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Platinum-Catalyzed Silaborative Coupling of 1,3-Dienes to Aldehydes: Regio- and Stereoselective Allylation with Dienes through Allylic Platinum Intermediates

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Synthetic application of organometallic compounds containing intermetallic σ-bonds has been developed by means of transition-metal catalysis involving activation of the σ-bonds. The σ-bonds between main-group elements such as Si−Si[1] and B−B[2] undergo insertion reactions with carbon−carbon multiple bonds, i.e., bismetalation reactions, whose usefulness has been demonstrated in stereoselective organic synthesis.[3] Insertion of 1,3-dienes with the intermetallic σ-bond promoted by transition metals is presumed to involve generation of π- or σ-allylic transition-metal complexes accompanying regio- and stereoselective formation of a carbon−main group metal bond.[4] However, the synthetic utilization of the allylic transition-metal intermediates generated in situ has not thoroughly been exploited, though some bismetalative dimerization reactions of 1,3-dienes has been described.[5]

Recently, we found that Si−B σ-bonds were effectively activated by palladium as well as platinum catalysts for regio- and stereoselective silaboration of C−C triple bonds.[6] It should be noted that the platinum complex also catalyzed the silaboration of terminal C−C double bonds, in which we proposed that insertion of alkenes into the Pt−B bond in a (silyl)(boryl)platinum intermediate is followed by reductive coupling with the silyl group on the platinum.[7] In this paper, we disclose a silaborative coupling of diene to aldehyde, which may involve 4-borylcrotylplatinum complex intermediates. The new three-component coupling reaction features the high regio- and stereoselectivity, providing homoallylic borane derivatives, which may be useful for further synthetic elaboration.

Scheme 1. Silaboration of 2,3-Dimethyl-1,3-butadiene Followed by Reaction with Benzaldehyde

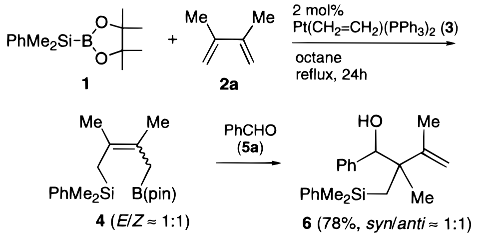


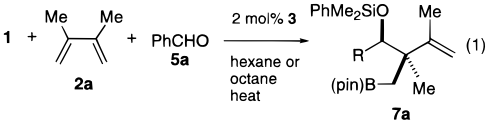
Table 1. Reaction of 2,3-Dimethylbutadiene (**2a**), Benzaldehyde (**5a**), and Silylborane **1** in the Presence of Platinum Catalyst **3**[a]

entry	PhCHO (**5a**) (equiv)	temp (°C)[b]	time (h)	product **7a** yield (%)[c]	ratio[d]
1[e]	1.5	120	2	74	81:19
2	1.5	80	4	78	95:5
3	1.5	50	8	61	98:2
4	1.0	80	4	63	93:7
5	3.0	80	4	85	96:4

[a] All reactions were carried out in hexane in the presence of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (**3**, 2 mol %) under nitrogen unless otherwise noted. [b] Bath temp. [c] Isolated yields. [d] Ratios of the syn and anti isomers determined by ^{1}H NMR. [e] A reaction in octane.

On the basis of the success of the silaboration of alkynes and alkenes, we attempted the reaction of silylborane **1** with 2,3-dimethyl-1,3-butadiene (**2a**) in the presence of a catalytic amount of $Pt(CH_2{=}CH_2)(PPh_3)_2$ (**3**) at 120 °C for 24 h in octane (Scheme 1). A 1,4-addition of the silicon−boron bond across the diene took place to give **4** in good yield, but in nearly 1:1 ratio of the *E* and *Z* isomers as judged by NMR spectroscopy of the resultant mixture.[1a,4] Addition of benzaldehyde (**5a**) to the reaction mixture including **4** afforded a homoallylic alcohol **6** having a silyl group as a 1:1 mixture of syn and anti isomers in good yield through allylboration of the aldehyde.[8]

