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Catalytic Asymmetric Hydrosilylation of Conjugated Dienes: Effective Control of Regio- and Enantioselectivities

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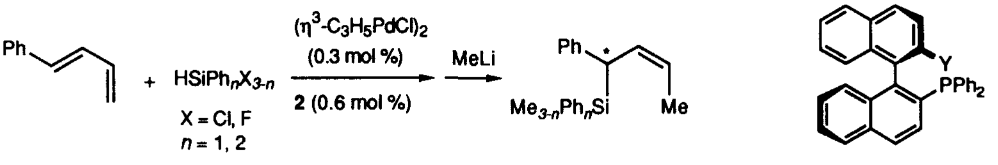
Abstract: Hydrosilylation of (*E*)-1-phenyl-1,3-butadiene with $HSiPh_nX_{3-n}$ (X = Cl, F; *n* = 1, 2) was catalyzed by palladium catalyst generated in situ from $(\eta^3\text{-}C_3H_5PdCl)_2$ and (*R*)-2-diphenylphosphino-1,1'-binaphthyl derivatives (**2**), giving optically active (*Z*)-1-phenyl-1-silyl-2-butenes (**1**) in good yields. The regio- and enantioselectivities of the reaction was found to be strongly affected by the structure of the hydrosilane and the phosphine ligand.

Optically active allylsilanes bearing a chiral carbon directly bonded to silicon are useful chiral building blocks for the synthesis of a wide range of optically active compounds.[1] Hayashi and his co-workers described an approach to these compounds which is based on palladium-catalyzed asymmeytric hydrosilylation of conjugated dienes with trichlorosilane.[2] Recently, they have used MOP (**2**, Y = OMe)[3] as a chiral ligand to attain high enantioselectivity of hydrosilylation. We have also found that asymmetric hydrosilylation of conjugated dienens, catalyzed by a palladium complex coordinated with (*R*)-2-diphenylphosphino-1,1'-binaphthyls (**2**), gives optically active allylsilanes **1**.[4] We report here that the enantio- and the regioselectivities of the reaction are decisively influenced by the kind of the hydrosilane and the substituent Y of **2**.



1a: *n* = 2
1b: *n* = 1

2a: Y = OH
2b: Y = OSi(*t*-Bu)Me_2

Hydrosilylation of (*E*)-1-phenyl-1,3-butadiene (4.5 mmol) with a hydrosilane (5.0 mmol) smoothly took place in the presence of $(\eta^3\text{-}C_3H_5PdCl)_2$ (1.5×10^{-2} mmol) and (*R*)-2-hydroxy-2'-diphenylphosphino-1,1'-binaphthyl (**2a**)[3a] (3.0×10^{-2} mmol) without solvent at 20 °C, giving (*S*)-(*Z*)-1-phenyl-1-silyl-2-butene (**1**) in good yields. The product was treated with excess methyllithium, purified by silica-gel column chromatography (hexane) and then analyzed by HPLC using chiral column (Daicel CHIRALCEL-OD, hexane) to determine the enantiomer excess (ee).[5] Results summarized in **Table 1** apparently show that the substituent on the hydrosilane exerts a strong influence on the enantioselectivity as well as the regioselectivity. The highest ee was obtained with $HSiPh_2F$, which gave a quantitative yield of (*S*)-**1a** with 66% ee (entry 1). Use of $HSiPhF_2$,

$HSiPh_2Cl$, or $HSiPhCl_2$ gave **1** with lower ee (entries 2-4). It is noteworthy that the presence of phenyl group on the hydrosilane is essential for the high regioselectivity. Replacement of the phenyl group by halogen markedly decreased the regioselectivity; the reaction of trichlorosilane gave a mixture of regioisomers (entries 5 and 10).

