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Asymmetric Hydrosilylation of Cyclopentadiene and Styrene with Chlorosilanes Catalyzed by Palladium Complexes of Chiral (β-N-Sulfonylaminoalkyl)phosphines[1)]

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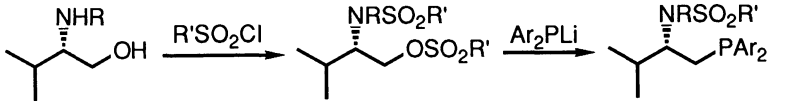
It was found that the palladium complexes of newly prepared chiral (β-aminoalkyl)phosphine derivatives bearing N-sulfonyl groups were efficient catalysts for asymmetric hydrosilylations of cyclopentadiene and styrene with chlorosilanes.

Asymmetric hydrosilylation is one of the useful methods for the synthesis of optically active compounds. Among them, asymmetric hydrosilylations of prochiral ketones catalyzed by chiral rhodium complexes have been studied extensively.[2,3)] Although several preparations of optically active allylsilanes and some other silanes by catalytic asymmetric hydrosilylation using chiral ferrocenylphosphines-palladium have been reported by Hayashi et al.,[4)] few highly efficient asymmetric hydrosilylations of olefinic substrates have been developed.

Here we report i) the preparation of new chiral (β-aminoalkyl)-phosphine derivatives bearing N-sulphonyl groups and ii) efficient asymmetric hydrosilylations of cyclopentadiene and styrene catalyzed by the chiral (β-N-sulfonylaminoalkyl)phosphine-palladium complexes.

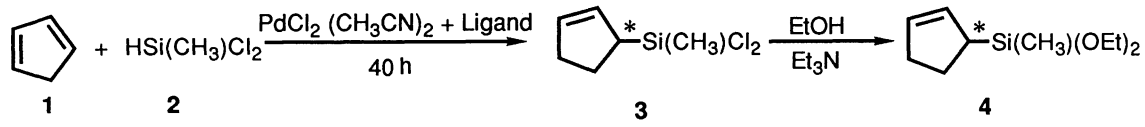
New chiral (S)-(N-sulfonylaminoalkyl)phosphines (**5a-c**, **6**, **7**) were prepared simply by both N-and O-sulfonylations of (S)-valinols with sulfonyl chlorides, followed by phosphination with lithium diarylphosphides (Scheme 1).

Asymmetric hydrosilylation of cyclopentadiene (**1**) with dichloromethylsilane (**2**) was carried out under an argon atmosphere in the presence



5a : R=H, R'=CH_3, Ar=C_6H_5
5b : R=H, R'=CH_3, Ar=$C_6H_4OCH_3$-*p*
5c : R=H, R'=CH_3, Ar=C_6H_4Cl-*p*
6 : R=H, R'=C_6H_5, Ar=C_6H_5
7 : R=CH_3, R'=CH_3, Ar=C_6H_5

Scheme 1.



1 2 3 4

Scheme 2.

Table 1. Asymmetric hydrosilylation of cyclopentadiene with dichloromethylsilane catalyzed by chiral phosphine-Pd(II) complexes.[a]

	Ligand ; R	Ar	Temp/°C	Yield of **3**/ % [b]	$[\alpha]_D^{18-24}$ of **4**/°	%e.e. [c]	(Confign.)
5a	$-NHSO_2CH_3$	-Ph	r.t.	83	-64.2	48	(*S*)
			0	82 (84)[d]	-80.8 (-82.5)[d]	61 (62)[d]	(*S*)
			-20	35	-93.8	71	(*S*)
5b	$-NHSO_2CH_3$	$-C_6H_4-OCH_3-p$	0	74	-82.9	62	(*S*)
5c	$-NHSO_2CH_3$	$-C_6H_4-Cl-p$	0	88	-67.9	51	(*S*)
6	$-NHSO_2C_6H_5$	-Ph	0	93	-70.9	53	(*S*)
7	$-N(CH_3)SO_2CH_3$	-Ph	0	84	-9.0	7	(*S*)
8a	$-N(CH_3)_2$	-Ph	r.t.	60	+0.9		(*R*)
8b	$-N(CH_3)_2$	$-C_6H_4-OCH_3-p$	r.t.	37	+1.1		(*R*)
8c	$-N(CH_3)_2$	$-C_6H_4-Cl-p$	r.t.	78	+1.0		(*R*)
9	$-OCH_2OCH_3$	-Ph	0	87	+48.7	37	(*R*)

