Palladium-Catalyzed Asymmetric Hydrosilylation of 4-Substituted 1-Buten-3-ynes. Catalytic Asymmetric Synthesis of Axially Chiral Allenylsilanes

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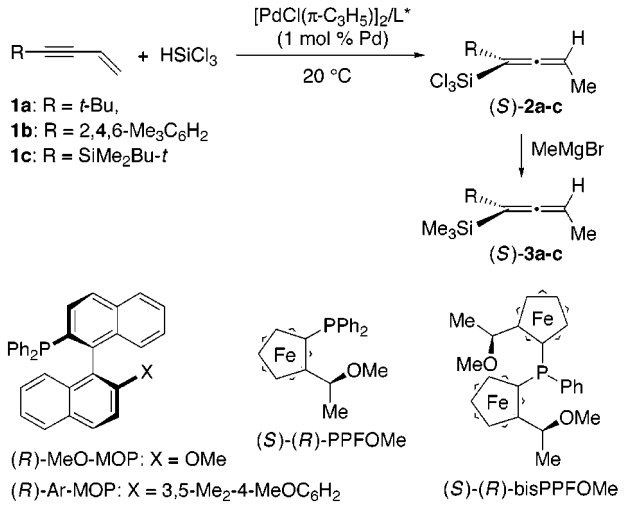
Allenylsilanes are useful intermediates in organic synthesis, reacting with a variety of electrophiles in a regiospecific manner.[1] For example, the reaction with carbonyl compounds provides a selective route to homopropargylic alcohols. Recently, considerable attention has been paid to the preparation of axially chiral allenylsilanes and their use for the asymmetric synthesis of homopropargylic alcohols.[2] However, to our best knowledge, only one report has appeared on the catalytic asymmetric synthesis of allenylsilanes, which was attained by rhodium-catalyzed asymmetric double hydrosilylation of a 1,3-diyne, giving a 1,3-bis(silyl)-1,2-propadiene derivative of 22% ee.[3] On the other hand, we have continued our studies on the palladium-catalyzed asymmetric hydrosilylation of olefins.[4] High enantioselectivity has been reported for various types of olefins including alkyl-substituted terminal alkenes, cyclic alkenes, styrene derivatives, and 1,3-dienes by use of axially chiral monodentate phosphine ligands.[5] The palladium-catalyzed hydrosilylation of 1,3-dienes with trichlorosilane is unique in that exclusive 1,4-addition takes place, giving allylsilanes with perfect selectivity, probably due to a contribution of π-allylpalladium intermediates.[6] We anticipated that a proper design of the catalytic reaction system would realize the regio- and enantioselective 1,4-addition to 1,3-enynes, giving axially chiral allenylsilanes. Here we report our results that allenylsilanes of up to 90% ee are obtained by the catalytic asymmetric hydrosilylation of 1,3-enynes.

We examined 1-buten-3-ynes containing various types of substituents at 4-position for the palladium-catalyzed hydrosilylation with trichlorosilane and found that the selectivity in giving allenylsilane is strongly dependent on the steric bulkiness of the substituent.[7] The selectivity is high for 1-buten-3-ynes containing sterically bulky groups such as *tert*-butyl, mesityl, or *tert*-butyldimethylsilyl, while it is low for those containing less bulky groups (Scheme 1).[8] In the reaction of 5,5-dimethyl-1-hexen-3-yne (**1a**, R = *tert*-Bu in RC≡C−CH═CH_2), we looked for the chiral phosphine ligand whose palladium complex catalyzes the hydrosilylation, forming allenylsilane in high yield with high enantioselectivity. Chelating bisphosphines such as binap cannot be used because the hydrosilylation is very slow, as has been usually observed in the palladium-catalyzed hydrosilylation with trichlorosilane.[5] The chiral monophosphines (MOPs) whose chirality is due to the binaphthyl axial chirality were not as effective for the present 1,3-enyne substrates as for other types of olefinic substrates.[5] The enantioselectivity was 27% and 18% with MeO-MOP[9] and Ar-MOP,[6,10] respectively. Much higher enantioselectivity was observed in the reaction with chiral ferrocenylmonophosphines based on the ferrocene planar chirality.[11,12] Of those reported so far, (*S*)-(*R*)-PPFOMe[12] showed the highest enantioselectivity. Thus, a mixture of **1a** (2.0 mmol), trichlorosilane (4.4 mmol), and 1.0 mol % of a palladium catalyst generated from [PdCl(π-C_3H_5)]$_2$ and (*S*)-(*R*)-PPFOMe (P/Pd = 2.2/1) was kept stirring at 20 °C for 9 h (entry 3 in Table 1). A GLC analysis indicated the formation of allenylsilane **2a** in 81% yield together with 19% of a mixture of dihydrosilylation products. Distillation under reduced pressure gave a 79% isolated yield of trichloro(allenyl)silane **2a**. Methylation with MeMgBr in Et_2O gave trimethyl(allenyl)silane **3a**, whose enantiomeric purity was determined to be 72% by GLC analysis using a chiral stationary phase column (CP-chiralsil-Dex CB). For higher enantioselectivity, we have prepared several new chiral ferrocenylmonophosphines. One of the best at this stage is (*S*)-(*R*)-bisPPFOMe, in which the phosphorus atom is bonded to two ferrocenyl moieties. Scheme 2 shows the preparation of (*S*)-(*R*)-bisPPFOMe[13] from (*S*)-*N*,*N*-dimethyl-1-((*R*)-2-bromoferrocenyl)ethylamine[14] (68% overall yield). The asymmetric hydrosilylation of **1a** catalyzed by a palladium complex of (*S*)-(*R*)-bisPPFOMe at 20 °C gave allenylsilane **2a** of 85% ee (entry 4). At a lower reaction

