

The Chemistry of Borylstannanes: Oxidative Addition to Palladium Species and Its Application to Palladium-Catalyzed Borylstannation of Alkynes

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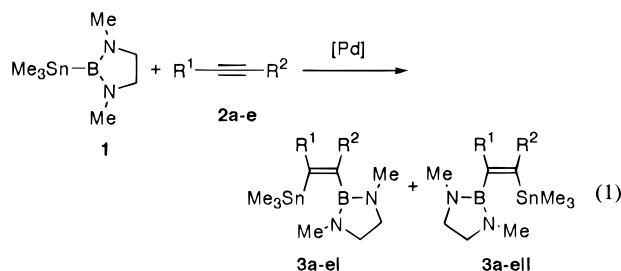
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Received August 21, 1996[⊗]

Summary: *cis* addition of the borylstannanes $\text{Me}_3\text{SnB}[\text{NMe}(\text{CH}_2\text{CH}_2)\text{NMe}]$ (**1**) and $\text{Me}_3\text{SnB}(\text{NEt}_2)_2$ (**4**) across alkynes was efficiently catalyzed at room temperature or 80 °C by $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}(\text{dba})_2$, $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$, or $\text{Me}_2\text{-Pd}[\text{PMe}_2(\text{CH}_2\text{CH}_2)\text{PMe}_2]$ to give (β -stannylalkenyl)borylanes in high yields. Treatments of **1** with $\text{Me}_2\text{Pd}[\text{PMe}_2(\text{CH}_2\text{CH}_2)\text{PMe}_2]$ and of **4** with *cis*- $\text{Me}_2\text{Pd}(\text{PPh}_2\text{Me})_2$ gave $[\{\text{MeN}(\text{CH}_2\text{CH}_2)\text{MeN}\}_2\text{B}](\text{Me}_3\text{Sn})\text{Pd}[\text{PMe}_2(\text{CH}_2\text{CH}_2)\text{PMe}_2]$ (**5**) and $[(\text{Et}_2\text{N})_2\text{B}](\text{Me}_3\text{Sn})\text{Pd}(\text{PPh}_2\text{Me})_2$ (**6**), respectively, with the former characterized by X-ray analysis. Complex **5**, when treated with 1-octyne, formed the corresponding (β -stannyl-1-octen-1-yl)borylane and could catalyze the addition reaction of **1** with 1-octyne.

Transition-metal-catalyzed addition reactions of inter-heteroatom bonds such as Si–Si,¹ Sn–Sn,^{1j, 2} Si–Sn,³ and B–B⁴ with unsaturated organic compounds have recently attracted increasing interest, since the resulting compounds are extremely useful as synthetic reagents and monomers for heteroatom-containing polymers. However, similar reactions of inter-heteroatom bonds for elements of two different groups are still very rare⁵ except for “ate” complexes,⁶ though the resulting

products having two different heteroatom–carbon bonds allow more elaborative synthetic applications, based on the difference in the intrinsic reactivities.⁷ With regard to the combinations of group 13 and 14 elements, a recent paper disclosed the inertness of borylsilanes in attempted reactions with alkynes and alkenes in the presence of transition-metal-complex catalysts.⁸ We report herein (1) the facile oxidative addition of borylstannanes to palladium complexes to afford *cis*-boryl-(stannyl)palladium species and (2) highly stereo- and regioselective palladium-catalyzed borylstannation of alkynes (eq 1) that involves oxidative addition in the catalytic cycle.⁹



a: $\text{R}^1 = n\text{-C}_6\text{H}_{13}$, $\text{R}^2 = \text{H}$; b: $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$; c: $\text{R}^1 = \text{R}^2 = \text{Ph}$;
d: $\text{R}^1 = \text{R}^2 = \text{COOMe}$; e: $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$

In a typical catalytic reaction, 1,3-dimethyl-2-(trimethylstannyl)-2-bora-1,3-diazacyclopentane (**1**; 1.1 mmol)¹⁰ and 1-octyne (**2a**; 1 mmol) were added at 0 °C to a benzene solution (1 mL) of $\text{Pd}(\text{PPh}_3)_4$ (1 mol %) and octane (50 μL , internal standard for GC) placed in a Schlenk tube. The mixture was warmed to room temperature and stirred for 1 h. GC and GC–MS (in conjunction with an NMR study) of the resulting mixture revealed that the starting materials were nearly completely consumed and that 1,3-dimethyl-2-(2-(*Z*)-(trimethylstannyl)-1-octen-1-yl)-2-bora-1,3-diazacyclopentane (**3aI**) was formed as the sole product in 98% yield. Evaporation of the mixture, addition of pentane (15 mL) to the residue, filtration, and Kugelrohr distillation of the filtrate (oven temperature 80 °C/3.4 $\times 10^{-3}$ Torr) afforded analytically pure **3aI** in 83% yield. A spectral study of **3aI**, inclusive of comparison of the

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[⊗] Abstract published in *Advance ACS Abstracts*, November 15, 1996.

