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Switch of Regioselectivity in Palladium-Catalyzed Silaboration of Terminal Alkynes by Ligand-Dependent Control of Reductive Elimination

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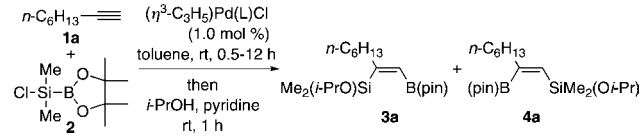
Abstract: The regioselectivity in the addition of silylboronic esters to terminal alkynes can be switched by the choice of phosphorus ligands on the palladium catalysts. The silaboration proceeds with normal regisoselectivity in the presence of (η^3-C_3H_5)Pd(PPh_3)Cl (1.0 mol %) to give 1-boryl-2-silyl-1-alkenes in high yields. In sharp contrast, selective formation of the inverse regioisomers, 2-boryl-1-silyl-1-alkenes, takes place when the reaction is carried out with a palladium catalyst bearing P(*t*-Bu)$_2$(biphenyl-2-yl). A reaction mechanism for the change of regioselectivity that involves reversible insertion/β-boryl elimination steps is proposed.

Transition-metal-catalyzed addition of the compounds H−E and E−E′ (E, E′ = B, Si, Sn, Ge, P, S, Se) across unsaturated carbon−carbon bonds has received much attention as a straightforward, atom-economical route to structurally defined, functionalized organic molecules.[1] One of the important objects with these catalyses is to switch the regio- and stereoselectivities of the additions by the nature of the catalysts. Such systems are well-established in H−E additions, as exemplified in the hydroboration of styrenes with HB(cat)[2] as well as in hydrosilylation,[3] hydrothiolation,[4] and hydrophosphination[5] of terminal alkynes. However, such regio- and stereochemical control in the addition of bimetallic E−E′ compounds has rarely been achieved.

Silaboration of terminal alkynes proceeds under mild conditions in the presence of palladium catalysts bearing an isocyanide or phosphorus ligand.[6] All of the reported catalysts resulted in regioselective formation of (*Z*)-1-boryl-2-silyl-1-alkenes via cis introduction of the boryl group to the terminal carbon and the silyl group to the internal carbon. Our interests have been directed toward efficient switching of the regio- and stereochemistry of silaboration. In this regard, we established palladium-catalyzed trans silaboration of terminal alkynes, which gives the *E* isomer with the same regioselectivity.[7] Herein, we describe a new palladium catalyst that changes the regioselectivity in silaboration of terminal alkynes.

Silaboration of 1-octyne (**1a**) with $ClMe_2Si$−B(pin) (**2**)[8] was carried out in toluene in the presence of (η^3-C_3H_5)Pd(L)Cl (1.0 mol %, L = tertiary phosphine)[9] (Table 1). The product was then treated with *i*-PrOH in the presence of pyridine to convert the Cl group on the silicon atom to an *i*-PrO group. A palladium complex having PPh_3 showed efficient catalyst activity for the addition at room temperature, giving (*Z*)-1-boryl-2-silyloct-1-ene **3a** in 94% yield with perfect regioselectivity for the normal product (entry 1). The reaction was also catalyzed by palladium complexes bearing trialkylphosphines (entries 2−4). Selective formation of **3a** was observed with P(*n*-Bu)$_3$ (entry 2), whereas a small amount of the (*E*)-2-boryl-1-silyloct-1-ene regioisomer **4a** was formed in the reaction with PCy_3 (entry 3). Formation of **4a** became more preferable with P(*t*-Bu)$_3$ and P(*t*-Bu)$_2$(2-MeC_6H_4) (entries 4 and 5), indicating that electron-rich and sterically demanding phosphines would change the regioselectivity of the reaction. We finally established that a palladium catalyst bearing P(*t*-Bu)$_2$(biphenyl-2-yl) (**5**) achieved high "abnormal" regioselectivity for formation of **4a** (**3a**:**4a** = 3:97; entry 6). Reactions with diphenyl- and dicyclohexyl analogues of **5** did not form **4a** (entries 7 and 8), indicating again the requirement of electron-donating, bulky triorganophosphines.[10]

Table 1. Ligand Effect on Pd-Catalyzed Silaboration of **1a**[a]

