carbon and the 2-position of the cyclopropane ring of **2a**, respectively, with cleavage of the 1,2-C−C bond in the cyclopropane ring. Furthermore, the formal 1,5-addition of silylborane provided the allylsilane **3a**, in which the geometry of the C═C bond was 100% *trans*. Under the optimized reaction conditions, VCP **2b** and **2c** bearing a substituent R^2 at the internal vinyl carbons afforded the corresponding products **3b** and **3c** selectively in good yields (entries 5 and 6). VCPs **2d** and **2e** having a substituent (R^1) at the terminal vinyl carbons provided respective products **3d** and **3e** in high yields even with use of smaller amounts of VCPs (entries 7 and 8).[13] Although the presence of more substituents on the vinyl group slightly lowered the product yields, the regio- and stereoselectivity were very high (entries 9 and 10). Reaction of 1,1-dicyclopropylethene (**2h**) afforded a double addition product **4** as a minor product along with the major formation of **3h** (eq 2; entry 11). The ratio of **3h** to **4** could be improved to 86:14 by use of a larger amount of **2h** (entry 12).



(2)

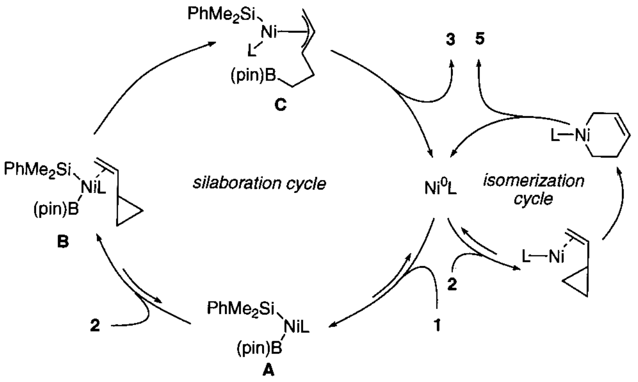
We found that the nickel-catalyzed silaboration of VCP **2a** was accompanied by ring-enlargement isomerization to 1-phenylcyclopentene.[14] Although nickel-catalyzed VCP−cyclopentene isomerization of VCPs having additional C═C or cyclopropyl groups was also demonstrated by using a $Ni(cod)_2-PBu_3$ (1:1) catalyst, no reaction took place for **2a**.[15] In sharp contrast to that report, the isomerization of **2a** was found to proceed in high yield (>95%) with the $Ni(acac)_2-DIBAH-PCy_3$ (1:1:1) system, even in the absence of the silylborane (eq 3).[16]



(3)

To elucidate the mechanistic relationship between the two competing Ni-catalyzed reactions of VCPs, i.e., silaboration and isomerization, we carried out the silaboration of **2a** (1.5 equiv) with varying PCy_3/Ni ratios (1:1−4:1; Ni: 5 mol %) at 90 °C for 1 h. Interestingly, the formation of **5** became dominant (ca. 90% yield based on **2a**; **3a**:**5** = 1:9) with the P/Ni ratio of 4:1, whereas ca. 1:1 formation of **3a** and **5** was observed for the P/Ni ratio of 1:1 (ca. 35% yield each based on **2a**). The change in the product distribution implies that the two reactions proceeded through different reaction pathways. A possible mechanism for the silaboration of VCPs may involve formation of (silyl)(boryl)nickel(II) intermediate **A** via oxidative addition of **1** onto a Ni(0) complex (Scheme 1). Coordination of VCPs onto the nickel (to form **B**) may be followed by migratory B−C bond formation with cleavage of the C−C bond, giving allylnickel species **C**. Subsequent reductive elimination of the Si−C bond proceeds facilely only at the allylic carbon *cis* to the silyl group without possible *syn*−*anti* as well as *cis*−*trans* isomerization of **C**, leading to the highly regioselective formation of **3**. The exclusive formation of the *trans*-alkenes may be rationalized by the preference for *s-trans* conformation of VCPs in the migratory B−C bond formation step.[10] The undesired VCP−cyclopentene isomerization may arise from direct interaction of VCPs with the Ni(0) species. The proposed catalytic cycle seems to be most probable in comparison with the other mechanistic possibilities from the following considerations: (1) Most stoichiometric reactions of VCPs with transition-metal complexes are driven by the formation of π-allyl complexes;[17] (2) the observed insensitivity of the reaction rate and yield to the substitution pattern at the C═C bonds of VCPs suggests that the insertion of the C═C is not involved in the cycle; and (3) our previous study on the Ni-catalyzed silaboration reaction strongly suggests that exclusive migration of the boryl group rather than the silyl group of the (silyl)(boryl)nickel(II) to the coordinated organic substrate is involved in the cycle.[2b,18]