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Table 1. Borylstannation of Alkynes^a

entry no.	alkyne (2)		temp (°C)	product (3)	
	R ₁	R ₂		yield ^b (%)	ratio (I/II) ^c
1	<i>n</i> -C ₆ H ₁₃	H	room temp	98 (83)	>99/1
2	Ph	H	room temp	97 (73)	>99/1
3 ^d	Ph	Ph	80	97 (78)	
4	MeOC(=O)	MeOC(=O)	80	91 (84)	
5	Ph	Me	80	97 (86)	85/15

^a All reactions were carried out in benzene using **1** (1.1 equiv), **2** (1.0 equiv), and Pd(PPh₃)₄ (1 mol %) for 1 h. ^b GC yields based on **2**. Figures in parentheses are isolated yields. ^c Determined by NMR. ^d For 3 h; isolated by recrystallization from pentane.

¹H NMR data with those of related vinylstannanes¹¹ and an NOE experiment,¹² confirmed the regio- and stereochemistry.

Besides Pd(PPh₃)₄, Pd(dba)₂ and Cl₂Pd(PPh₃)₂ also exhibited catalytic activity under similar conditions (5 mol % catalyst, room temperature, 3 h) to afford **3aI** quantitatively. Me₂Pd(dmpe)¹³ (dmpe = 1,2-bis(dimethylphosphino)ethane) was inactive at room temperature, but it did promote the reaction at 80 °C to give **3aI** in 93% yield in 8 h. On the other hand, Pt(PPh₃)₄, which was a good catalyst for diboration of alkynes,⁴ was totally ineffective.

The Pd(PPh₃)₄-catalyzed borylstannation appears to be quite general. As summarized in Table 1,¹⁴ ethynylbenzene also reacted at room temperature to give only **3bI** in an excellent yield. Internal alkynes were less reactive, but the borylstannation proceeded smoothly at 80 °C to provide corresponding *cis*-addition products (entries 3–5). Unsymmetrical internal alkynes gave a mixture of regioisomers, as exemplified by the phenylpropene reaction; optimization to achieve higher control in the regioselectivity has not been carried out yet. With regard to the borylstannane, Me₃SnB(NEt₂)₂ (**4**)¹⁵ also reacted with various alkynes very similarly to **1**. For instance, the Pd(PPh₃)₄-catalyzed reactions with ethynylbenzene (1 mol % catalyst) or 1-octyne (5 mol % catalyst) at room temperature over 3 h quantitatively gave the corresponding (*β*-stannylalkenyl)boranes. However, the resulting adducts were somewhat thermally unstable and attempted isolation by distillation resulted

(12) Irradiation at 2.48 ppm (allylic protons) exhibited a 7% enhancement of the vinylic proton at 6.39 ppm, suggesting that **3aI** is the *Z* isomer.

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(14) All catalytic reactions were carried out in the same way as in the typical example with some exceptions in the reaction temperature and/or time, which were indicated in Table 1. The workup procedure was also the same except for **3c**, which was recrystallized from pentane.

