

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

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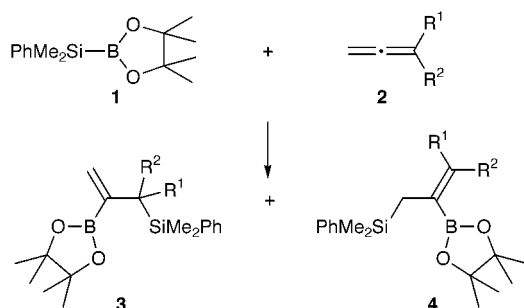
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A borylsilane regioselectively adds to 1,2-dienes in the presence of palladium complexes to afford high yields of alkenylboranes having allylsilane moieties, whereas a borylstannane gives a 1 : 2 telomer with 3-methylbuta-1,2-diene due to borylstannylative 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.<sup>1</sup> Although several studies on the transition-metal-catalysed reactions of 1,2-dienes with Si–Si,<sup>2</sup> Sn–Sn,<sup>3</sup> Si–Sn,<sup>3</sup> Ge–Sn<sup>4</sup> and B–B bonds<sup>5</sup> have been reported, similar reactions of B–Si or B–Sn bonds have received little attention.<sup>6,7</sup> In the course of our investigation on the transition-metal-catalysed additions of these bonds to unsaturated organic compounds,<sup>8,9</sup> 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<sub>2</sub>(dba)<sub>3</sub> (2.5 mol%; dba = dibenzylideneacetone) and etpo as ligand [10 mol%; etpo = 4-ethyl-2,6,7-trioxo-1-phosphabicyclo[2,2,2]octane, P(OCH<sub>2</sub>)<sub>3</sub>CEt] 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<sub>2</sub>Cl<sub>2</sub> as eluent) gave analytically pure **3a** in 88% yield.<sup>†</sup>

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.<sup>†</sup> Under similar



Scheme 1

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).

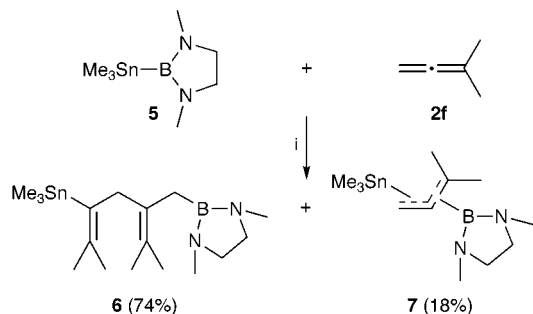
The regioselectivity of the Pd–etpo-catalysed borylsilylation of 1,1-disubstituted propa-1,2-dienes was strongly influenced by the nature of substituents. For example, the reaction of 1,1-diphenylpropa-1,2-diene **2e** with **1** selectively proceeded at the terminal double bond to give **4e** in 94% 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<sub>2</sub>(dba)<sub>3</sub> (2.5 mol%)–PPh<sub>3</sub> (10 mol%) (entry 7). The use of the Pd<sub>2</sub>(dba)<sub>3</sub> (2.5 mol%)–PMe<sub>3</sub> (10 mol%) system was less effective, giving a mixture containing **3f** as major product (**3f** : **4f** = 71 : 29, entry 8).

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<sub>2</sub>=CH<sub>2</sub>)Pt(PPh<sub>3</sub>)<sub>2</sub> (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

Table 1 Borylsilylation of 1,2-dienes<sup>ab</sup>

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

<sup>a</sup> Reaction conditions: borylsilane **1** (0.33 mmol), 1,2-dienes (1.0 mmol), catalyst Pd<sub>2</sub>(dba)<sub>3</sub> (2.5 mol%)–etpo (10.0 mol%), THF (1 ml), 80 °C, 9 h unless otherwise noted. <sup>b</sup> Si = SiMe<sub>2</sub>Ph, B = B(OCMe<sub>2</sub>)<sub>2</sub>. <sup>c</sup> Isolated yields based on the amount of the borylsilane **1**. Figures in parentheses are GC yields. <sup>d</sup> Determined by <sup>1</sup>H NMR spectroscopy. <sup>e</sup> A large excess of 1,2-diene was used. <sup>f</sup> Pd<sub>2</sub>(dba)<sub>3</sub> (2.5 mol%)–PPh<sub>3</sub> (10.0 mol%) was used as catalyst. <sup>g</sup> Pd<sub>2</sub>(dba)<sub>3</sub> (2.5 mol%)–PMe<sub>3</sub> (10.0 mol%) was used as catalyst. <sup>h</sup> Run in the presence of (CH<sub>2</sub>=CH<sub>2</sub>)Pt(PPh<sub>3</sub>)<sub>2</sub> (5 mol%) at 80 °C for 3 h.



