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Regio- and Stereoselective 1,4-Borylstannation of 1,3-Dienes Promoted by Palladium Catalysts

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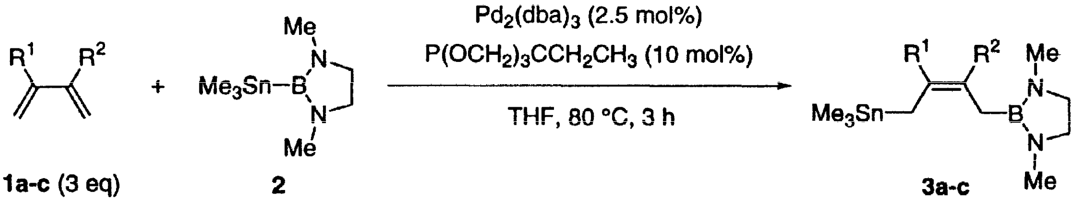
Abstract

Regio- and stereoselective 1,4-addition of borylstannane **2** to 1,3-dienes smoothly proceeds in the presence of catalytic amounts of $Pd_2(dba)_3$ and $P(OCH_2)_3CEt$, giving high yields of (*Z*)-1-boryl-4-stannyl-2-butenes **3**. The reaction of **3** with aldehyde provides a facile method for preparing various homoallyl alcohols.

Keywords: addition reactions; boron and compounds; tin and compounds; dienes

Transition-metal-catalyzed addition reactions of metal-metal bonds such as Si-Si [1], Ge-Ge [2], Sn-Sn [3], and B-B [4] to 1,3-dienes have attracted considerable attention as a general and straightforward route to allylmetals, which are extremely useful reagents in organic synthesis [5]. However, methodologies to simultaneously introduce two different metals starting with conjugated dienes have not been extensively explored [6]. Recently, we have found that borylstannanes [7] and borylsilanes [8] regio- and stereoselectively add to various alkynes in the presence of palladium catalysts. We report herein the palladium-catalyzed 1,4-addition reactions of borylstannane **2** to conjugated dienes to give adducts **3** containing both allyl-Sn and -B moieties (Scheme 1) [9].



Scheme 1

The following procedure for the preparation of **3a** is representative (Table 1). A mixture of 0.005 mmol of $Pd_2(dba)_3$ and 0.02 mmol of $P(OCH_2)_3CEt$ (etpo = 4-ethyl-2,6,7-trioxa-1-phospha-bicyclo[2.2.2]octane) in tetrahydrofuran (0.5 ml) was heated in a J.Young valve-equipped Schlenk tube at 80 °C for 5 min. To this solution were added 0.2 mmol of 1,3-dimethyl-2-trimethylstannyl-2-bora-1,3-diazacyclopentane (**2**) and 0.6 mmol of isoprene at room temperature. The resulting mixture was then heated at 80 °C for 3 h. Evaporation of the solvent, addition of hexane to the residue to separate the catalyst, filtration, and bulb-to-bulb distillation of the concentrated filtrate (72-74 °C/1.3 x 10^{-3} mmHg) gave **3a** (52.6 mg, 80% yield) [10]. The reaction exhibited

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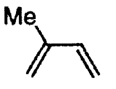
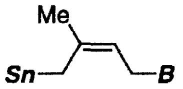
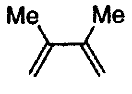
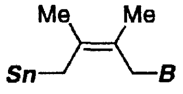
extremely high regio- and stereoselectivity; ^{1}H NMR spectroscopy and GC-MS analysis of the reaction mixture showed that there were no significant side products.