Since the lack of stereoselectivity was presumed to be due to isomerization of the primarily formed *E* or *Z* alkenes **4** under the reaction conditions, we examined the silaboration reaction in the presence of **5a**, which would trap **4** before the isomerization, if any. The reaction at 120 °C proceeded smoothly (2 h) until silylborane **1** was completely consumed and provided an aldehyde adduct without the formation of the primary silaboration product **4**. However, to our surprise, the product was not **6** but **7a**, i.e., silyl-protected homoallylic alcohol having boryl group at the terminal carbon of the diene (eq 1; Table 1, entry 1).



The unexpected B−C and C−C bond formation along with Si−O bond formation took place even at 80 °C to give **7a** with high (95:5) stereoselectivity in 78% yield (Table 1, entry 2). The reaction at lower temperature (50 °C) improved the diastereoselectivity up to 98:2, but resulted in decrease in yield (Table 1, entry 3). Molar amount of the aldehyde employed was also important to attain high yield and stereoselectivity (Table 1, entries 4 and 5). Use of 3 molar amounts of **5a** gave the highest yield

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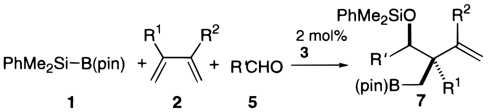
Table 2. Reaction of Dienes (**2**), Aldehydes (**5**), and Silylborane **1** in the Presence of Platinum Catalyst 3[a]

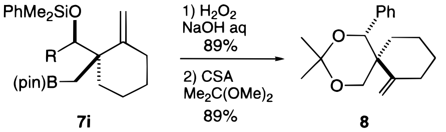


entry	dienes (R^1, R^2)	aldehydes (R′)	temp (°C)[b]	products **7** yield (%)	ratio
1	**2b** (H,Ph)	**5a** (Ph)	120	**b** (79)	99:1
2	**2b**	**5b** (*p*-MeOPh)	120	**c** (77)	99:1
3	**2b**	**5c** (*o*-MeOPh)	120	**d** (83)	99:1
4	**2b**	**5d** (*p*-NCPh)	120	**e** (80)	99:1
5	**2b**	**5e** (*n*-Hex)	120	**f** (71)	93:7
6	**2b**	**5f** (*c*-Hex)	120	**g** (60)	96:4
7[c,d]	**2c** (H,H)	**5a** (Ph)	50	**h** (63)	95:5
8[c]	**2d** (-$(CH_2)_4$-)	**5a** (Ph)	80	**i** (60)	99:1

[a] All reactions were carried out in octane using 1.5 equiv of aldehyde unless otherwise noted. [b] Bath temp. [c] 3.0 equiv of aldehydes. [d] A reaction in hexane under atmospheric pressure of 1,3-butadiene.

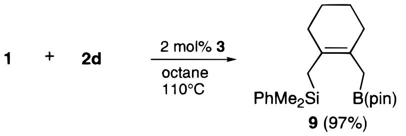
as well as high stereoselectivity (Table 1, entry 5), while use of 1 molar equivalent of **5a** resulted in an unsatisfactory yield with slight decrease in stereoselectivity (Table 1, entry 4).

The silaborative diene−aldehyde coupling reaction was applicable to unsymmetrical 2-phenyl-1,3-butadiene (**2b**), though higher temperature was required for the completion of the reactions. Thus, in the reaction with **5a**, the B−C and C−C bond formation occurred at the less substituted C═C bond with another C═C bond having the phenyl group left intact (Table 2, entry 1). Benzaldehyde derivatives having methoxy group at either para (**5b**) and ortho (**5c**) position as well as that having a *p*-cyano group (**5d**) similarly gave the corresponding coupling products **7** with the high regio- and stereoselectivities in good yields (Table 2, entries 2−4). Diene **2b** also reacted with aliphatic aldehyde **5e** in 71% yield with a diastereoselectivity of 93:7 (Table 2, entry 5). Higher selectivity was attained in the reaction of branched aliphatic aldehyde **5f** (Table 2, entry 6). It is noted that a reaction of **1** and **5a** under butadiene (**2c**) atmosphere (1 atm) at 50 °C furnished the corresponding coupling product **7h** in 63% yield with 95:5 stereoselectivity (Table 2, entry 7). The silaborative coupling to **5a** also took place with diene **2d**, in which two C═C bonds are fixed in a *s-cis* fashion, giving **7i** with almost complete diastereoselectivity (Table 2, entry 8). Treatment of **7i** with basic hydrogen peroxide followed by acetonidation afforded **8** as a single diastereomer (eq 2).



