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

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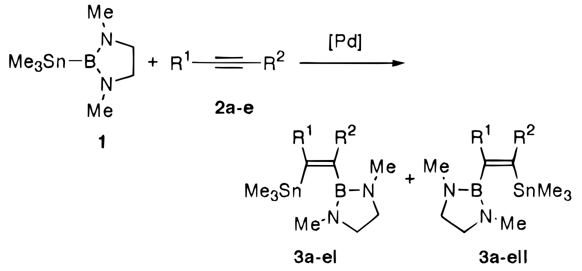
*Summary: cis addition of the borylstannanes $Me_3SnB[NMe(CH_2CH_2)NMe]$ (**1**) and $Me_3SnB(NEt_2)_2$ (**4**) across alkynes was efficiently catalyzed at room temperature or 80 °C by $Pd(PPh_3)_4$, $Pd(dba)_2$, $Cl_2Pd(PPh_3)_2$, or $Me_2Pd[PMe_2(CH_2CH_2)PMe_2]$ to give (β-stannylalkenyl)boranes in high yields. Treatments of **1** with $Me_2Pd[PMe_2(CH_2CH_2)PMe_2]$ and of **4** with cis-$Me_2Pd(PPh_2Me)_2$ gave $[\{MeN(CH_2CH_2)MeN\}B](Me_3Sn)Pd[PMe_2(CH_2CH_2)PMe_2]$ (**5**) and $[(Et_2N)_2B](Me_3Sn)Pd(PPh_2Me)_2$ (**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)borane 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−B[4] 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 rare[5] 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]



(1)

a: $R^1 = n\text{-}C_6H_{13}$, $R^2 = H$; **b**: $R^1 = Ph$, $R^2 = H$; **c**: $R^1 = R^2 = Ph$; **d**: $R^1 = R^2 = COOMe$; **e**: $R^1 = Ph$, $R^2 = Me$

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 $Pd(PPh_3)_4$ (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 × 10^{-3} Torr) afforded analytically pure **3aI** in 83% yield. A spectral study of **3aI**, inclusive of comparison of the

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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	n-C_6H_{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 $Pd(PPh_3)_4$ (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 vinylstannanes[11] and an NOE experiment,[12] confirmed the regio- and stereochemistry.

Besides $Pd(PPh_3)_4$, $Pd(dba)_2$ and $Cl_2Pd(PPh_3)_2$ also exhibited catalytic activity under similar conditions (5 mol % catalyst, room temperature, 3 h) to afford **3aI** quantitatively. $Me_2Pd(dmpe)$[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, $Pt(PPh_3)_4$, which was a good catalyst for diboration of alkynes,[4] was totally ineffective.

The $Pd(PPh_3)_4$-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, $Me_3SnB(NEt_2)_2$ (**4**)[15] also reacted with various alkynes very similarly to **1**. For instance, the $Pd(PPh_3)_4$-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 in deterioration of the products, which did not gave satisfactory analytical data.

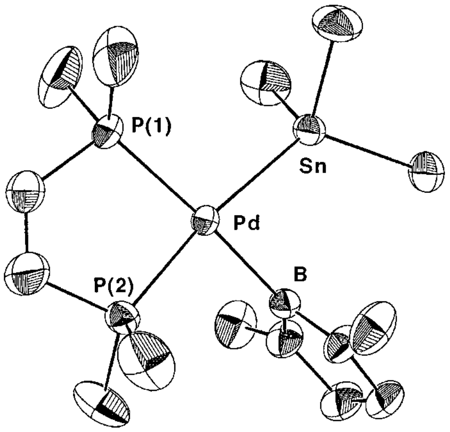
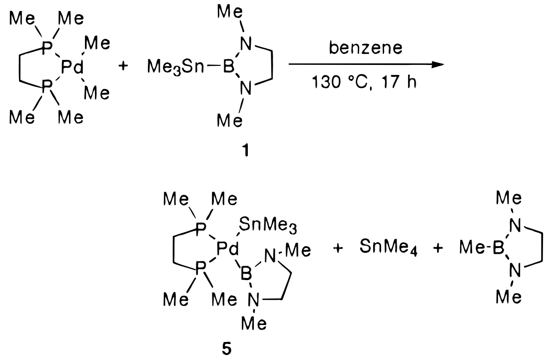


Figure 1. ORTEP drawing of complex **5**. Selected bond distances (Å): Pd−P(1), 2.338(2); Pd−P(2), 2.280(2); Pd−Sn, 2.577(1); Pd−B, 2.077(6). Selected bond angles (deg): Sn−Pd−P(1), 102.9(1); P(1)−Pd−P(2), 86.3(1); P(2)−Pd−B, 91.2(2); B−Pd−Sn, 79.3(2).