Etpo-based palladium complexes were highly effective precursors for catalysts to promote the 1,4-borylstannation of 1,3-dienes; the reaction of isoprene with **2** catalyzed by $PdCl_2(MeCN)_2$-2etpo (5 mol%) gave **3a** in 81% yield under the same conditions [11]. Although $Pd(PPh_3)_4$ and $Pd(dba)_2$ are efficient catalysts for the 1,2-borylstannation of alkynes [7a], these catalysts did not work when applied to the reaction of isoprene with **2**. Use of $PdCl_2(PPh_3)_2$ in the same reaction caused a rather extensive β-hydride elimination reaction of the intermediate, affording a significant amount of a 1-boryl-3-methyl-1,3-butadiene (**4**; 28%) [12] along with **3a** (35%) (See Scheme 2). $HSnMe_3$ which was extruded through the β-hydride elimination was converted to $(SnMe_3)_2$ (23 %). A remarkable solvent effect was found in the reaction; comparison of the yields after heating at 80 °C for 1 h revealed that the addition was faster in more polar solvents: e.g., THF (81 %) > benzene (37 %) > hexane (0 %).

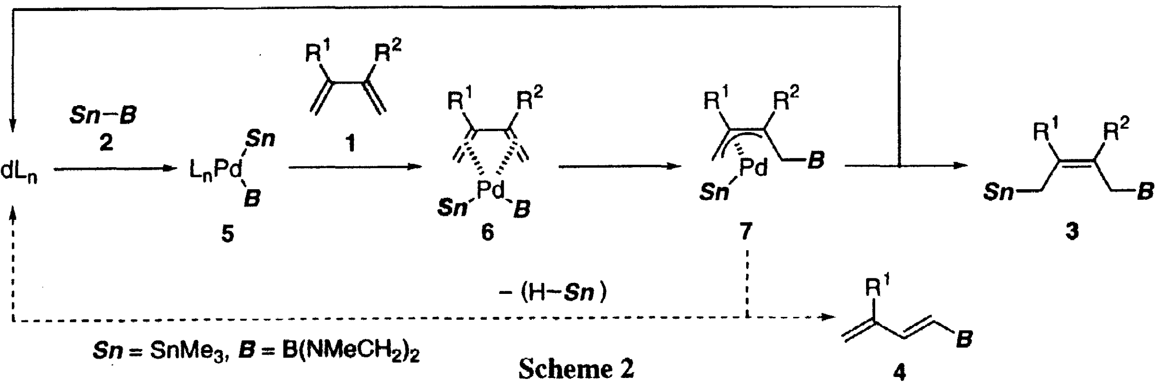
Table 1 summarizes the representative results. Under the same conditions, 1,4-addition of borylstannane **2** to 1,3-butadiene smoothly took place, selectively furnishing a (*Z*)-1-boryl-4-stannyl-2-butene (**3b**) in 87% yield. The configuration of **3b** was determined by the coupling constant (J = 10.4 Hz) between the two vinylic protons [13]. 2,3-Dimethyl-1,3-butadiene (**1c**) was slightly less reactive than isoprene and 1,3-butadiene, and a longer reaction time (5 h) was needed to achieve a satisfactory yield of **3c**. However, 1,3-cyclohexadiene and 1,4-diphenyl-1,3-butadiene failed to react with **2** even at 110 °C, presumably due to the steric congestion induced upon their coordination to a palladium species (*vide infra*). The structure of the boryl group strongly affected the reactivity of the borylstannanes under the present conditions. For instance, the reaction of isoprene with Me_3Sn-B(pinacolate) used in place of **2** resulted in extensive disproportionation of the borylstannane, giving a mixture of bis(pinacolato)diboron and hexamethyldistannane, both of which were unreactive toward isoprene under the conditions.