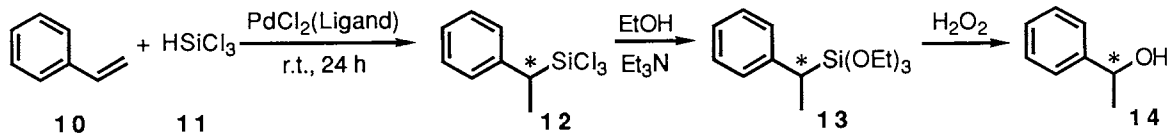
a) [**1**]/[**2**]/[Pd]=1/2/10^{-3}. Palladium catalysts were prepared *in situ* by mixing dichlorobis(acetonitrile)palladium(II) with 1 equiv. of ligands. b) Yield based on **1**. c) Ref. 4a. d) The palladium complex catalyst isolated was used.

of 0.1 mol% of N-sulfonyl-substituted aminophosphines (**5a-c**, **6**, **7**)-palladium complexes prepared in situ by mixing the ligand and dichlorobis-(acetonitrile)palladium. The results are summarized in Table 1. The palladium complexes of **5a-c** and **6** bearing a N-methylsulfonyl group and a N-phenylsulfonyl group, respectively, were catalytically active even at 0 °C giving (S)-3-(dichloromethyl)cyclopentene (**3**) in high yields.[5,6] In the case of **5a** the enantioselectivities were higher at lower temperatures and at -20 °C the highest optical yield (71% ee (S)) was obtained. The substituents on each phenyl group of **5b,c** did not have a dramatic influence on the enantioselection. Since N-methyl-N-methylsulfonyl derivative (**7**) showed much lower selectivity than **5a**, the NH group of the sulfonamides was considered to be important for giving high selectivity. On the other hand, both valphos (**8a**)[7] itself and its derivatives (**8b-c**) showed catalytic activity at room temperature, but the selectivity was very low.

Then, in order to clarify the role of the substituted amino groups, we prepared another analogue (**9**)[8] bearing a methoxymethyloxy group in place of the substituted amino group. It was of interest that the palladium complex of this ligand showed the reverse enantioselectivity

in comparison with those of the sulfonamide derivatives under the same reaction conditions, giving the (R)-product in 37% ee.

These results may imply that the β-substituents of the alkylphosphine ligands play much more important roles than the phosphino groups on their enantioselectivities.



10 11 12 13 14

Scheme 3.

Table 2. Asymmetric hydrosilylation of styrene with trichlorosilane catalyzed by sulfonylaminoalkylphosphine-Pd(II) complexes.[a)]

Ligand ;	R	Ar	Yield of 12 /%[b)]	%e.e.[c)]	(Confign.)
5a	-$NHSO_2CH_3$	-Ph	57[d)]	64.8	(*S*)
5b	-$NHSO_2CH_3$	-C_6H_4-OCH_3-*p*	60	51.8	(*S*)
5c	-$NHSO_2CH_3$	-C_6H_4-Cl-*p*	88	58.9	(*S*)
6	-$NHSO_2C_6H_5$	-Ph	81	50.7	(*S*)

a) [10]/[11]/[Pd]=1/2/10^{-3} b) Yield based on 10. c) Determined by HPLC analysis of 14 (DAICEL Chiralcel OB, hexane/2-propanol=9/1). d) Yield of 13 from 10.

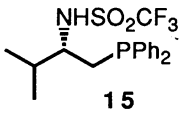
Next, the asymmetric hydrosilylation of styrene (10) with trichlorosilane (11) was carried out in the presence of 0.1 mol% of the palladium-N-sulfonylaminophosphines (5a-c, 6) complexes prepared. The results are summarized in Table 2. The reaction proceeded smoothly to give regioselectively the corresponding hydrosilylation product (12) with good to moderate enantioselectivities.[9,10)] In these cases, as well as the hydrosilylation of 1, the substituents on each phenyl group of the phosphino group did not give a dramatic effect on the selectivity.

