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Palladium-Catalyzed Asymmetric Silaboration of Allenes

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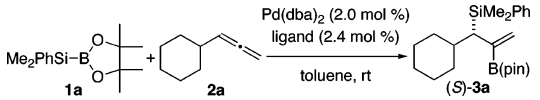
The synthesis of stereodefined organometallic compounds has attracted much attention because of the increasing demand for stereoselective construction of complex organic molecules. Allylsilanes are recognized as one of the most important classes of organometallic reagents in synthetic organic chemistry.[1] Their unique features involve stability, reactivity, and functional group tolerability, which make these particular compounds synthetically attractive. Further interest has been focused on the synthetic use of optically active allylsilanes, which enable asymmetric allylations via highly efficient chirality transfer.[2] To take advantage of these features of allylsilanes, much effort has been devoted to catalytic asymmetric synthesis of highly enantioenriched allylsilanes via asymmetric Grignard cross-coupling,[3] hydrosilylation of 1,3-dienes,[4] and allylic substitution.[5] However, these reactions are limited to the synthesis of simple allylsilanes that do not carry functional groups at their C═C bonds.[6]

We have developed Pd-catalyzed silaboration of terminal allenes for the efficient synthesis of the allylsilanes that bear boryl groups at their β-positions.[7,8] We have reported that highly diastereoselective formation of optically active β-borylallylsilanes was achieved under double asymmetric induction conditions using an optically active ligand and a chiral auxiliary on the boron atom of the silylborane.[9] The use of the pinanedioxy group as the chiral auxiliary was critical in obtaining high stereoselectivity. Our efforts were then focused on exploring a catalytic asymmetric synthesis that does not rely on the stoichiometric use of a chiral auxiliary. Herein, we describe an asymmetric silaboration of terminal allenes using an achiral silylborane with a Pd catalyst having an optically active monodentate phosphine ligand.

Silaboration of cyclohexylallene (**2a**) with $Me_2PhSiB(pin)$ (**1a**) was examined in the presence of Pd catalysts bearing chiral monodentate phosphorus ligands (entries 1−6 in Table 1). The reactions proceeded smoothly at room temperature, giving **3a** in 84−99% yields with varying enantiomeric excesses (ees) (12−74% ee). Whereas (+)-NMDPP, (*S*)-MONOPHOS, and (*S*)-MOP gave poor selectivities (entries 1, 2, and 5), (*R*,*R*)-**4**[10] and (*S*)-QUINAP showed moderate selectivities (63 and 51% ee, entries 3 and 4). The highest selectivity was attained with (*R*)-**5a** (Ar = Ph, 74% ee, entry 6), suggesting that 1,1′-binaphth-2-yl was the chiral group of choice in the asymmetric silaboration of allenes.

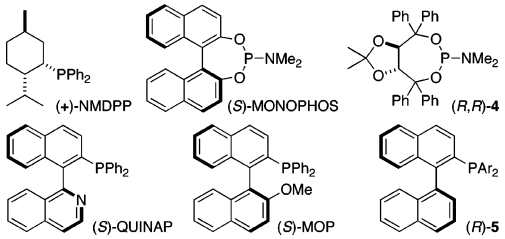
We then modified the diarylphosphino group on the 1,1′-binaphthyl skeleton (entries 7−17 in Table 1).[11] A derivative with a *p*-MeO group showed an appreciable increase in ee (entry 7), whereas a *p*-CF_3 derivative resulted in a significant drop in ee (entry 8). Among the tolyl derivatives examined, *p*- and *m*-tolyl derivatives (*R*)-**5d** and (*R*)-**5e** showed higher ees than the parent (*R*)-**5a** ligand (entries 9 and 10), although almost no enantioselectivity was attained with the *o*-tolyl derivative (*R*)-**5f** (entry 11). We observed the highest selectivity with the 3,5-dimethylphenyl derivative (*R*)-**5g**, which afforded **3a** with 84% ee at room temperature (entry 12). The same levels of enantioselectivity were attained with analogous phosphines (*R*)-**5h** and (*R*)-**5i** having 3,5-substituents (entries 13 and 14). It is interesting to note that the ees dropped to 47−59% when phosphines having CF_3, *t*-Bu, and Me_3Si groups at their 3,5-positions on the phenyl group were used (entries 15−17).