Table 1. 1,4-Borylstannation of 1,3-dienes with **2**.[a]

Substrate	Product[b]	Yield (%)[c]
 **1a**	 **3a**	83 (80)
 **1b**	 **3b**	95 (87)[d]
 **1c**	 **3c**	87 (84)[e]

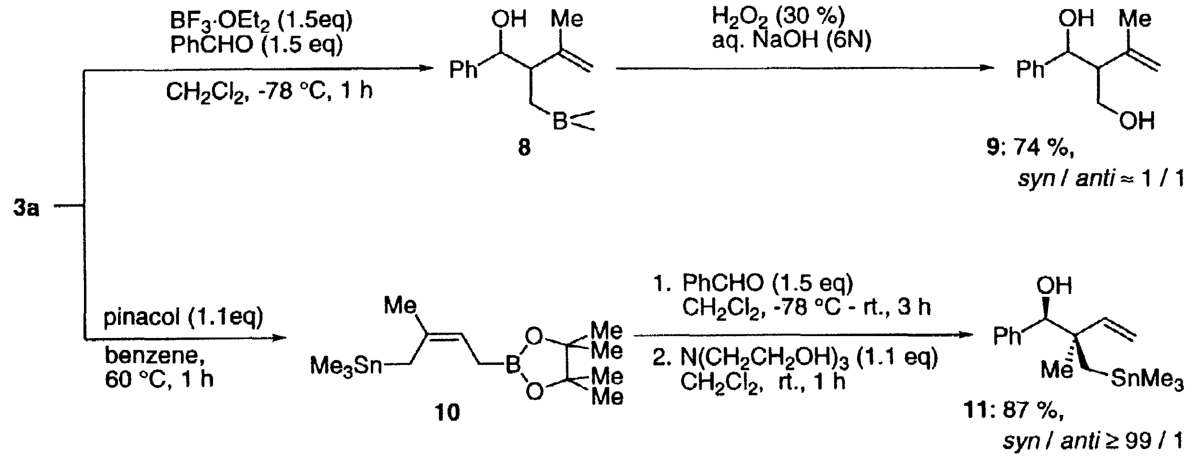
[a] Reactions were carried out in THF using **1** (3.0 equiv), **2** (1.0 equiv), and $Pd_2(dba)_3$ (2.5 mol%)-etpo (10 mol%) for 3 h at 80 °C. [b] *Sn* = $SnMe_3$, *B* = $B(NMeCH_2)_2$. [c] GC yields based on the charged amount of borylstannane **2**. Figures in parentheses are isolated yields. [d] 1,3-Butadiene (6.0 equiv). [e] Reaction time (5 h).

On the basis of the regio- and stereoselectivity observed here, the mechanism of the present reaction can be as shown in Scheme 2. The oxidative addition of the Sn-B bond to a Pd (0) species generating a boryl(stannyl)palladium(II) species **5** has already been established by us [7a]. Coordination of a 1,3-diene to **5**, followed by insertion of one of the olefinic linkages to the B-Pd bond affords **7**. The preferential reaction of the Pd-B bond rather than the Pd-Sn bond is strongly supported by the regioselective introduction of the boryl group onto the less hindered carbon of isoprene (R^1 = Me, R^2 = H). The reductive elimination of **7**, in which the stannyl group selectively migrates to the less hindered terminal carbon of the π-allyl ligand, gives addition product **3** and regenerates the Pd(0) species. The formation of **4** as a byproduct is also in line with this mechanistic proposal.



Scheme 2

The utility of this chemistry is exemplified by the highly regioselective allylation of an aldehyde with **3a** (Scheme 3). Thus, in the presence of $BF_3 \cdot OEt_2$, the reaction of **3a** with benzaldehyde selectively occurred at the allyltin moiety to give **8** [14]. Oxidation of the resulting B-C bond with H_2O_2 under the basic conditions afforded diol **9** in a good overall yield (74%). In contrast, compound **10**, prepared *in situ* by treating **3a** with pinacol, reacted with benzaldehyde exclusively at the allylborane moiety without the aid of a Lewis acid [15], affording a good yield of **11** with high stereoselectivity [16].



Scheme 3

In summary, the Pd-catalyzed 1,4-borylstannation of 1,3-dienes provides a highly regio- and stereoselective method for preparing various 1-boryl-4-stannyl-2-butenes, which proved to be versatile reagents for the selective allylation of aldehyde. We are currently studying the application of the present reaction to synthetic chemistry involving asymmetric synthesis.