**Scheme 2** Reagents and conditions: i, Pd<sub>2</sub>(dba)<sub>3</sub> (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, PhMe<sub>2</sub>Si-(BNMeCH<sub>2</sub>CH<sub>2</sub>NMe) failed to undergo the addition reaction with **2f** even at elevated temperatures (e.g. 110 °C) in the presence of the Pd<sub>2</sub>(dba)<sub>3</sub>-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<sub>2</sub>(dba)<sub>3</sub>-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<sup>-3</sup> mmHg) afforded analytically pure **6** in 63% yield.† The structure of **6** was determined by NMR spectroscopy; its <sup>119</sup>Sn NMR spectrum displayed a signal at δ -49.6 assignable to tin attached to an alkenyl group.<sup>3,4</sup> In addition, the <sup>13</sup>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<sub>H</sub> 0.32 and 0.34 (both s, 6H, SiCH<sub>3</sub>), 1.03 (s, 12H, OCCH<sub>3</sub>), 1.20 (d, *J* 7.6, 3H, CCH<sub>3</sub>), 2.52 (q, *J* 7.6, 1H, CH), 5.52 (d, *J* 2.9, 1H, =CH<sub>2</sub>), 6.24 (s, *J* 2.9, 1H, =CH<sub>2</sub>), 7.18–7.24 (m, 3H, arom), 7.51–7.59 (m, 2H, aromatic); δ<sub>C</sub> -5.3 and -3.5 (SiCH<sub>3</sub>), 14.8 (CCH<sub>3</sub>), 25.0 (OCCH<sub>3</sub>), 26.8 (CH), 83.3 (OCCH<sub>3</sub>), 126.3 (=CH<sub>2</sub>), 127.9, 129.1, 134.6, 138.5 (arom), 145.3 (br s, =CB); δ<sub>Si</sub> -1.7; δ<sub>B</sub> 30.4. For **3b**: δ<sub>H</sub> 0.41 and 0.45 (both s, 6H, SiCH<sub>3</sub>), 0.99 and 1.01 (both s, 12H, OCCH<sub>3</sub>), 3.21 (s, 3H, OCH<sub>3</sub>), 4.28 (s, 1H, CH), 5.97 (d, *J* 4.0, 1H, =CH<sub>2</sub>), 6.29 (d, *J* 4.0, 1H, =CH<sub>2</sub>), 7.17–7.25 (m, 3H, arom), 7.67–7.72 (m, 2H, arom); δ<sub>C</sub> -5.6 and