Table 1. Screening of Chiral Ligands for Palladium-Catalyzed Silaboration of **2a**[a]



entry	ligand	yield (%)[b]	ee (%)[c]
1	(+)-NMDPP	84	37[d]
2	(*S*)-MONOPHOS	85	16
3	(*R*,*R*)-**4**	99	63[d]
4[e]	(*S*)-QUINAP	84	51
5[e]	(*S*)-MOP	96	12
6[e]	(*R*)-**5a** (Ar = Ph)	98	74
7	(*R*)-**5b** (Ar = 4-$MeOC_6H_4$)	88	77
8	(*R*)-**5c** (Ar = 4-$CF_3C_6H_4$)	99	53
9	(*R*)-**5d** (Ar = 4-MeC_6H_4)	93	77
10	(*R*)-**5e** (Ar = 3-MeC_6H_4)	98	78
11	(*R*)-**5f** (Ar = 2-MeC_6H_4)	67[f]	13
12	(*R*)-**5g** (Ar = 3,5-$Me_2C_6H_3$)	99	84
13	(*R*)-**5h** [Ar = 3,5-$(MeOCH_2)_2C_6H_3$]	99	84
14	(*R*)-**5i** (Ar = 3,5-Me_2−4-$MeOC_6H_2$)	98	81
15	(*R*)-**5j** [Ar = 3,5-$(CF_3)_2C_6H_3$]	85	53
16	(*R*)-**5k** (Ar = 3,5-$^t Bu_2$−4-$MeOC_6H_2$)	99	59
17	(*R*)-**5m** [Ar = 3,5-$(Me_3Si)_2C_6H_3$]	83	47

[a] **1** (0.40 mmol), **2a** (0.48 mmol), $Pd(dba)_2$ (8.0 μmol), and ligand (9.6 μmol) were stirred in toluene (0.2 mL) at room temperature for 3−15 h unless otherwise noted. [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase column. [d] (*R*)-**3a** was formed as major isomer. [e] CpPd(η^3-allyl) (1.0 mol %) and ligand (1.1 mol %) were used. [f] Yield after 140 h.



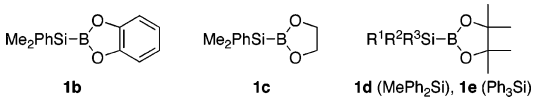


Figure 1. Silylboranes used in the asymmetric silaboration.

Silylboranes bearing different substituents on the boron and silicon atoms were applied to the asymmetric silaboration of **2a** with the Pd/(*R*)-**5g** catalyst under the same conditions as those described in Table 1 (Figure 1). Silylboranes derived from catechol (**1b**, 27% ee) and ethylene glycol (**1c**, 40% ee) gave much lower selectivity than **1a**. Enantioselectivity was found to be improved significantly by use of the more sterically hindered diphenylmethylsilyl derivative (**1d**), affording the corresponding β-borylallylsilane

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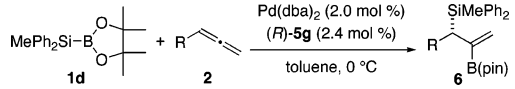
Table 2. Asymmetric Silaboration of Various Allenes[a]



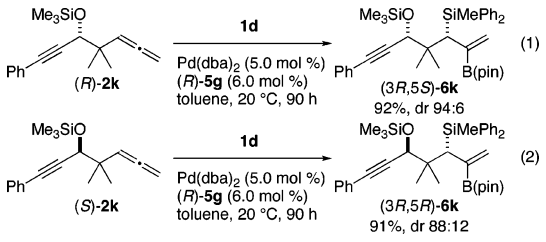
entry	R	product	yield (%)[b]	ee (%)[c]
1	*cyclo*-C_6H_{11} (**2a**)	**6a**	90	91[d]
2	$Me_2PhSiOCH_2C(Me)_2$ (**2b**)	**6b**	97	92[d]
3	$OHCC(Me)_2$ (**2c**)	**6c**	95	93[d]
4	Ph (**2d**)	**6d**	93	88
5	4-MeC_6H_4 (**2e**)	**6e**	94	89
6	2-MeC_6H_4 (**2f**)	**6f**	93	90
7	1-naphthyl (**2g**)	**6g**	86	90
8	Me (**2h**)	**6h**	96	80[d]
9	$Ph(CH_2)_2$ (**2i**)	**6i**	91	82[d]
10[e]	$AcOCH_2C(Me)_2$ (**2j**)	**3j**	91	90