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[10] **3a**: ^{1}H NMR (C_6D_6) δ 0.14 (s, J_{HSn} = 52.2 Hz, 9H, $SnCH_3$), 1.60 (d, J = 7.7 Hz, 2H, BCH_2), 1.68 (d, J = 1.2 Hz, J_{HSn} = 12.0 Hz, 3H, C=CCH_3), 1.83 (s, J_{HSn} = 67.8 Hz, 2H, $SnCH_2$), 2.62 (s, 6H, NCH_3), 2.97 (s, 4H, NCH_2), 5.20 (t, J = 7.7 Hz, 1H, C=CH). ^{13}C NMR (C_6D_6) δ -9.3 (J_{CSn} = 314 Hz), 11.8 (broad), 17.6 (J_{CSn} = 308 Hz), 26.0, 34.0, 51.6, 117.2, 132.8. ^{11}B NMR (C_6D_6) δ 32.0. ^{119}Sn NMR (C_6D_6) δ -1.2. Irradiation at 1.68 ppm (allylic protons) exhibited a 1 % enhancement of the vinylic proton at 5.20 ppm, suggesting that **3a** is (*Z*)-isomer. Elemental analysis: Calcd for $C_{12}H_{27}BN_2Sn$: C, 43.83; H, 8.27; N, 8.52. Found: C, 43.33; H, 8.38; N, 8.69.

[11] Several catalysts have been examined for 1,4-borylstannation of isoprene with **2** in C_6D_6 at 80 °C for 3 h. The NMR yields of adduct **3** [catalyst] increased as follows: 0 % $[Cl_2Pd(P\textit{o}\text{-tolyl}_3)_2]$ ≈ 0 % $[Cl_2Pd\{P(C_6F_5)_3\}_2]$ < 18 % $[Cl_2Pd(PBu_3)_2]$ < 46% $[Cl_2Pd(PPh_3)_2]$ < 58 % $[Cl_2Pd(PMe_3)_2]$ < 61% $[Cl_2Pd(MeCN)_2$ + 2etpo].

[12] **4**: ^{1}H NMR (C_6D_6) δ 1.84 (d, J = 0.6 Hz, 3H, C=CCH_3), 2.64 (s, 6H, NCH_3), 2.99 (s, 4H, NCH_2), 5.03 (s, 1H, C=CH), 5.06 (q, J = 0.6 Hz, 1H, C=CH), 5.89 (d, J = 18.7 Hz, 1H, C=CH), 6.94 (d, J = 18.7 Hz, 1H, C=CH). ^{13}C NMR (C_6D_6) δ 18.1, 34.3, 51.9, 117.2, 122.0 (broad), 144.1, 146.4. ^{11}B NMR (C_6D_6) δ 30.0. HRMS for $C_9H_{17}BN_2$ calcd 164.1484, found 164.1511.

[13] **3b**: Bp. 68 °C/1.5 x 10^{-3} mmHg. ^{1}H NMR (C_6D_6) δ 0.13 (s, J_{HSn} = 52.6 Hz, 9H, $SnCH_3$), 1.70 (d, J = 7.5 Hz, 2H, BCH_2), 1.84 (d, J = 8.7 Hz, J_{HSn} = 67.2 Hz, 2H, $SnCH_2$), 2.62 (s, 6H, NCH_3), 2.96 (s, 4H, NCH_2), 5.47 (td, J = 7.5, 10.4 Hz, 1H, C=CH), 5.59 (td, J = 8.7, 10.4 Hz, 1H, C=CH). ^{13}C NMR (C_6D_6) δ -9.9 (J_{HSn} = 318 Hz), 10.9 (broad), 12.4 (J_{CSn} = 312 Hz), 34.0, 51.6, 126.0, 128.2. Elemental analysis: Calcd for $C_{11}H_{25}BN_2Sn$: C, 41.96; H, 8.00; N, 8.90. Found: C, 41.49; H, 8.00; N, 9.44.

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