-4.5 (SiCH<sub>3</sub>), 24.9 and 25.0 (OCCH<sub>3</sub>), 58.4 (OCH<sub>3</sub>), 78.7 (CH), 83.3 (OCCH<sub>3</sub>), 126.7 (=CH<sub>2</sub>), 127.9, 129.3, 135.0, 137.8 (arom), =CB not observed; δ<sub>Si</sub> -5.9; δ<sub>B</sub> 30.0. For **3c**: δ<sub>H</sub> 0.32 (s, 6H, SiCH<sub>3</sub>), 1.02 (s, 12H, OCCH<sub>3</sub>), 2.11 (s, 2H, SiCH<sub>2</sub>), 5.49 (s, 1H, =CH<sub>2</sub>), 6.09 (s, 1H, =CH<sub>2</sub>), 7.18–7.23 (m, 3H, arom), 7.51–7.54 (m, 2H, arom); δ<sub>C</sub> -3.0 (SiCH<sub>3</sub>), 24.6 (SiCH<sub>2</sub>), 24.9 (OCCH<sub>3</sub>), 83.4 (OCCH<sub>3</sub>), 128.0 (arom), 128.3 (=CH<sub>2</sub>), 129.1, 134.3 (arom), 138.9 (br s, =CB), 139.3 (arom); δ<sub>Si</sub> -4.1; δ<sub>B</sub> 30.2. For **3d**: δ<sub>H</sub> 0.45 (s, 6H, SiCH<sub>3</sub>), 1.11 (s, 12H, OCCH<sub>3</sub>), 1.27 (s, 3H, =CCH<sub>3</sub>), 1.33 (s, 6H, CCH<sub>3</sub>), 1.82 (s, 3H, =CCH<sub>3</sub>), 7.18–7.21 (m, 3H, arom), 7.57–7.61 (m, 2H, arom); δ<sub>C</sub> -3.7 (SiCH<sub>3</sub>), 23.5 (=CCH<sub>3</sub>), 25.5 (OCCH<sub>3</sub>), 27.2 (=CCSi), 27.4 (=CCH<sub>3</sub>), 27.8 (CCH<sub>3</sub>), 82.9 (OCCH<sub>3</sub>), 127.6, 128.9, 135.1 (arom), 136.4 (=CMe<sub>2</sub>), 139.3 (arom), =CB not observed; δ<sub>Si</sub> 1.7; δ<sub>B</sub> 31.1. For **3e**: δ<sub>H</sub> 0.39 (s, 6H, SiCH<sub>3</sub>), 0.94 (s, 12H, OCCH<sub>3</sub>), 2.36 (s, 2H, SiCH<sub>2</sub>), 6.96–7.21 (m, 11H, arom), 7.30–7.35 (m, 2H, arom), 7.43–7.48 (m, 2H, arom); δ<sub>C</sub> -1.5 (SiCH<sub>3</sub>), 23.1 (SiCH<sub>2</sub>), 24.9 (OCCH<sub>3</sub>), 83.2 (OCCH<sub>3</sub>), 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<sub>2</sub>), =CB not observed; δ<sub>Si</sub> -2.6; δ<sub>B</sub> 31.4. For **3f**: δ<sub>H</sub> 0.36 (s, 6H, SiCH<sub>3</sub>), 1.02 (s, 12H, OCCH<sub>3</sub>), 1.30 (s, 6H, CCH<sub>3</sub>), 5.45 (s, 1H, =CH<sub>2</sub>), 6.19 (s, 1H, =CH<sub>2</sub>), 7.18–7.23 (m, 3H, arom), 7.53–7.54 (m, 2H, arom); δ<sub>C</sub> -4.8 (SiCH<sub>3</sub>), 24.8 (CCH<sub>3</sub>), 24.9 (OCCH<sub>3</sub>), 29.0 (SiCH<sub>2</sub>), 83.0 (OCCH<sub>3</sub>), 127.1 (=CH<sub>2</sub>), 127.7, 129.0, 135.2, 138.1 (arom), 149.6 (br s, =CB); δ<sub>Si</sub> 1.2; δ<sub>B</sub> 30.6. For **4f**: δ<sub>H</sub> 0.36 (s, 6H, SiCH<sub>3</sub>), 1.05 (s, 12H, OCCH<sub>3</sub>), 1.52 (s, 3H, =CCH<sub>3</sub>), 2.15 (s, 2H, SiCH<sub>2</sub>), 2.21 (s, 3H, =CCH<sub>3</sub>), 7.18–7.23 (m, 3H, arom), 7.56–7.59 (m, 2H, arom); δ<sub>C</sub> -2.0 (SiCH<sub>3</sub>), 21.2 (SiCH<sub>2</sub>), 22.5 (=CCH<sub>3</sub>), 24.6 (=CCH<sub>3</sub>), 25.1 (OCCH<sub>3</sub>), 82.7(OCCH<sub>3</sub>), 122.0 (br s, =CB), 127.9, 129.0, 134.2, 140.4 (arom), 145.9 [=C(CH<sub>3</sub>)<sub>2</sub>]; δ<sub>Si</sub> -3.6; δ<sub>B</sub> 30.7. For **6**: bp 116–118 °C/5.4 × 10<sup>-3</sup> mmHg; δ<sub>H</sub> 0.29 (s, *J*<sub>H<sub>Sn</sub></sub> 52.1, 9H, SnCH<sub>3</sub>), 1.71–1.76 (m, 11H, 3CH<sub>3</sub>C= and BCH<sub>2</sub>), 1.83 (s, *J*<sub>H<sub>Sn</sub></sub> 12.5, 3H, =CCH<sub>3</sub>), 2.57 (s, 6H, NCH<sub>3</sub>), 2.96 (s, 4H, NCH<sub>2</sub>), 3.22 [s, *J*<sub>H<sub>Sn</sub></sub> 67.6, 2H, (=C)<sub>2</sub>CH<sub>2</sub>]; δ<sub>C</sub> -7.2 (*J*<sub>C<sub>Sn</sub></sub> 324.8, SnCH<sub>3</sub>), 16.2 (br s, BCH<sub>2</sub>), 19.8 (*J*<sub>C<sub>Sn</sub></sub> 54.8, =CCH<sub>3</sub>), 20.9 (=CCH<sub>3</sub>), 21.6 (CCH<sub>3</sub>), 28.3 (*J*<sub>C<sub>Sn</sub></sub> 53.8, =CCH<sub>3</sub>), 33.5 (NCH<sub>3</sub>), 38.8 (*J*<sub>C<sub>Sn</sub></sub> 50.7, CH<sub>2</sub>), 51.8 (NCH<sub>2</sub>), 122.5 (C), 130.9 (C), 136.8 (*J*<sub>C<sub>Sn</sub></sub> 525.5, C), 141.3 (*J*<sub>C<sub>Sn</sub></sub> 32.1, C); δ<sub>B</sub> 31.7; δ<sub>Sn</sub> -49.6; *m/z* (EI, 70 eV) 398 ([M]<sup>+</sup>, 0.9%), 383 ([M - Me]<sup>+</sup>, 5), 233 ([M - SnMe<sub>3</sub>]<sup>+</sup>, 100).

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