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Palladium-catalysed borylsilylation and borylstannylative dimerization of 1,2-dienes

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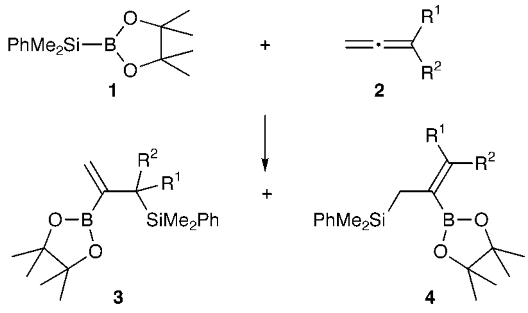
A borylsilane regioselectively adds to 1,2-dienes in the presence of palladium complexes to afford high yields of alkenylboranes having allylsilane moieties, whereas a borylstannane gives a 1 : 2 telomer with 3-methylbuta-1,2-diene due to borylstannylative dimerization.

Addition reactions of metal–metal bonds to 1,2-dienes provide a straightforward route to organometallic compounds having both vinylic and allylic metal moieties, which are versatile reagents in organic synthesis.[1] Although several studies on the transition-metal-catalysed reactions of 1,2-dienes with Si–Si,[2] Sn–Sn,[3] Si–Sn,[3] Ge–Sn[4] and B–B bonds[5] have been reported, similar reactions of B–Si or B–Sn bonds have received little attention.[6,7] In the course of our investigation on the transition-metal-catalysed additions of these bonds to unsaturated organic compounds,[8,9] we have found that palladium catalysts effectively promote the reactions with 1,2-dienes, giving the corresponding adducts with extremely high regioselectivity (Scheme 1).

The following procedure is representative (Table 1, entry 1). A mixture of $Pd_2(dba)_3$ (2.5 mol%; dba = dibenzylideneacetone) and etpo as ligand [10 mol%; etpo = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane, $P(OCH_2)_3CEt$] in THF (1 ml) was heated at 80 °C for 5 min, while the color of the solution turned to green from red. To this solution were added 2-dimethylphenylsilyl-4,4,5,5-tetramethyl-2-bora-1,3-dioxacyclopentane **1** (0.33 mmol), buta-1,2-diene **2a** (1.0 mmol) and decane (30 μl; as internal standard for GC analysis), and the reaction mixture was heated at 80 °C. GC-MS analysis of the mixture indicated the complete consumption of the borylsilane **1** after 9 h and quantitative formation of a borylsilylation product **3a** (98% GC yield). It should be noted that the NMR analysis of the reaction mixture indicated the lack of formation of regioisomers like **4a**. Thus, the addition of the B–Si bond smoothly proceeded at the internal double bond of **2a**, and the boryl group was regioselectively introduced to the central carbon, leading to the exclusive formation of alkenylborane moiety. Purification of the crude product by TLC (silica gel; hexane–CH_2Cl_2 as eluent) gave analytically pure **3a** in 88% yield.†

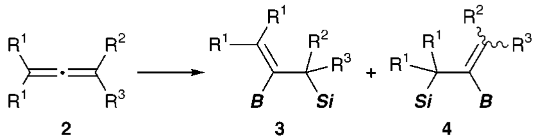
Representative results of the reactions between **1** and various 1,2-dienes **2a–f** are summarized in Table 1. All of the products listed have exhibited satisfactory spectral data.† Under similar conditions, another monosubstituted 1,2-diene, **2b**, also underwent the borylsilylation at the internal double bond, affording **3b** in 86% yield as the sole product (entry 2). Propa-1,2-diene **2c** and sterically congested 2,4-dimethylpenta-2,3-diene **2d** effectively participated in the borylsilylation with high regioselectivity (entries 3 and 4).