Further, in order to gain more efficient catalysts, we designed and prepared new chiral ligands, (S)-(N-sulfonylaminoalkyl)phosphines (15[11)] and 16); the former bearing a trifluoromethylsulfonyl group as a more electron-withdrawing group and the latter bearing a t-butyl group as a sterically more bulky skeleton. Hydrosilylations of cyclopentadiene (1) and styrene (10) were carried out under the same conditions as shown in Tables 1 and 2. The results summarized in Table 3 show that both the palladium complexes of 15 and 16 gave higher selectivities than that of 5a in the hydrosilylation of 1, but the selectivity of the complex of 15 decreased in the hydrosilylation of 10. Electronic effects of

Table 3. Asymmetric hydrosilylation of cyclopentadiene and styrene catalyzed by sulfonylaminoalkylphosphine-Pd(II) complexes[a)]

Substrate	Ligand	Temp/° C	React. time /h	Yield /%[b)]	$[\alpha]_D^{22}$/°	%e.e.	(Confign.)
1	**15**	0	40	**3** 84	**4** -96.0	72[c)]	(*S*)
1	**16**	0	40	**3** 84	**4** -90.7.	68[c)]	(*S*)
10	**15**	r.t.	24	**12** 63		16.3[d)]	(*S*)
10	**16**	r.t.	24	**12** 90		63.0[d)]	(*S*)

a) [**1**]/[**2**]/[Pd]=1/2/10^{-3}, [**10**]/[**11**]/[Pd]=1/2/10^{-3}, The palladium complex catalyst isolated was used.
b) Yield based on **1** or **10**. c) Calculated on the basis of the reported value (Ref. 4a). d) Determined by HPLC analysis of **14** (DAICEL Chiralcel OB, hexane/2-propanol=9/1).



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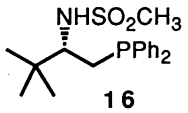

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the sulfonamide groups were considered to play important roles on their enantioselections.

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2) I. Ojima and K. Hirai, "Asymmetric Synthesis," ed by J. D. Morrison, Academic Press, New York (1985), Vol. 5, p. 103.
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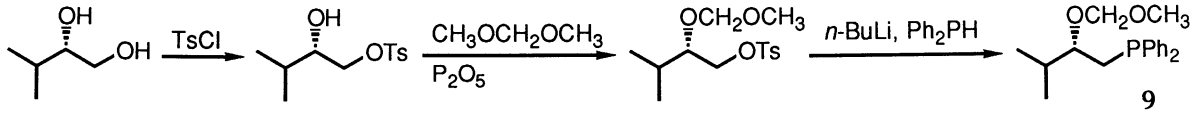
4) a) T. Hayashi, K. Kabeta, T. Yamamoto, K. Tamao, and M. Kumada, Tetrahedron Lett., 24, 5661 (1983); b) T. Hayashi, K. Tamao, Y. Katsuro, I. Nakae, and M. Kumada, ibid., 21, 1871 (1980); c) T. Hayashi and K. Kabeta, ibid., 26, 3026 (1985); d) Y. Matsumoto, T. Hayashi, I. Morikawa, and Y. Ito, 36th Symposium on Organometallic Chemistry, Japan, 1989, 295.
5) The product (**3**) was converted to diethoxysilyl derivative (**4**), the optical yield of which was calculated on the basis of the reported value (Ref. 4a).
6) The hydrosilylation of **1** with trichlorosilane (**11**) did not proceed smoothly under the similar conditions.
7) T. Hayashi, M. Konishi, M. Fukushima, K. Kanehira, T. Hioki, and M. Kumada, J. Org. Chem., 48, 2195 (1983).
8) The ligand **9** was prepared in the following manner.



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9) After leading to triethoxysilyl derivative (**13**), the product was further converted to α-phenethyl alcohol (**14**) [cf. K. Tamao, E. Nakajo, and Y. Ito, J. Org. Chem., 52, 4412 (1987)]. The enantiomeric excess of **14** was determined by HPLC analysis using a chiral column, Chiralcel OB.
10) The hydrosilylation of **10** with dichloromethylsilane (**2**) did not proceed smoothly under the similar conditions.
11) The ligand **15** was prepared from (S)-valinol via N-t-butoxycarbonylation, O-tosylation, phosphination, N-deprotection, and N-trifluoromethylsulfonylation.

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