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(16) Boryl(stannyl)palladium complex **5**: mp 120 °C; ¹H NMR (C₆D₆) δ 0.59 (s, 9H, J_{H-Sn} = 34.3 Hz, SnCH₃), 0.89–1.06 (m, 16H, PCH₃ and PCH₂), 2.83 (s, 6H, NCH₃), 3.23–3.41 (m, 4H, NCH₂); ¹³C NMR (C₆D₆) δ -4.5 (dd, J_{C-P} = 5.5, 11.5 Hz, SnCH₃), 14.3 (dd, J_{C-P} = 3.4, 16.7 Hz, PCH₃), 14.5 (dd, J_{C-P} = 2.7, 11.0 Hz, PCH₃), 29.2 (dd, J_{C-P} = 20.1, 22.1 Hz, PCH₂), 30.0 (dd, J_{C-P} = 19.9, 21.9 Hz, PCH₂), 37.3 (NCH₃), 53.9 (d, J_{C-P} = 5.2 Hz, NCH₂); ¹¹⁹Sn NMR (C₆D₆) δ -29.2 (J_{Sn-P_{trans}} = 1666 Hz); ¹¹B NMR (C₆D₆) δ 46.9; ³¹P NMR (C₆D₅CD₃ at -40 °C) δ 14.0 (J_{P_{cis}-Sn} = 167 Hz, P_{cis} to the stannyl ligand; the Sn satellites did not display splitting due to ¹¹⁷Sn and ¹¹⁹Sn nuclei), 18.4 (J_{P_{trans}-P_{cis}} = 7 Hz, J_{P_{trans}-Sn} = 1671 Hz, P_{trans} to the stannyl ligand); DI-MS (EI) *m/z* (relative intensity) 518 (M⁺ for **5** having ¹¹¹B, ¹⁰⁶Pd, and ¹²⁰Sn isotopes, 2.6; molecular peaks corresponding to other isotopes were also observed), 507 (32), 506 (28), 505 (67), 504 (47), 503 (92), 502 (86), 501 (100), 500 (69), 499 (63), 498 (40), 497 (22), 393 (24), 391 (34), 390 (24), 389 (52), 388 (18), 387 (18), 353 (15), 352 (15), 260 (22), 258 (45), 256 (51), 255 (44), 254 (21), 243 (10), 241 (17), 135 (17), 122 (16), 111 (37), 97 (61), 96 (26). Anal. Calcd for C₁₃H₃₅BN₂P₂Sn: C, 30.18; H, 6.82; N, 5.42. Found: C, 30.55; H, 6.79; N, 5.30.

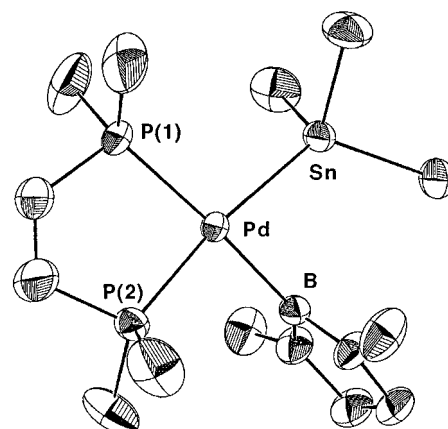
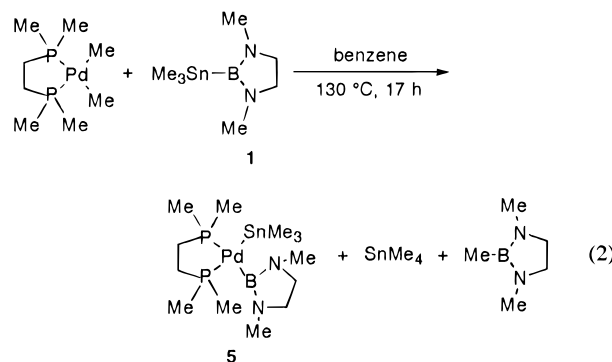


Figure 1. ORTEP drawing of complex **5**. Selected bond distances (Å): Pd–P(1), 2.338(2); Pd–P(2), 2.280(2); Pd–Sn, 2.577(1); Pd–B, 2.077(6). Selected bond angles (deg): Sn–Pd–P(1), 102.9(1); P(1)–Pd–P(2), 86.3(1); P(2)–Pd–B, 91.2(2); B–Pd–Sn, 79.3(2).

in deterioration of the products, which did not give satisfactory analytical data.

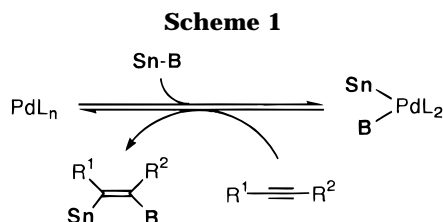
The catalysis is envisioned to be triggered by oxidative addition of the B–Sn bond. Although we have been unable to provide any evidence for oxidative addition between borylstannanes and Pd(PPh₃)₄, we did find that heating a benzene-*d*₆ (1 mL) solution of Me₂Pd(dmpe) (2.25 mmol) and **1** (2.6 equiv) at 130 °C over 17 h in a sealed NMR tube quantitatively formed a *cis* adduct (**5**) along with SnMe₄ (84%) and MeB[NMe(CH₂CH₂)NMe] (91%) (eq 2). Adduct **5** displays satisfactory ¹H, ¹³C, ³¹P, ¹¹B, and ¹¹⁹Sn NMR spectra and MS and analytical data.¹⁶ Recrystallization from a toluene-pentane (1:4)