Scheme 1

The regioselectivity of the Pd–etpo-catalysed borylsilylation of 1,1-disubstituted propa-1,2-dienes was strongly influenced by the nature of substituents. For example, the reaction of 1,1-diphenylpropa-1,2-diene **2e** with **1** selectively proceeded at the terminal double bond to give **4e** in 94% yield (entry 5), whereas the borylsilylation of 3-methylbuta-1,2-diene **2f** took place at both the internal and terminal double bonds, affording a regioisomeric mixture of **3f** and **4f** with a 52 : 48 ratio (entry 6). The low regioselectivity of the latter reaction could be successfully improved by tuning the phosphorus ligands; the best result (**3f** : **4f** = 100 : 0) was achieved by using $Pd_2(dba)_3$ (2.5 mol%)–PPh_3 (10 mol%) (entry 7). The use of the $Pd_2(dba)_3$ (2.5 mol%)–PMe_3 (10 mol%) system was less effective, giving a mixture containing **3f** as major product (**3f** : **4f** = 71 : 29, entry 8).

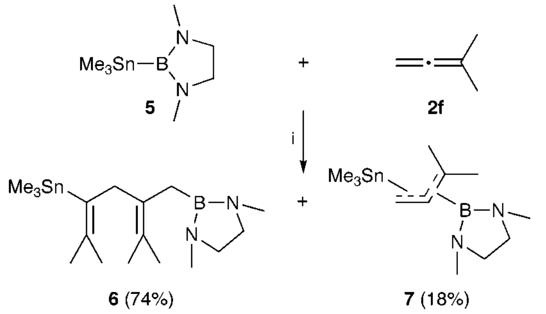
Table 1 Borylsilylation of 1,2-dienes[ab]



Entry	1,2-Diene 2	R¹	R²	R³	Yield (%)[c]	**3** : **4**[d]
1	**2a**	H	Me	H	88 (98)	100 : 0
2	**2b**	H	OMe	H	86 (93)	100 : 0
3[e]	**2c**	H	H	H	91 (96)	—
4	**2d**	Me	Me	Me	92 (94)	—
5	**2e**	H	Ph	Ph	94	0 : 100
6	**2f**	H	Me	Me	84 (85)	52 : 48
7[f]	**2f**	H	Me	Me	(90)	100 : 0
8[g]	**2f**	H	Me	Me	(90)	71 : 29
9[h]	**2f**	H	Me	Me	87 (94)	0 : 100

[a] Reaction conditions: borylsilane **1** (0.33 mmol), 1,2-dienes (1.0 mmol), catalyst $Pd_2(dba)_3$ (2.5 mol%)–etpo (10.0 mol%), THF (1 ml), 80 °C, 9 h unless otherwise noted. [b] ***Si*** = $SiMe_2Ph$, ***B*** = $B(OCMe_2)_2$. [c] Isolated yields based on the amount of the borylsilane **1**. Figures in parentheses are GC yields. [d] Determined by ^1H NMR spectroscopy. [e] A large excess of 1,2-diene was used. [f] $Pd_2(dba)_3$ (2.5 mol%)–PPh_3 (10.0 mol%) was used as catalyst. [g] $Pd_2(dba)_3$ (2.5 mol%)–PMe_3 (10.0 mol%) was used as catalyst. [h] Run in the presence of $(CH_2{=}CH_2)Pt(PPh_3)_2$ (5 mol%) at 80 °C for 3 h.

To our surprise, the regioselectivity of this reaction completely changed when the reaction was conducted with a platinum catalyst. Thus, in the presence of a catalytic amount of $(CH_2{=}CH_2)Pt(PPh_3)_2$ (5 mol%), the B–Si bond of **1** preferentially added to the terminal double bond of **2f**, furnishing **4f** as the sole product (94% GC yield, entry 9). However, application of this catalyst to the borylsilylation of monosubstituted



Scheme 2 *Reagents and conditions*: i, Pd$_2$(dba)$_3$ (2.5 mol%)–etpo (10 mol%), THF, 50 °C, 3 h.

1,2-dienes such as **2a** made the reaction sluggish, resulting in the formation of a mixture of many products.

The reactivities of borylsilanes in the present reaction were strongly influenced by the structure of the boryl group. For instance, $\mathrm{PhMe_2Si{-}(\overline{BNMeCH_2CH_2N}Me)}$ failed to undergo the addition reaction with **2f** even at elevated temperatures (*e.g.* 110 °C) in the presence of the Pd$_2$(dba)$_3$–etpo system.

