Palladium-catalyzed Asymmetric Hydrosilylation of Styrene and Its Derivatives with Chiral Phosphoramidite Ligands Containing Chiral Ferrocenyl Amine

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Asymmetric hydrosilylation was one of the most effective methods, which provided optically active organosilanes as a synthetically useful intermediate in organic synthesis.¹ One useful transformation is the Tamao–Fleming oxidation, which is an oxidation reaction of carbon–silicone bond to afford optically active alcohols with retention of configuration.² Palladium–monophosphorus ligand complex is the well-known catalysts in asymmetric hydrosilylation of olefins. Among various types of monophosphines, the monodentate phosphine (MOP)-type ligands were known as a highly reactive and enantioselective ligands.³ Ferrocene-based monophosphine ligands such as L1 were also highly effective ligands in asymmetric hydrosilylation of olefins (Figure 1).⁴

Recently, chiral phosphoramidite ligands which were easily prepared from readily available compounds with a good stability⁵ were applied to asymmetric hydrosilylation of styrene and its derivatives.⁶ As well as the Feringa ligand (L2),^{6a} phosphoramidites which had 1,1'spirobiindane backbone^{6b} or BINOL backbone with unsymmetric secondary amines^{6c} demonstrated that these ligands were highly efficient for the Pd-catalyzed asymmetric hydrosilylation of styrenes. Chiral phosphoramidite ligands (L3a) derived from bis((R)-1-ferrocenylethyl)amine, introduced by Zheng and co-workers, were used in the Cucatalyzed asymmetric 1,4-conjugate addition.7 Thus, we attempted to prepare whole diastereomers of the ferrocenyl amines and to prepare all the phosphoramidite ligands from (S)-BINOL and these diastereomeric ferrocenyl amines in order to evaluate their utility in asymmetric hydrosilylation of styrenes as a chiral ligand, focusing on the effect of the diastereomeric ferrocenyl amino group on the ligands in



their enantioselectivity. In this context, we synthesized all the diastereomeric phosphoramidites from (*S*)-BINOL and diastereomeric bis(1-ferrocenylethyl)amines. Two racemic (*R*,*R*)- and (*S*,*S*)-4 and one *meso* (*R*,*S*)-4 were obtained by the substitution reaction between the appropriate ammonium salt 2 and the primary amine 3, respectively, starting from each of enantiomerically pure *N*,*N*-dimethylaminoethylferrocene (1).^{7,8} Diastereomeric phosphoramidite ligands L3 were easily prepared from (*S*)-BINOL, bis(1-ferrocenylethyl)amines 4, and PCl₃ in the presence of trimethylamine (Scheme 1).

With these phosphoramidite ligands in hands, we examined the reactivity and enantioselectivity of the hydrosilylation of styrene (5a) using these diastereomeric ferrocenyl phosphoramidite ligands (Table 1). The catalytic reactions were performed without solvent with 1.0 mol % of palladium catalysts generated in situ by mixing $[PdCl(\pi-C_3H_5)]_2$ and L3 (Pd/P = 1/2). The reactions proceeded smoothly at 20° C in 20 h to give optically active 1-phenyl-1-(trichlorosilyl)ethane (6a). After Tamao-Fleming oxidation, enantioselectivities of the hydrosilylation were deduced from enantiomeric excess of 1-phenylethan-1-ol (7a). It was found that (S_a, R_c, R_c) -L3a, which had the same absolute configuration with Feringa ligand (L2), showed the highest enantioselectivity among the ligands we examined (entry 1). Employment of (S_a, S_c, S_c) -L3b as a chiral ligand resulted in a low reactivity and enantioselectivity. Interestingly, (S_a, R_c, S_c) -L3c, which had mesosecondary amino-moiety, showed higher enantioselectivity than (S_a, S_c, S_c) -L3b (entries 2 and 3). In our previous study of asymmetric hydrosilylation of styrenes,⁹ we proved that phenyl substituents at the 3,3'-positions of the binaphthyl were effective to increase enantioselectivity of the reaction, whereas (S_a, R_c, R_c) -L3d, which was a modified ligand of (S_a, R_c, R_c) -L3a, gave negative effects on enantioselectivity with the opposite absolute configuration of the product (entry 4).

Next, we also examined asymmetric hydrosilylation of styrene derivatives with the ligand **L3a**, which showed the highest enantioselectivity for styrene in this study. The hydrosilylation of 4-methylstyrene (5b) led to the (R)-products in excellent yield and moderate enantioselectivity (entry 5) and excellent enantioselectivity of 97% ee was



Scheme 1. Synthesis of chiral ferrocenyl secondary amines and phosphoramidite ligands.

Table 1. Asymmetric hydrosilylation of styrenes using L3.^a



 $(S_{a^{\prime}}R_{c^{\prime}}R_{c})\text{-}\textbf{L3d}$

Entry	Ligands	Substrate	R	$\operatorname{Yield}^{b}(\%)$	$\% ee^c$
1	L3a	5a	Н	85	91 (<i>R</i>)
2	L3b	5a	Н	41	62 (<i>R</i>)
3	L3c	5a	Н	85	73 (<i>R</i>)
4	L3d	5a	Н	93	68 (S)
5	L3a	5b	4-CH ₃	97	72 (<i>R</i>)
6	L3a	5c	2-CH ₃	96	97 (R)
7^d	L3a	5d	4-MeO	99	91 (<i>R</i>)
8	L3a	5e	4-Cl	91	91 (<i>R</i>)

^{*a*} Hydrosilylation was performed with 2.0 mmol of **5** at 20 °C in 20 h. The catalyst was generated *in situ* by mixing $[PdCl(\pi-C_3H_5)]_2$ and **L3**. The initial ratio of **5**/HSiCl₃/Pd/L**3** was 1.0/1.2/0.010/0.020.

 b Isolated yield of **6** by bulb-to-bulb distillation.

^c Determined by HPLC analyses of **7** with a chiral stationary column (Daicel Chiralpak OD-H, OB-H and AD-H).

^d Reaction was completed within 1 h.

obtained in the reaction of 2-methylstyrene (5c) (entry 6). We found that the reactivities and enantioselectivities were good enough for 4-methoxystyrene and 4-chlorostyrene (entries 7 and 8). Notably, the hydrosilylation of 4-methoxystyrene showed a high catalytic activity. The reaction was completed within 1 h at 20° C.

In summary, it is demonstrated that a palladium catalyst coordinating with phosphoramidite ligand (S_a, R_c, R_c) -L3a from (S)-BINOL and chiral bis((R)-1-ferrocenylethyl) amine shows a high catalytic activity and enantioselectivity up to 97% ee in asymmetric hydrosilylation of styrene and its derivatives. The hydrosilylation of various olefin substrates using these ligands is in progress.

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Supporting Information. Experimental details and analytical data are available in the online version of this article.

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