Modification of Chiral Monodentate Phosphine (MOP) Ligands for Palladium-Catalyzed Asymmetric Hydrosilylation of Styrenes

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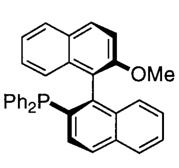
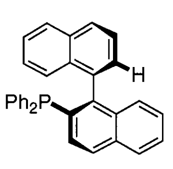
In the palladium-catalyzed asymmetric hydrosilylation of styrene with trichlorosilane, several chiral monophosphine ligands, (*R*)-2-diarylphosphino-1,1'-binaphthyls (**2**), were examined for their enantioselectivity. The highest enantioselectivity was observed in the reaction with (*R*)-2-bis[3,5-bis-(trifluoromethyl)phenyl]phosphino-1,1'-binaphthyl (**2g**) , which gave (*S*)-1-phenylethanol of 98% ee after oxidation of the hydrosilylation product.

Catalytic asymmetric hydrosilylation of alkenes has been recognized to be one of the most useful methods for the asymmetric transformation of prochiral alkenes into optically active alcohols.[1] We have previously reported that the asymmetric hydrosilylation of simple terminal alkenes such as 1-octene[2] and cyclic alkenes such as norbornene[3] is efficiently catalyzed by a palladium complex coordinated with 2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl (MeO-MOP (**1**))[4] and that 2-diphenylphosphino-1,1'-binaphthyl (H-MOP (**2a**)) is more enantioselective than MeO-MOP for the hydrosilylation of styrene derivatives.[5,6] However, unfortunately, the enantioselectivity with H-MOP was still not high enough, especially for the styrene derivatives containing electron-donating groups on the phenyl ring. Thus, for example, hydrosilylation of 4-methylstyrene and 4-methoxystyrene with trichlorosilane in the presence of palladium/H-MOP catalyst gave 1-(4-methylphenyl)ethanol of 89% ee and 1-(4-methoxyphenyl)ethanol of 61% ee, respectively, while the reaction of styrene gave 1-phenylethanol of 93% ee.[6] We have further modified H-MOP ligand on the diphenylphosphino group and found that introduction of bis[3,5-bis(trifluoromethyl)phenyl]phosphino group greatly enhances both the enantioselectivity and catalytic activity in the palladium-catalyzed asymmetric hydrosilylation of styrene derivatives. Here we report the preparation of (*R*)-2-bis[3,5-bis(trifluoromethyl)-phenyl]phosphino-1,1'-binaphthyl (**2g**) and its use for the hydrosilylation of styrene derivatives.

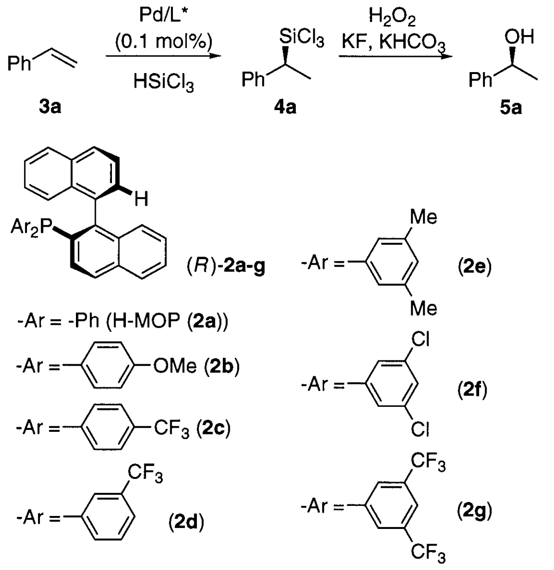


(*S*)-MeO-MOP (**1**)



(*R*)-H-MOP (**2a**)

First, H-MOP ligand (**2a**) was modified on the diphenylphosphino group by introduction of methoxy group or trifluoromethyl group on the phenyl ring, and these substituted H-MOP ligands were examined for their enantioselectivity in the palladium-catalyzed asymmetric hydrosilylation of styrene (**3a**) with trichlorosilane (Scheme 1). The hydrosilylation was carried out at 0 °C without solvent in the presence of 0.1 mol% of the palladium catalyst generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ with two equiv (to palladium) of the H-MOP ligand. The hydrosilylation product, 1-trichlorosilyl-1-phenylethane (**4a**) was oxidized into 1-phenylethanol (**5a**) with hydrogen peroxide in the presence of potassium fluoride, which is known to proceed with retention of configuration at the stereogenic carbon center.[7] The enantiomeric purity of **5a** was determined by HPLC analysis with a chiral stationary phase column (Table 1). It was found that the enantioselectivity is not strongly dependent on the electron-withdrawing or electron-donating characters of the *para*-substituents, H-MOP(*p*-OMe) (**2b**) and H-MOP(*p*-CF_3) (**2c**) giving (*S*)-**5a** of 92% ee (entry 2) and 93% ee (entry 3), respectively. These values are almost the same as that observed with unsubstituted H-MOP (**2a**) (entry 1). On the other hand, higher enantioselectivity (95% ee) was observed with H-MOP(*m*-CF_3) (**2d**) (entry 4). Based on the higher selectivity observed with the *meta*-substitution, three H-MOP ligands, H-MOP(*m,m*-2Me) (**2e**), H-MOP(*m,m*-2Cl) (**2f**), and H-MOP(*m,m*-2CF_3) (**2g**), were also prepared, all of which are disubstituted at *meta,meta*-positions. Of the three ligands, bis-trifluoromethylated ligand **2g** was found to be most effective ligand giving (*S*)-**5a** of 97% ee (entry 7). In addition to the high enantioselectivity, the reaction with **2g** is much faster than that with other ligands. The reaction in the presence of the palladium/**2g** catalyst was so exothermic that the reaction temperature is difficult to be kept 0 °C under the standard reaction conditions where no solvents were used. The reaction diluted with benzene (1.0 M solution) in the presence of 0.1 mol% of the palladium/**2g** catalyst was completed in 1 h at 0 °C (entry 7).