Scheme 1



Application of the present silaboration reaction to vinylcyclobutanes was quite successful (eq 4; Table 2). Although higher temperature and concentration as well as larger catalyst loading were required, the reaction of VCBs (1.5−3.0 equiv) with **1** afforded **7a**−**c** with 100% *trans* C═C double bonds in good yields via cleavage of the C−C bond in the cyclobutane ring.[19,20] The characteristic regioselectivity for the introduction

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(13) VCPs **2d** and **2e** were used as mixtures of *E* and *Z* isomers. *E*/*Z* ratios: 76/24 for **2d**; 7/93 for **2e**.

(14) Hudlicky, T.; Reed, J. W. In *Comprehensive Organic Synthesis*, Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, p 899.

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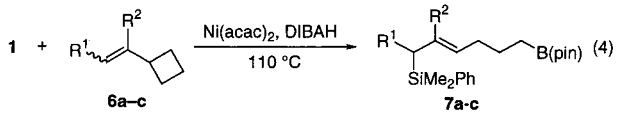
(16) Besides **2a** (>95%), VCPs **2b** (>95%), **c** (<5%), **f** (40%), **g** (50%), and **h** (90%) underwent the nickel-catalyzed isomerization under the same reaction conditions. The values in parentheses indicate the conversion of the VCPs after 8 h at 90 °C. As for reactions of VCPs **2d** and **2e**, products were not identifiable due to the low conversion. In these reactions, *cis* isomers were more rapidly consumed than the corresponding *trans* isomers.

(17) Khusnutdinov, R. I.; Dzhemilev, U. M. *J. Organomet. Chem.* **1994**, *471*, 1.

(18) We have proposed that not only the Ni-catalyzed silaborations, but also Pd- and Pt-catalyzed silaborations generally proceed via insertion into the boron−metal bond.[1−3] Recently, Ozawa et al. reported that stoichiometric reaction of *cis*-$(PhMe_2Si)[(pin)B]Pt(PR_3)_2$ with phenylacetylene proceeded via exclusive insertion of the triple bond into the B−Pt bond, giving *cis*-$(PhMe_2Si)[(pin)BHC{=}CPh]Pt(PR_3)_2$ in high yield, which subsequently underwent reductive elimination cleanly on heating. Sagawa, T. ; Asano, Y.; Ozawa, F. The 48th Symposium on Organometallic Chemistry, Japan, Yokohama, September 18−19, 2001; Abstract PA234.

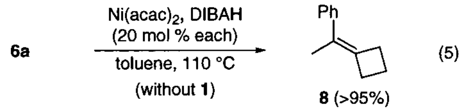
Table 2. Nickel-Catalyzed Reaction of VCBs 6 with 1[a]



entry	VCP (R^1, R^2)	equiv[b]	product (% yield)[c]
1	**6a** (H, Ph)	3.0	**7a** (65)
2	**6b** (Ph, Me)	3.0	**7b** (69)
3	**6c** (Ph, Ph)	1.5	**7c** (77)

[a] Reactions were carried out on a 0.4 mmol scale at 110 °C in the presence of a nickel catalyst prepared from $Ni(acac)_2$ (20 mol %) and DIBAH (20 mol %). [b] Molar equiv of **6** based on **1**. [c] Isolated yield based on **1**.

of the silyl and the boryl groups to the allylic and ω-positions, respectively, indicates that the silaboration of VCBs proceeds via essentially the same mechanism as that proposed for VCP silaboration. It is interesting to note that the VCB silaboration was accompanied by a side reaction that was quite different from that for VCP silaboration (eq 5). Unlike the VCP−cyclopentene isomerization, selective double-bond isomerization occurred to give methylenecyclobutane derivative **8** without any detectable VCB−cyclohexene isomerization. In the absence of **1**, almost quantitative formation of **8** was observed under the same reaction conditions.



In summary, we report that new silaboration reactions of VCPs and VCBs were efficiently catalyzed by nickel complexes. The silaboration was accompanied by C−C bond cleavage of the cyclopropane and cyclobutane ring, resulting in highly regio- and stereoselective formation of (ω-borylalkyl)-substituted (*E*)-allylsilanes. These findings may open up new possibilities of relatively unexplored bis- and hydrometalation chemistry of vinylcycloalkanes.

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

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