In contrast to the borylsilylation of 1,2-dienes, the B–Sn bond of borylstannane **5** underwent the palladium-catalysed addition reaction with 3-methylbuta-1,2-diene **2f**, predominantly yielding telomer **6** having both vinyl–Sn and allyl–B moieties (74% GC yield) along with an isomeric mixture of simple borylstannylation products **7** (18% GC yield) (Scheme 2). The reaction proceeded smoothly at 50 °C in the presence of the Pd$_2$(dba)$_3$–etpo system and was complete within 3 h. The purification of the reaction mixture by bulb-to-bulb distillation (116–118 °C/5.4 × 10^{-3} mmHg) afforded analytically pure **6** in 63% yield.† The structure of **6** was determined by NMR spectroscopy; its ^{119}Sn NMR spectrum displayed a signal at δ −49.6 assignable to tin attached to an alkenyl group.[3,4] In addition, the ^{13}C NMR spectrum showed a broad signal at δ 16.2 indicative of an allylic carbon bonded to boron. Further studies on the reaction mechanism are in progress.

In conclusion, the transition-metal-catalysed addition reaction of B–Si or B–Sn bonds to 1,2-dienes provides a selective and facile route to organometallic compounds containing both vinyl- and allyl-metal moieties. In view of the different reactivities of these metal moieties in electrophilic substitution, the products will find considerable synthetic applications for complex organic molecules.