[a] **1d** (0.40 mmol), **2** (0.48 mmol), $Pd(dba)_2$ (8.0 μmol), and (*R*)-**5g** (9.6 μmol) were stirred in toluene (0.2 mL) at 0 °C for 22−90 h unless otherwise noted. [b] Isolated yield. [c] Determined by HPLC analysis with a chiral stationary phase column. [d] Determined after transforming **6** into corresponding β-hydroxysilane. See Supporting Information. [e] Reaction with **1a** at −10 °C in the presence of 4.0 mol % of catalyst.

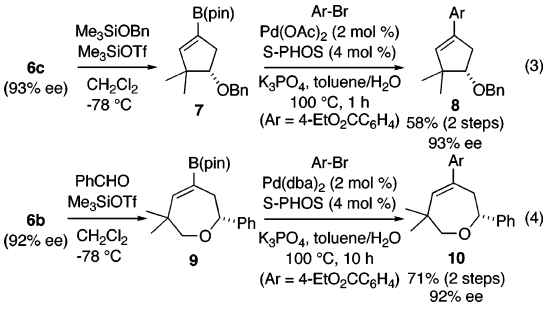
6a with 89% ee. The more sterically demanding triphenylsilyl derivative (**1e**) did not react at all under the same reaction conditions.

Under the optimized conditions using the Pd/(*R*)-**5g** catalyst and the silylborane **1d**, various allenes were subjected to enantioselective silaboration at 0 °C (Table 2). The enantioselectivity was improved to 91% ee in the reaction of **2a** (entry 1). The silaboration of allenes having *sec*- and *tert*-alkyl groups gave the corresponding products **6** with high ees (91−93% ee, entries 1−3). The same level of enantioinduction was observed in the reaction of phenylallene (**2d**) and its derivatives **2e**−**g** (88−90% ee, entries 4−7). On the other hand, methyl or primary alkyl-substituted allenes gave the corresponding β-borylallylsilanes with lower ees (entries 8 and 9). These results indicate that the enantioselectivity largely depends on the bulkiness of the substituents of the allenes. An additional example is shown by the reaction of **1a** with bulky **2j**, providing **3j** with 90% ee (entry 10).

To examine the chemoselectivity of the silaboration, a pair of asymmetric silaborations of enantiomeric allenynes (*R*)- and (*S*)-**2k** was carried out at 20 °C (eqs 1 and 2). The additions of **1d** took place exclusively at the allene moiety rather than the carbon−carbon triple bond to give **6k** in high yields.[12] Diastereomeric ratios of the products were slightly affected by the stereochemistry of the original stereogenic carbon centers (94:6 for the matched pair, 88:12 for the mismatched pair).



The allylsilane aldehyde **6c** (93% ee) cyclized via oxonium intermediate formation in the presence of Me_3SiOTf with Me_3-SiOBn, giving boryl-substituted cyclopentene **7** (eq 3).[13] On the other hand, reaction of **6b** (92% ee) with PhCHO afforded seven-membered cyclic alkenylborane **9** (eq 4).[14] Suzuki−Miyaura cross-coupling of the alkenylborane products (**7** and **9**) with ethyl 4-bromobenzoate under the conditions using 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-PHOS)[15] gave the corresponding alkenylarenes (**8** and **10**) in 58 and 71% total yield, respectively. The ees of **8** and **10** were found to be 93 and 92% ee, respectively, indicating the cyclization steps proceeded with perfect chirality transfer.



In conclusion, we have demonstrated Pd-catalyzed asymmetric silaboration of terminal allenes with an achiral silylborane, affording synthetically useful β-borylallylsilanes with high ees.

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

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