solution afforded colorless parallelepipeds (68%),¹⁷ the structure of which was unequivocally verified by X-ray diffraction (*vide infra*). Oxidative addition between *cis*-Me₂Pd(PPhMe₂)₂ and **4** also proceeded cleanly under much milder conditions (60 °C, 46 h) to give an adduct (**6**) along with SnMe₄ and MeB(NEt₂)₂. The adduct being an oil prevents X-ray crystallography, but the spectral data, ³¹P NMR in particular (–19.2 and –16.6 ppm, ²J_{PP} = 17 Hz), suggest that it also has a *cis* configuration.

The structure of **5**, the first boryl(stannyl)palladium complex, is planar (Figure 1); the distortion from planarity is very small since the repulsion between the four ligands is reduced by the arrangement of the

(17) X-ray data for **5**: SnPdP₂N₂BC₁₃H₃₅, triclinic, space group *P*1, colorless prism, *a* = 9.656(2) Å, *b* = 10.553(1) Å, *c* = 12.442(2) Å, α = 90.61(1)°, β = 90.75(1)°, γ = 116.93(1)°, *V* = 1130.1(3) Å³, *Z* = 2, *R* = 0.0340, *R*_w = 0.0551, GOF = 0.206.

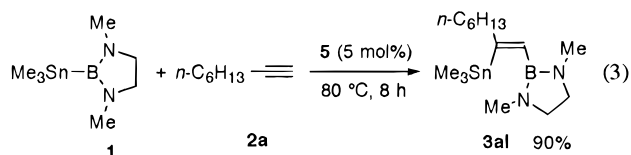


diazaborolane ring, which is nearly perpendicular to the BSnPdP₂ mean plane. The Pd-P(1) bond (2.338(2) Å) is longer than the Pd-P(2) bond (2.280(2) Å). This indicates that the boryl ligand is stronger in *trans* influence than the stannyl ligand.

The boryl(stannyl)palladium complexes were found to react with alkynes. For instance, complex **5** (0.05 mmol) in benzene-*d*₆ (0.4 mL) reacted with an excess (2.8 equiv) of 1-octyne at 80 °C to afford **3aI** (36%) in 8 h.¹⁸ In addition, the borylstannylation of 1-octyne with **1** proceeded at 80 °C over 8 h in the presence of complex **5** (5 mol %) used as catalyst to give **3aI** in 90% yield (eq 3).

(18) Ethyl propiolate proved to be much more reactive toward complex **5** than 1-octyne. When **5** was treated with ethyl propiolate (1.1 equiv) in benzene-*d*₆ (0.4 mL) at room temperature for 30 min, ¹H NMR of the reaction mixture displayed signals presumably assignable to [(*Z*)-2-(ethoxycarbonyl)-2-stannylethenyl]palladium species. For instance, the proton *trans* to the stannyl group exhibited satellites as two doublets centered at 8.04 ppm with coupling constants of 157 and 150 Hz due respectively to ¹¹⁹Sn and ¹¹⁷Sn nuclei, both the chemical shift¹⁹ and the coupling constants¹¹ being in good agreement with the known values. Accordingly, we tentatively conclude that the acetylenic bond was inserting into the Sn–Pd bond (stannyl palladation), at least in this particular case.

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On the basis of these results, one can safely conclude that the boryl(stannyl)palladium species is involved in the catalytic cycle of the borylstannylation (Scheme 1).

In summary, we have developed the palladium-catalyzed borylstannylation of alkynes, which is initiated by the oxidative addition of the B–Sn bond. This paper offers another useful demonstration to verify the power of transition-metal catalysis to activate the inter-heteroatom bonds. Extensions to other combinations of heteroatoms as well as synthetic applications of the (β -stannylalkenyl)boranes will be the subjects of forthcoming papers.

Acknowledgment. We are grateful to the Japan Science and Technology Corporation (JST) for the partial financial support through the CREST (Core Research for Evolutional Science and Technology) program.

Supporting Information Available: Text giving detailed experimental procedures and characterization data for the (β -stannylalkenyl)boranes and the boryl(stannyl)palladium complexes and text and tables giving full details of the crystal structure analysis of **5** (12 pages). Ordering information is given on any current masthead page.

OM9607199