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Notes and references

† Selected *data* for **3a**: δ_{H} 0.32 and 0.34 (both s, 6H, SiCH$_3$), 1.03 (s, 12H, OCCH$_3$), 1.20 (d, *J* 7.6, 3H, CCH$_3$), 2.52 (q, *J* 7.6, 1H, CH), 5.52 (d, *J* 2.9, 1H, =CH$_2$), 6.24 (s, *J* 2.9, 1H, =CH$_2$), 7.18–7.24 (m, 3H, arom), 7.51–7.59 (m, 2H, aromatic); δ_{C} −5.3 and −3.5 (SiCH$_3$), 14.8 (C*C*H$_3$), 25.0 (OC*C*H$_3$), 26.8 (CH), 83.3 (O*C*CH$_3$), 126.3 (=CH$_2$), 127.9, 129.1, 134.6, 138.5 (arom), 145.3 (br s, =CB); δ_{Si} −1.7; δ_{B} 30.4. For **3b**: δ_{H} 0.41 and 0.45 (both s, 6H, SiCH$_3$), 0.99 and 1.01 (both s, 12H, OCCH$_3$), 3.21 (s, 3H, OCH$_3$), 4.28 (s, 1H, CH), 5.97 (d, *J* 4.0, 1H, =CH$_2$), 6.29 (d, *J* 4.0, 1H, =CH$_2$), 7.17–7.25 (m, 3H, arom), 7.67–7.72 (m, 2H, arom); δ_{C} −5.6 and −4.5 (SiCH$_3$), 24.9 and 25.0 (OCCH$_3$), 58.4 (OCH$_3$), 78.7 (CH), 83.3 (O*C*CH$_3$), 126.7 (=CH$_2$), 127.9, 129.3, 135.0, 137.8 (arom), =CB not observed; δ_{Si} −5.9; δ_{B} 30.0. For **3c**: δ_{H} 0.32 (s, 6H, SiCH$_3$), 1.02 (s, 12H, OCCH$_3$), 2.11 (s, 2H, SiCH$_2$), 5.49 (s, 1H, =CH$_2$), 6.09 (s, 1H, =CH$_2$), 7.18–7.23 (m, 3H, arom), 7.51–7.54 (m, 2H, arom); δ_{C} −3.0 (SiCH$_3$), 24.6 (SiCH$_2$), 24,9 (OC*C*H$_3$), 83.4 (O*C*CH$_3$), 128.0 (arom), 128.3 (=CH$_2$), 129.1, 134.3 (arom), 138.9 (br s, =CB), 139.3 (arom); δ_{Si} −4.1; δ_{B} 30.2. For **3d**: δ_{H} 0.45 (s, 6H, SiCH$_3$), 1.11 (s, 12H, OCCH$_3$), 1.27 (s, 3H, =CCH$_3$), 1.33 (s, 6H, CCH$_3$), 1.82 (s, 3H, =CCH$_3$), 7.18–7.21 (m, 3H, arom), 7.57–7.61 (m, 2H, arom); δ_{C} −3.7 (SiCH$_3$), 23.5 (=C*C*H$_3$), 25.5 (OC*C*H$_3$), 27.2 (=C*C*Si), 27.4 (=C*C*H$_3$), 27.8 (C*C*H$_3$), 82.9 (O*C*CH$_3$), 127.6, 128.9, 135.1 (arom), 136.4 (=*C*Me$_2$), 139.3 (arom), =CB not observed; δ_{Si} 1.7; δ_{Bi} 31.1. For **3e**: δ_{H} 0.39 (s, 6H, SiCH$_3$), 0.94 (s, 12H, OCCH$_3$), 2.36 (s, 2H, SiCH$_2$), 6.96–7.21 (m, 11H, arom), 7.30–7.35 (m, 2H, arom), 7.43–7.48 (m, 2H, arom); δ_{C} −1.5 (SiCH$_3$), 23.1 (SiCH$_2$), 24.9 (OC*C*H$_3$), 83.2 (O*C*CH$_3$), 126.7, 126.9, 127.8, 127.9, 128.5, 129.0, 130.0 (two peaks), 134.2, 140.1, 143.4, 145.9 (arom), 149.7 (=CPh$_2$), =CB not observed; δ_{Si} −2.6; δ_{B} 31.4. For **3f**: δ_{H} 0.36 (s, 6H, SiCH$_3$), 1.02 (s, 12H, OCCH$_3$), 1.30 (s, 6H, CCH$_3$), 5.45 (s, 1H, =CH$_2$), 6.19 (s, 1H, =CH$_2$), 7.18–7.23 (m, 3H, arom), 7.53–7.54 (m, 2H, arom); δ_{C} −4.8 (SiCH$_3$), 24.8 (C*C*H$_3$), 24.9 (OC*C*H$_3$), 29.0 (SiCH$_2$), 83.0 (O*C*CH$_3$), 127.1 (=CH$_2$), 127.7, 129.0, 135.2, 138.1 (arom), 149.6 (br s, =CB); δ_{Si} 1.2; δ_{B} 30.6. For **4f**: δ_{H} 0.36 (s, 6H, SiCH$_3$), 1.05 (s, 12H, OCCH$_3$), 1.52 (s, 3H, =CCH$_3$), 2.15 (s, 2H, SiCH$_2$), 2.21 (s, 3H, =CCH$_3$), 7.18–7.23 (m, 3H, arom), 7.56–7.59 (m, 2H, arom); δ_{C} −2.0 (SiCH$_3$), 21.2 (SiCH$_2$), 22.5 (=C*C*H$_3$), 24.6 (=C*C*H$_3$), 25.1 (OC*C*H$_3$), 82.7(O*C*CH$_3$), 122.0 (br s, =CB), 127.9, 129.0, 134.2, 140.4 (arom), 145.9 [=*C*(CH$_3$)$_2$]; δ_{Si} −3.6; δ_{B} 30.7. For **6**: bp 116–118 °C/5.4 × 10^{-3} mmHg; δ_{H} 0.29 (s, J_{HSn} 52.1, 9H, SnCH$_3$), 1.71–1.76 (m, 11H, 3CH$_3$C= and BCH$_2$), 1.83 (s, J_{HSn} 12.5, 3H, =CCH$_3$), 2.57 (s, 6H, NCH$_3$), 2.96 (s, 4H, NCH$_2$), 3.22 [s, J_{HSn} 67.6, 2H, (=C)$_2$CH$_2$]; δ_{C} −7.2 (J_{CSn} 324.8, SnCH$_3$), 16.2 (br s, BCH$_2$), 19.8 (J_{CSn} 54.8, =C*C*H$_3$), 20.9 (=C*C*H$_3$), 21.6 (C*C*H$_3$), 28.3 (J_{CSn} 53.8, =C*C*H$_3$), 33.5 (NCH$_3$), 38.8 (J_{CSn} 50.7, CH$_2$), 51.8 (NCH$_2$), 122.5 (C), 130.9 (C), 136.8 (J_{CSn} 525.5, C), 141.3 (J_{CSn} 32.1, C); δ_{B} 31.7; δ_{Sn} −49.6; *m/z* (EI, 70 eV) 398 ([M]$^+$, 0.9%), 383 ([M − Me]$^+$, 5), 233 ([M − SnMe$_3$]$^+$, 100).

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