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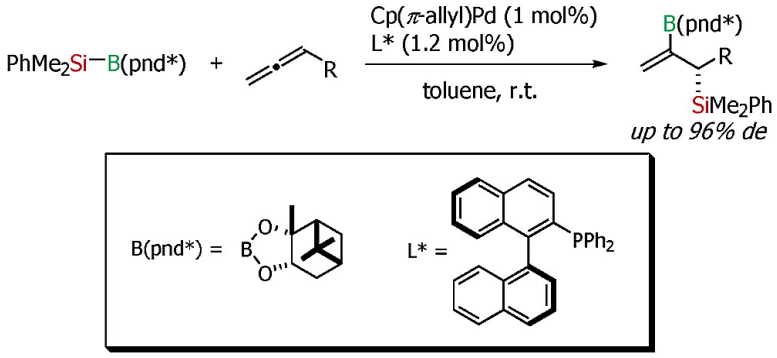

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Enantioface-Selective Palladium-Catalyzed Silaboration of Allenes via Double Asymmetric Induction

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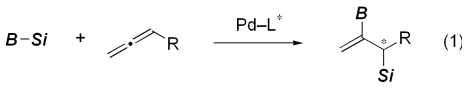
Transition metal-catalyzed additions of metal-containing σ-bonds across carbon−carbon multiple bonds have attracted much interest in synthetic organic chemistry, because these reactions provide synthetically useful organometallic compounds, which are otherwise difficult to prepare. In particular, enantioselective versions of the σ-bond addition processes have been gaining considerable attention with the increasing demand for chiral organometallic reagents for asymmetric organic synthesis. Studies on asymmetric hydrometalation reactions have been motivated not only by their synthetic potential, but also by the ease of M−H bond activation, which allows the extensive survey of a variety of catalyst systems.[1] On the other hand, only a few asymmetric bis-metalations have been reported to date.[2−5] Although the highly enantioselective bis-silylation of α,β-unsaturated ketones using a Pd-BINAP catalyst has been reported,[2] asymmetric bis-metalations of unactivated C=C bonds have only achieved moderate enantioface selectivities.[3,4] It is likely that the difficulty associated with the activation of the intermetallic σ-bonds has hampered the development of asymmetric bis-metalations.

Our recent efforts have focused on transition metal-catalyzed reactions of silylboranes with unsaturated organic molecules.[1,6] We were particularly interested in silaboration of terminal allenes to provide synthetically useful β-borylallylsilanes via regioselective addition of the Si−B bond to the internal C=C bond.[7,8] Herein, we describe enantioface-selective silaboration of terminal allenes as the first asymmetric addition of a metal-containing σ-bond across an allene C=C bond (eq 1).

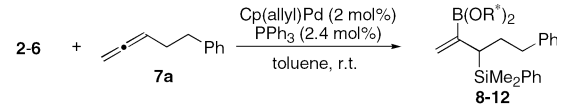


(1)

The original conditions for the silaboration of allenes used a ligand/palladium ratio greater than 2:1. These require high temperatures to drive the reactions to proceed.[7,8] We found that the use of (η^5-cyclopentadienyl)(π-allyl)palladium [Cp(allyl)Pd] with tertiary phosphines in a 1:1 ratio allowed us to perform the silaboration of allenes at room temperature.[9,10] Using the new monophosphine-palladium (1:1) catalyst system, we initially examined the reactions of silylboranes bearing a series of chiral auxiliaries on the boron atom.

Silylboranes **2**−**6** bearing diol-derived chiral auxiliaries were prepared[11] and subjected to reactions with 5-phenyl-1,2-pentadiene (**7a**) in the presence of a catalyst prepared from Cp(allyl)Pd with PPh_3 (1:1.2).[12] All of the reactions proceeded at room temperature to give high yields, affording silaboration products **8**−**12** with perfect regioselectivity (Table 1). The diastereomeric ratios, however, varied significantly with the chiral auxiliaries. Although silylboranes **2**−**5**, derived from acyclic diols, resulted in poor