Scheme 1



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(7) 1-Buten-3-ynes containing substituents at the 1 or 2 position do not produce any allenylsilanes.

(8) For example, the reaction of dec-1-en-3-yne (R = *n*-Hex in RC≡C−CH═CH_2) gave a complex mixture of the hydrosilylation products which consist of less than 20% of the allenylsilane.

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(13) (*S*)-(*R*)-bisPPFOMe: $[\alpha]^{20}_D$ +447.4 (*c* 1.1, benzene); ^{1}H NMR (C_6D_6) δ 1.54 (d, *J* = 6.5 Hz, 3H), 1.70 (d, *J* = 6.4 Hz, 3H), 2.78 (s, 3H), 3.44 (s, 3H), 3.61 (s, 5H), 4.07 (s, 5H), 4.13 (t, *J* = 2.4 Hz, 1H), 4.16 (t, *J* = 2.4 Hz, 1H), 4.29 (m, 1H), 4.35 (m, 1H), 4.39 (m, 1H), 4.40 (m, 1H), 4.68 (qd, *J* = 6.5, 2.8 Hz, 1H), 4.95 (qd, *J* = 6.4, 2.9 Hz, 1H), 7.03-7.11 (m, 3H), 7.76−7.79 (m, 2H).

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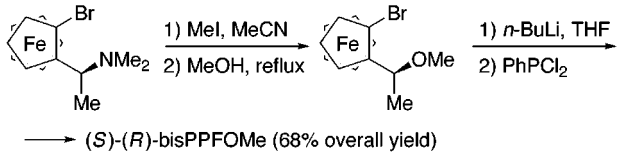
Table 1. Asymmetric Hydrosilylation of 1,3-Enynes **1** with Trichlorosilane Catalyzed by Chiral Phosphine−Palladium Complexes Forming Allenylsilanes **2**[a]

entry	enyne **1**	L*	temp (°C)	time (h)	product	yield (%)[c,d]	% ee[b] (config)
1	**1a**	(*R*)-MeO-MOP	20	18	**2a**	59	27 (*S*)
2	**1a**	(*R*)-Ar-MOP	20	24	**2a**	72	18 (*S*)
3	**1a**	(*S*)-(*R*)-PPFOMe	20	9	**2a**	81	72 (*S*)
4	**1a**	(*S*)-(*R*)-bisPPFOMe	20	48	**2a**	59	85 (*S*)
5	**1a**	(*S*)-(*R*)-bisPPFOMe	0	160	**2a**	37	90 (*S*)
6[e]	**1b**	(*S*)-(*R*)-PPFOMe	20	18	**2b**	54	56 (*S*)
7[e]	**1b**	(*S*)-(*R*)-bisPPFOMe	20	64	**2b**	90	77 (*S*)
8	**1c**	(*S*)-(*R*)-PPFOMe	20	36	**2c**	94	61 (*S*)
9	**1c**	(*S*)-(*R*)-bisPPFOMe	20	160	**2c**	40	68 (*S*)