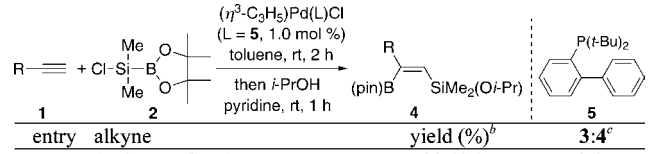


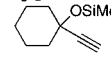
entry	L	yield (%)[b]	**3a**:**4a**[c]
1	PPh_3	94	>99:1
2	P(*n*-Bu)$_3$	87	>99:1
3	PCy_3	92	96:4
4	P(*t*-Bu)$_3$	55	68:32
5	P(*t*-Bu)$_2$(2-MeC_6H_4)	92	85:15
6	P(*t*-Bu)$_2$(biphenyl-2-yl) **5**	92, 90[d]	3:97
7	PPh_2(biphenyl-2-yl)	93	>99:1
8	PCy_2(biphenyl-2-yl)	96	97:3

[a] **1a** (0.24 mmol), **2** (0.20 mmol), and (η^3-C_3H_5)Pd(L)Cl (2.0 μmol) were stirred in toluene (0.1 mL) at room temperature for 0.5−12 h. The mixture was then reacted with pyridine (0.36 mmol) and *i*-PrOH (0.30 mmol) at room temperature for 1 h. [b] GC yield based on **2**. [c] Determined by GC analysis of the crude mixture. [d] Isolated yield in a 0.4 mmol scale reaction.

Various 1-alkynes **1** were subjected to silaboration using the Pd/**5** catalyst (Table 2).[11] Primary-alkyl-substituted **1b**−**h** reacted smoothly

Table 2. Pd/**5**-Catalyzed Silaboration of Terminal Alkynes[a]



entry	alkyne	yield (%)[b]	**3**:**4**[c]
1	**1b** (R = *n*-C_4H_9)	99 (**4b**)	3:97
2	**1c** (R = *n*-C_8H_{17})	92 (**4c**)	3:97
3	**1d** [R = *t*-$BuMe_2SiO(CH_2)_2$]	91 (**4d**)	3:97
4	**1e** [R = *t*-$BuMe_2SiO(CH_2)_3$]	90 (**4e**)	3:97
5	**1f** [R = $AcO(CH_2)_3$]	94 (**4f**)	3:97
6	**1g** [R = $Cl(CH_2)_3$]	85 (**4g**)	2:98
7	**1h** [R = $NC(CH_2)_3$]	80 (**4h**)	2:98
8	**1i** (R = *cyclo*-C_6H_{11})	89 (**4i**)	5:95
9[d]	**1j** [R = *t*-$BuMe_2SiOCH(Me)$]	62 (**4j**)	4:96
10[d]	 **1k**	61 (**4k**)	10:90
11	**1l** (R = Ph)	83 (**4l**)	18:82
12	**1m** (R = 4-$MeOC_6H_4$)	80 (**4m**)	13:87
13	**1n** (R = 4-$F_3CC_6H_4$)	no reaction	-

[a] **1** (0.48 mmol), **2** (0.40 mmol), and (η^3-C_3H_5)Pd(L)Cl (L = **5**, 4.0 μmol). For details, see the Supporting Information. [b] Isolated total yield of **3** and **4**. [c] Determined by GC of the crude mixture. [d] Using 3.0 mol % Pd at 50 °C for 24 h.

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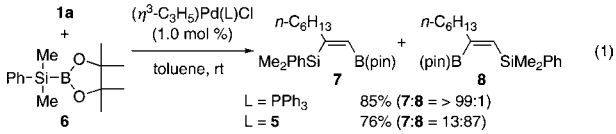
with **2** to give **4b**−**h** in 80−99% yield with high regioselectivity for the reverse addition (**3**:**4** = 2:98−3:97; entries 1−7). Functional groups such as silyloxy (entries 3 and 4), AcO (entry 5), Cl (entry 6), and CN groups (entry 7) were tolerated under the conditions. The regioselective silaboration was also applicable to sterically more hindered **1i** (entry 8). Although the silaborations of **1j** and **1k** derived from secondary and tertiary alcohols were rather slow, the regioselectivity was still acceptable (entries 9 and 10). In contrast, a lower **3**:**4** ratio was observed in the reaction of phenylethyne (**1l**) (entry 11). The electron-rich aromatic alkyne **1m** reacted faster than **1l** to give the adduct with a better **3**:**4** ratio (entry 12), whereas no reaction took place with the electron-deficient alkyne **1n** (entry 13).

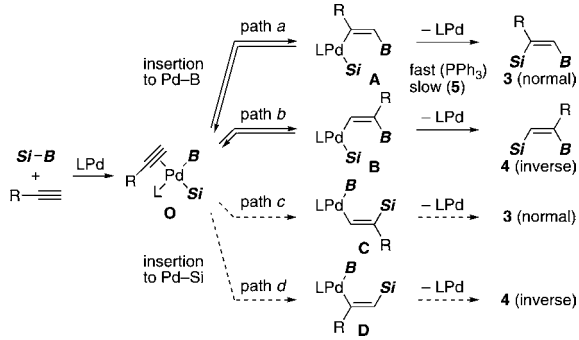
The ligand-dependent change in regioselectivity was also observed in the addition of $Me_2PhSi-B(pin)$ (**6**) to **1a** (eq 1).