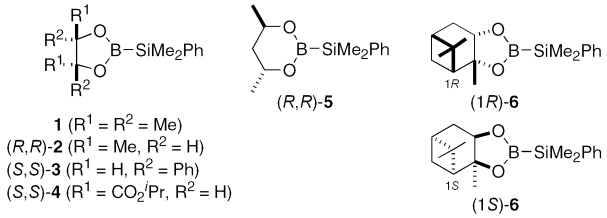
Table 1. Reaction of **7a** with Silylboranes Bearing Chiral Auxiliaries in the Presence of a Palladium-PPh_3 Catalyst[a]



entry	silylborane	product (% yield)[b]	dr[c]	% de
1	(*R*,*R*)-**2**	**8** (86)	51:49	2
2	(*S*,*S*)-**3**	**9** (94)	52:48	4
3	(*S*,*S*)-**4**	**10** (90)	68:32	36
4	(*R*,*R*)-**5**	**11** (85)	58:42	16
5	(1*R*)-**6**	**12a** (96)	81:19	62

[a] A mixture of silylborane **2**−**6** (0.5 mmol) and **7a** (0.6 mmol) in toluene (0.25 mL) was stirred at room temperature in the presence of Cp(allyl)Pd (2 mol %) with PPh_3 (2.4 mol %). [b] NMR yield (anisole as an internal standard). [c] Diastereomeric ratio determined by HPLC or ^{1}H NMR (400 MHz).

diastereoselectivities (entries 1−4), silylborane **6**, derived from pinanediol, gave an isomer ratio greater than 4:1 (entry 5).



We then examined chiral monodentate phosphine ligands **13**−**15** in the reaction of **6** with **7a** (Table 2). To evaluate matched and mismatched chiral ligand-auxiliary combinations, we carried out the reactions using both enantiomers of **6**. When the phosphoramidite ligand **13** was used with either enantiomer (1*S*)-**6** or (1*R*)-**6**,[13] the diastereoselectivity was considerably lower than that occurring with achiral PPh_3. The diastereoselectivity was significantly improved when the ligand was switched to the ferrocene derivatives **14**.[14] The matched pairs (**14a**/(1*R*)-**6** and **14b**/(1*R*)-**6**) afforded **12a** with 81% de. Although **14a** and **14b** showed the same diastereoselectivity in the matched cases, the results for the mismatched pairs (−1% for **14a**/(1*S*)-**6** vs −34% for **14b**/(1*S*)-**6**) indicated that the 3,5-bis(trifluoromethyl)phenyl derivative (**14b**) effects larger stereochemical induction than does **14a**. Finally, MOP ligands **15a** and **15b** were tested.[15] The 2′-methoxy derivative **15a** gave almost the same diastereoselectivity as that obtained by the PPh_3 catalyst system, indicating that the ligands had no strong influence on the enantioface selection. To our surprise, however, a remarkably high enantioface selectivity (89% de) was recorded with

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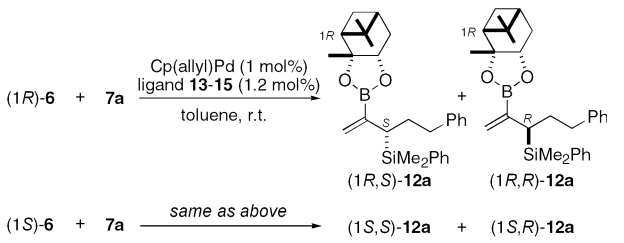
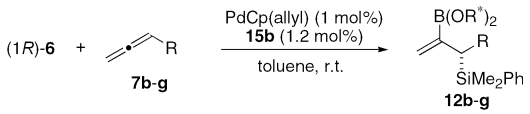
Table 2. Screening of Chiral Ligands for Palladium-Catalyzed Silaboration of **7a** with (1*R*)-**6** and (1*S*)-**6**



	reaction of (1*S*)-**6**			reaction of (1*R*)-**6**		
ligand	% yield[b]	(1*S*,*R*):(1*S*,*S*)[c]	% de[c]	% yield[b]	(1*R*,*S*):(1*R*,*R*)[c]	% de[c]
13	95	71:29	43	88	62:38	24
14a	98	50:50	−1	91	90:10	81
14b	99	33:67	−34	95	90:10	81
15a	73	78:22	55	88	83:17	65
15b	96	37:63	−27	**99**[d]	**94:6**	**89**

[a] Silylborane **6**, **7a** (1.2 equiv), Cp(allyl)Pd (1 mol %), and **13**−**15** (1.2 mol %) were reacted in toluene at room temperature. [b] NMR yield unless otherwise noted. [c] Diastereomeric ratio determined by HPLC. [d] Isolated yield.