The most striking feature of the present reaction is that the enantioselectivity can be *reversed* when (*R*)-2-(*tert*-butyldimethylsilyl)oxy-2'-diphenylphosphino-1,1'-binaphthyl (**2b**)[3b] is used as a chiral ligand. Thus, the hydrosilylation of 1-phenyl-1,3-butadiene catalyzed by $(\eta^3\text{-}C_3H_5PdCl)_2$/**2b** afforded (*R*)-**1** under the same conditions (entries 6-9). The highest ee of (*R*)-**1** (56% ee) was attained by the reaction of $HSiPh_2Cl$ (entry 8). These results suggest that coordination of 2-OH group of phosphine ligand **2a** with a silane plays an important role in determining the absolute configuration of allylsilane **1**.[6]

Table 1 Asymmetric Hydrosilylation of (*E*)-1-Phenyl-1,3-butadiene with Phenyl(halo)silanes Catalyzed by $(\eta^3\text{-}C_3H_5PdCl)_2$ / **2**[a]

Entry	Ligand	Hydrosilane	Conditions	Yield[b] (%)	% ee (*confign*)	$[\alpha]^{20}_D$[c]
1	**2a**	$HSiPh_2F$	20 °C, 12 h	96 (**1a**)	66 (*S*)	-6.35°
2	**2a**	$HSiPhF_2$	20 °C, 12 h	95 (**1b**)	45 (*S*)	-4.98°
3	**2a**	$HSiPh_2Cl$	20 °C, 12 h	90 (**1a**)	34 (*S*)	-3.25°
4	**2a**	$HSiPhCl_2$	50 °C, 12 h	91 (**1b**)	17 (*S*)	-
5	**2a**[d]	$HSiCl_3$	80 °C, 12 h	-	-	-
6	**2b**	$HSiPh_2F$	20 °C, 3 h	92 (**1a**)	9 (*R*)	-
7	**2b**	$HSiPhF_2$	20 °C, 3 h	91 (**1b**)	29 (*R*)	+3.26°
8	**2b**	$HSiPh_2Cl$	20 °C, 3 h	94 (**1a**)	56 (*R*)	+5.36°
9	**2b**	$HSiPhCl_2$	20 °C, 3 h	97 (**1b**)	31 (*R*)	-
10	**2b**[e]	$HSiCl_3$	80 °C, 12 h	-	-	-

[a] Reactions were carried out with hydrosilane (5.0 mmol) and (*E*)-1-phenyl-1,3-butadiene (4.5 mmol) in the presence of $(\eta^3\text{-}C_3H_5PdCl)_2$ (1.5×10^{-2} mmol) and **2** (3.0×10^{-2} mmol). [b] Isolated yield. [c] (*c* 0.89-1.12, $CHCl_3$). [d] Inseparable mixture of regio- and stereoisomers was obtained. [e] A 2.5 : 1 mixture of (*Z*)-1-phenyl-1-trichlorolsilyl-1,3-butadiene ((*R*), 15% ee) and (*E*)-1-phenyl-3-trichlorosilyl-1-butene was obtained in 74% yield.

REFERENCES AND NOTES

1. (a) Hatanaka, Y.; Goda, K.; Hiyama, T. *Tetrahedron Lett.* **1994**, *35*, 1279. (b) Hayashi, T.; Matsumoto, Y.; Itoh, Y. *Organometallics*, **1987**, *6*, 884, and references cited therein.
2. (a) Hayashi, T.; Kabeta, K.; Yamamoto,T.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 5661. (b) Hayashi, T.; Kabeta, K. *Ibid.* **1985**, *26*, 3023. (c) Hayashi, T.; Matsumoto, Y.; Morikawa, I.; Ito, Y. *Tetrahedron Asymm.* **1990**, *1*, 151.
3. (a) Kurz, L.; Lee, G.; Morgans, Jr., D.; Waldyke, M. J.; Wars, T. *Tetrahedron Lett.* **1990**, *31*, 6321. (b) Uozumi, Y.; Tanahashi, A.; Lee, S. L.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945. (c) For asymmetric reactions catalyzed by a palladium complex bearing MOP as a chiral ligand, see: Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y. *J. Am. Chem. Soc.*, **1994**, *116*, 775, and references cited therein.
4. This work is presented in part at the 63rd Anniversary Meeting of the Chemical Society of Japan, Tokyo, April, 1992; 1F243.
5. To determine the absolute configuration, **1** was converted into known (*Z*)-1-phenyl-2-buten-1-ol according to the literature procedure: see ref 2c.
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