[a] The asymmetric hydrosilylation was carried out with enyne **1** (2.0 mmol) and trichlorosilane (4.4 mmol) in the presence of 1 mol % of the catalyst generated from $[PdCl(\pi\text{-}C_3H_5)]_2$ and L* (Pd/P = 1/2.2). [b] Determined by GLC analysis of trimethylsilane **3a** with a chiral stationary phase column (CP-chiralsil-Dex CB) and by HPLC analysis of homopropargylic alcohol **4** with a chiral stationary column (Daicel Chiralcel OD-H). [c] Determined by GLC analysis. [d] A mixture of dihydrosilylation products was also formed: 34%, 24%, 19%, 1%, 0%, 29%, 0%, 4%, and 1% for entries 1, 2, 3, 4, 5, 6, 7, 8, and 9, respectively. [e] With 1.1 equiv of trichlorosilane.

Scheme 2

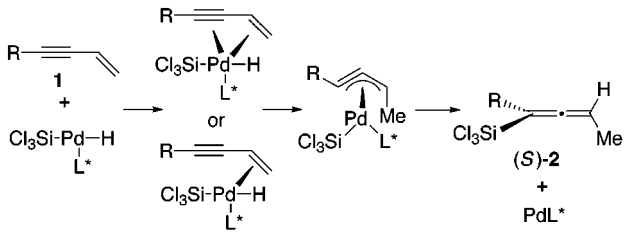


temperature (0 °C), the enantioselectivity was increased to 90% ee (entry 5). In the hydrosilylation of 1-buten-3-ynes substituted at the 4-position with mesityl (**1b**) and *tert*-butyldimethylsilyl (**1c**), the enantioselectivity was also higher with (*S*)-(*R*)-bisPPFOMe than with other chiral ligands, though it is still not high enough (entries 6−9).

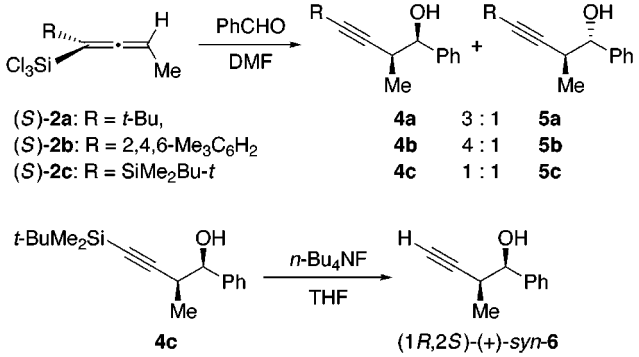
Considering the reaction mechanism we have studied for the palladium-catalyzed hydrosilylation of styrenes and 1,3-dienes with trichlorosilane,[15] the present asymmetric hydrosilylation of 1,3-enynes forming allenylsilanes probably proceeds through the catalytic cycle involving hydropalladation of the terminal alkene, forming a π-propargyl(silyl)palladium intermediate (Scheme 3). The steric bulkiness of the substituent at the 4 position must be important in retarding the hydropalladation of the alkyne moiety.

The enantiomerically enriched allenylsilanes **2** were allowed to react with benzaldehyde in DMF at 0 °C to give homopropargylic alcohols, which consist of syn and anti isomers, **4** and **5**, in a ratio ranging between 4:1 and 1:1 (Scheme 4). Their enantiomeric purities, determined by HPLC analysis with a chiral stationary phase column, were found to be the same as that of the allenylsilane, demonstrating that the axial chirality of allenylsilanes is completely transferred to the central chirality of homopropargylic alcohols in the S_E' reaction with an aldehyde.

Scheme 3



Scheme 4



The absolute configuration of syn homopropargylic alcohol **4** was determined to be (1*R*,2*S*) by correlation with known alcohol (+)-(1*R*,2*S*)-**6**[16] or by NMR studies of the MTPA esters of **4a**.[17] The *S* configuration of allenyl(trichloro)silanes **2** is deduced from the 2*S* configuration of the homopropargyl alcohols **4** on the assumption that the reaction of allenyl(trichloro)silane with aldehyde proceeds via a cyclic transition state.[18]

To summarize, we have shown the first successful example of preparation of axially chiral allenylsilanes by asymmetric catalysis. High enantioselectivity (up to 90%) was achieved by use of a new chiral monophosphine ligand which contains two planar chiral ferrocenyl moieties on the phosphorus atom. As an example of the reaction of the allenyl(trichloro)silanes obtained, they were transformed into homopropargylic alcohols without loss of their enantiomeric purity.

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data for the products (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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