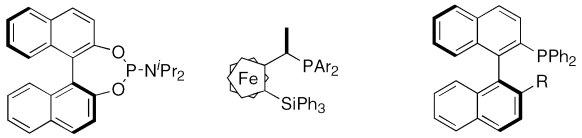
Table 3. Silaboration of Allenes with (1*R*)-**6** in the Presence of a **15b**−Palladium Catalyst[a]



entry	allene	% yield[b]	ratio	% de[c]
1	**7b** (R = CH_3)	92	93:7	86
2	**7c** (R = $CH_2CH_2OSiMe_2Ph$)	91	94:6	88
3	**7d** (R = *c*-Hex)	95	98:2	96
4	**7e** (R = Ph)	95	96:4	92
5	**7f** (R = *p*-$MeOC_6H_4$)	96	95:5	91
6	**7g** (R = *p*-$CF_3C_6H_4$)	92	96:4	92

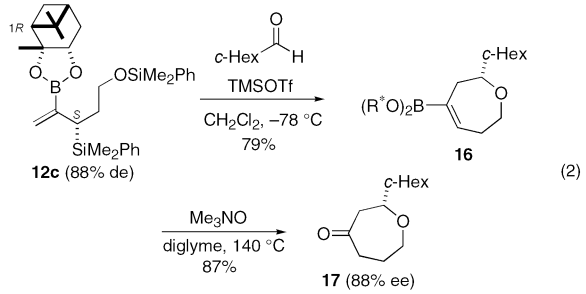
[a] Silylborane (1*R*)-**6**, allenes **7b**−**g** (1.2 equiv), Cp(allyl)Pd (1.0 mol %), and **15b** (1.2 mol %) were reacted in toluene at room temperature. [b] Isolated yield. [c] Diastereomeric ratio determined by ^{1}H NMR (500 MHz).

15b lacking a substituent at the 2′ position.



The optimized reaction conditions using **15b** were applied to the asymmetric silaboration of a series of terminal allenes (Table 3). Diastereomeric excesses comparable to that of **7a** were obtained in the silaboration of terminal allenes **7b** and **7c** bearing nonbranched alkyl groups (entries 1 and 2). The stereoselectivity reached 96% in the reaction of allene **7d**, bearing a sterically more demanding alkyl group (entry 3). Under these reaction conditions, arylallenes **7e**−**7g** also provided the corresponding β-borylallylsilanes in high stereoselectivities (entries 4−6). No marked effect of the *p*-substituents of the arylallenes on the diastereoselectivity and the reaction efficiency was observed. Application of this catalyst system to the reaction of achiral silylborane **1** with **7a**, however, led to only a moderate enantioselectivity (68% ee), indicating that the chiral pinanedioxy group on the boron atom plays an important role in the enantioface discrimination.

The enantioenriched β-borylallylsilane **12c** (88% de), obtained from allene **7c**, bearing a terminal siloxy group, was subjected to a Markó-type cyclization (eq 2).[7c,16] The seven-membered ring formation with cyclohexanecarboxaldehyde took place effectively, giving an enantioenriched oxacyclic alkenylborane **16**. Oxidation of **16** afforded cyclic ketone **17** with 88% ee, indicating that the stereochemical course of the reaction of **12c** relies solely on the silicon-bound chiral center via flawless chirality transfer, with no influence of the boron-bound chiral auxiliary.



(2)

In summary, we have demonstrated enantioface selective addition of silylboranes across an internal C=C bond of allenes, using a new palladium catalyst system. Further improvement of the catalytic system, as well as the synthetic application of the new chiral allylsilanes, is now being undertaken in this laboratory.

Supporting Information Available: Detailed experimental procedures and spectral data for the new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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