Scheme 1.

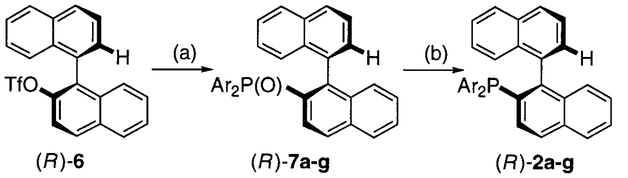
Table 1. Asymmetric hydrosilylation of styrene (**3a**) with trichlorosilane catalyzed by palladium complexes of (*R*)-H-MOP and its derivatives **2a-g**[a]

Entry	Ligand (Ar)	Temp /°C	Time /h	Yield /%[b] of **4a**	% ee[c] (config)[d]
1	C_6H_5 (**2a**)	0	12	100	93 (*S*)
2	4-$MeOC_6H_4$ (**2b**)	0	24	89	92 (*S*)
3	4-$CF_3C_6H_4$ (**2c**)	0	11	92	93 (*S*)
4	3-$CF_3C_6H_4$ (**2d**)	0	15	81	95 (*S*)
5	3,5-$Me_2C_6H_3$ (**2e**)	0	16	95	92 (*S*)
6	3,5-$Cl_2C_6H_3$ (**2f**)	0	20	89	94 (*S*)
7[e]	3,5-$(CF_3)_2C_6H_3$ (**2g**)	0	1	93	97 (*S*)
8	3,5-$(CF_3)_2C_6H_3$ (**2g**)	–20	24	85	98 (*S*)

[a] The hydrosilylation was carried out without solvent unless otherwise noted. The catalyst was generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and a chiral phosphine ligand **2**. The initial ratio of styrene/$HSiCl_3$/Pd/P is 1/1.2/0.001/0.002. [b] Isolated yield by bulb-to-bulb distillation. [c] Determined by HPLC analysis of (3,5-dinitrophenyl)carbamate ester of alcohol **5a** with a chiral stationary phase column (Sumichiral OA-4700, hexane/dichloroethane/ethanol = 50/15/1). [d] Determined by optical rotation of **5a**. For entry 8, $[\alpha]_D^{22}$ –48.8 (*c* 1.61, dichloromethane). [e] In benzene (1.0 M solution).

Higher enantioselectivity (98% ee) was observed in the reaction carried out at –20 °C (entry 8). The 98% ee observed here is by far the highest of the enantioselectivities reported for asymmetric hydrosilylation of styrene.[8]

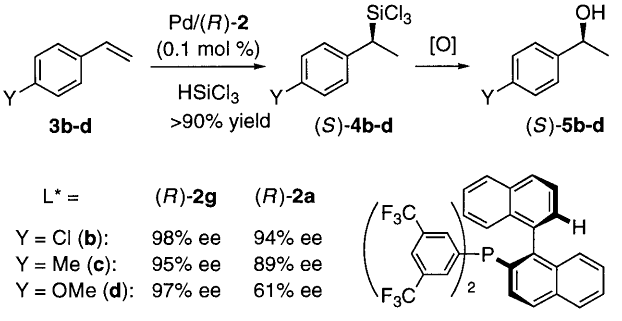
The H-MOP ligands **2** that contain substituted diarylphosphino groups at 2-position on the 1,1'-binaphthyl skeleton were prepared[9] starting from (*R*)-2-trifluoromethanesulfonyloxy-1,1'-binaphthyl (**6**)[4] (Scheme 2). Diarylphosphinyl groups were introduced at the 2-position by the palladium-catalyzed cross-coupling type reaction[2,4,10] and the phosphine oxide was reduced with trichlorosilane and triethylamine according to the reported procedures.[4]



(a) HP(O)Ar_2, $Pd(OAc)_2$, dppb, *i*-Pr_2NEt, DMSO, 100 °C, 24 h. 61% (**7b**), 65% (**7c**), 79% (**7d**), 97% (**7e**), 64% (**7f**), 75% (**7g**).
(b) $HSiCl_3$, Et_3N, PhMe, reflux, 15 h. 91% (**2b**), 80% (**2c**), 93% (**2d**), 90% (**2e**), 74% (**2f**), 72% (**2g**).

Scheme 2.

The high efficiency of (*R*)-H-MOP(*m*,*m*-$2CF_3$) (**2g**) was also observed in the asymmetric hydrosilylation of styrene derivatives substituted on the phenyl ring **3b–3d** (Scheme 3). The regioselectivity in forming benzylic silanes was always perfect, as is usually observed in the palladium-catalyzed hydrosilylation of styrene derivatives.[6,8] The enantioselectivity is generally very high with H-MOP(*m*,*m*-$2CF_3$) (**2g**) irrespective of the electron-withdrawing or electron-donating characters of the substituents on the phenyl, ranging between 95% and 98% ee. Although the difference in enantioselectivity between unsubstituted H-MOP (**2a**) and H-MOP(*m*,*m*-$2CF_3$) (**2g**) is not very large for the *p*-chlorostyrene (**3b**), the enantioselectivity was greatly improved for the styrenes substituted with electron-donating groups, methyl (**3c**) and methoxy (**3d**).



Scheme 3.

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9 Specific rotations ($[\alpha]_D^{20}$ (*c* 0.8–1.0 in $CHCl_3$)) of (*R*)-**2** are as follows: –91.2° (**2b**). –69.9° (**2c**). –53.6° (**2d**). –52.7° (**2e**). –38.3° (**2f**). –22.2° (**2g**).

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