(1)

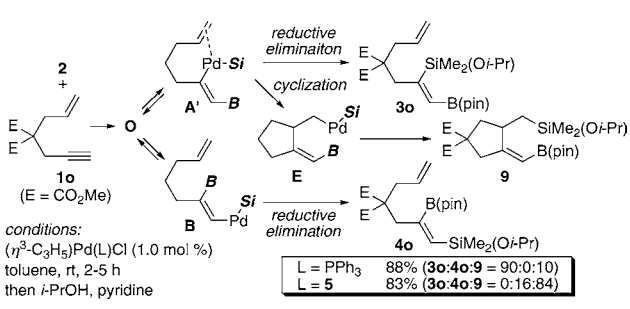
We assume that the "normal" silaboration, which forms **3**, proceeds through formation of intermediate **A** by insertion of an alkyne into the B−Pd bond of intermediate **O**, with B−C bond formation occurring at the terminus of the alkyne (path *a*, Scheme 1).[12] Another possibility, the formation of intermediate **C** via insertion of the alkyne into the Si−Pd bond of **O** (path *c*), can be neglected because of the much higher energy of the intermediate as determined by theoretical studies.[13] Likewise, any routes through insertion into the Si−Pd bond of **O** (path *d*) can be neglected for the same energetic reason. It is reasonable to assume that product **4** with inverse regiochemistry is obtained through formation of intermediate **B**, which is derived by regioisomeric insertion of an alkyne into the B−Pd bond of **O** (path *b*).

Scheme 1. Possible Mechanism



To gain insight into the mechanism, reactions of 1,6-enyne **1o** were carried out in the presence of either PPh_3 or **5** (Scheme 2). In the presence of PPh_3, **1o** selectively afforded uncyclized product **3o**. The

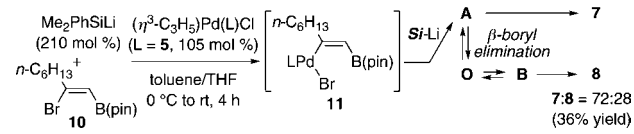
Scheme 2. Pd-Catalyzed Silaboration of 1,6-Enyne **1o** with **2**



formation of **3o** can be reasonably explained by the "normal" pathway involving formation of **A**′. The failure of the cyclization (to form **9**) suggests that the reductive elimination step with the PPh_3/Pd catalyst is faster than the cyclization step. In contrast, reaction of **1o** in the presence of **5** as a ligand gave cyclization product **9** in good yield with minor formation of **4o**. The formation of **9** is inconsistent with the formation of **B** in the "abnormal" path using **5**, while the formation of inverse addition product **4o** is consistent with the mechanism. We assume that in the silaboration using **5**, formation of **A**′ is still kinetically favored, but the subsequent reductive elimination is significantly retarded by the effect of ligand **5**. Alternatively, **A**′ undergoes cyclization with the intramolecular C═C bond to give **9** as the major product. The formation of **4o** can be explained by β-boryl elimination from **A**′ back to **O** followed by formation of **B**.[14,15] The formation of **4** in the reaction shown in Table 2 is also explained by the reversible insertion/β-boryl elimination (Scheme 1), by which product formation finally takes place from **B**. Steric interactions between the bulky ligand and the substituent on the double bond may destabilize intermediate **A**, leading the equilibrium to the formation of **B**.

The possibility of β-boryl elimination from **A** was confirmed by the reaction of (*Z*)-1-boryl-2-bromo-1-octene **10**, which was prepared separately, with $Me_2PhSiLi$ (Scheme 3). The reaction afforded regioisomeric **7** and **8** in a 72:28 ratio in the presence of the Pd/**5** complex, while neither product was formed in the absence of the palladium complex. These results indicate that **7** is obtained through formation of complex **11** followed by silylation to form **A**.[16] Formation of **8** may be rationalized by the β-boryl elimination from **A**, resulting in formation of **O**, which provides **8** via **B**.

Scheme 3. Reaction of **10** with $Me_2PhSiLi$ Mediated by Pd/**5**



In conclusion, we have achieved reversal of regioselectivity in the silaboration of terminal alkynes. Mechanistic details, which involve unique ligand control of reductive elimination, are now under investigation in this laboratory.

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Supporting Information Available: Experimental details and characterization data for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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