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 $Pd(PPh_3)_4$, we did find that heating a benzene-d_6 (1 mL) solution of $Me_2Pd(dmpe)$ (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 $SnMe_4$ (84%) and $MeB[NMe(CH_2CH_2)NMe]$ (91%) (eq 2). Adduct **5** displays satisfactory ^1H, ^{13}C, ^{31}P, ^{11}B, and ^{119}Sn 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*-$Me_2Pd(PPhMe_2)_2$ and **4** also proceeded cleanly under much milder conditions (60 °C, 46 h) to give an adduct (**6**) along with $SnMe_4$ and $MeB(NEt_2)_2$. The adduct being an oil prevents X-ray crystallography, but the spectral data, ^{31}P NMR in particular (−19.2 and −16.6 ppm, $^2J_{PP}$ = 17 Hz), suggest that it also has a *cis* configuration.



(2)

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

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(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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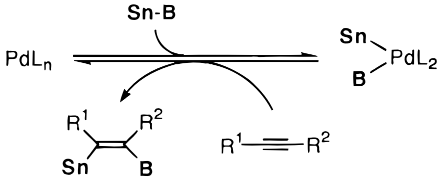
(16) Boryl(stannyl)palladium complex **5**: mp 120 °C; ^1H NMR (C_6D_6) δ 0.59 (s, 9H, J_{H-Sn} = 34.3 Hz, $SnCH_3$), 0.89−1.06 (m, 16H, PCH_3 and PCH_2), 2.83 (s, 6H, NCH_3), 3.23−3.41 (m, 4H, NCH_2); ^{13}C NMR (C_6D_6) δ −4.5 (dd, J_{C-P} = 5.5, 11.5 Hz, $SnCH_3$), 14.3 (dd, J_{C-P} = 3.4, 16.7 Hz, PCH_3), 14.5 (dd, J_{C-P} = 2.7, 11.0 Hz, PCH_3), 29.2 (dd, J_{C-P} = 20.1, 22.1 Hz, PCH_2), 30.0 (dd, J_{C-P} = 19.9, 21.9 Hz, PCH_2), 37.3 (NCH_3), 53.9 (d, J_{C-P} = 5.2 Hz, NCH_2); ^{119}Sn NMR (C_6D_6) δ −29.2 ($J_{Sn-P_{trans}}$ = 1666 Hz); ^{11}B NMR (C_6D_6) δ 46.9; ^{31}P NMR ($C_6D_5CD_3$ 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 ^{117}Sn and ^{119}Sn 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 ^{11}B, ^{106}Pd, and ^{120}Sn 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 $C_{13}H_{35}BN_2P_2PdSn$: C, 30.18; H, 6.82; N, 5.42. Found: C, 30.55; H, 6.79; N, 5.30.

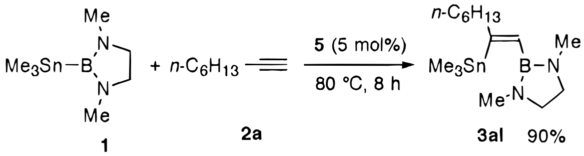
(17) X-ray data for **5**: $SnPdP_2N_2BC_{13}H_{35}$, triclinic, space group $P\bar{1}$, colorless prism, a = 9.656(2) Å, b = 10.553(1) Å, c = 12.442(2) Å, α = 90.61(1)°, β = 90.75(1)°, γ = 116.93(1)°, V = 1130.1(3) Å^3, Z = 2, R = 0.0340, R_w = 0.0551, GOF = 0.206.

Scheme 1



diazaborolane ring, which is nearly perpendicular to the BSnPdP$_2$ 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 **3al** (36%) in 8 h.[18] In addition, the borylstannation 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 **3al** in 90% yield (eq 3).



(3)

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

In summary, we have developed the palladium-catalyzed borylstannation 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.

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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.

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[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, ^{1}H 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 ^{119}Sn and ^{117}Sn nuclei, both the chemical shift[19] and the coupling constants[11] 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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