(2)

It is remarked again that the *s-cis* diene **2d** reacted with **1** in the absence of aldehydes to give 1,4-silaboration product **9** in high yield (eq 3).



(3)

The finding that the platinum-catalyzed reaction did not take place with **1** and **5a** in the absence of diene **2a** suggests that some reactive platinum intermediate may be formed from silylborane **1** and dienes in the presence of the platinum catalyst. We propose the following mechanism for the platinum-catalyzed silaborative diene−aldehyde coupling (Scheme 2).[9] Oxidative addition of the Si−B bond onto the platinum(0) complex and subsequent coordination of a diene with *s-cis* conformation may form (boryl)(silyl)(diene)platinum(II) intermediate **A**. Insertion of the coordinated diene to the B−Pt bond takes place with regioselective B−C bond formation at the terminal carbon of the less-substituted C═C bond to give (4-borylcrotyl)(organosilyl)platinum(II) complex **B** having a cis geometry. The *cis*-crotylplatinum complex **B** can react with an aldehyde with C−C bond formation at the position γ to the platinum atom to give (alkoxy)(silyl)platinum(II) **C**,[10] which undergoes a reductive elimination to give the coupling product **7** with Si−O bond formation. The finding that the silaborative diene−aldehyde coupling reaction proceeds at lower temperature than the silaboration of dienes in the absence of aldehydes suggests that the reductive elimination of a Si−C bond from **B** is sufficiently slow to allow the further reaction of **B** with aldehydes. The observed high stereoselectivity may be attributed to the cyclic transition state, in which platinum serves as intramolecular Lewis acid (Chart 1). Presumably, in the absence of the aldehydes, the *cis*-crotylplatinum intermediate **B** may be gradually isomerized to the trans isomer, resulting in the formation of the *E* alkene via the subsequent reductive elimination.

Scheme 2. Possible Mechanism for the Silaborative Coupling of Dienes to Aldehydes

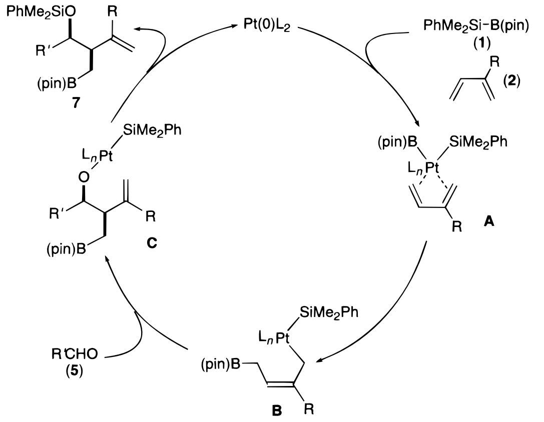
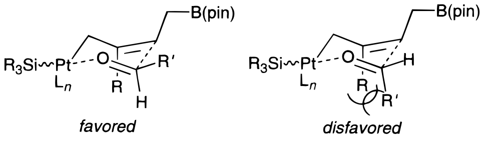


Chart 1



In summary, a new catalytic C−C bond forming reaction involving the regio- and stereoselective formation of allylic platinum intermediates from 1,3-dienes through the activation of the Si−B bond has been reported. The highly stereoselective reaction of the platinum intermediate with aldehydes may lead to further exploitation of new synthetically useful reactions.

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Supporting Information Available: Detailed experimental procedures, characterization of the new compounds, and stereochemical assignment of **7** (7 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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