Asymmetric Hydrosilylation of Styrenes Catalyzed by Palladium−MOP Complexes: Ligand Modification and Mechanistic Studies

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In the palladium-catalyzed asymmetric hydrosilylation of styrene (**3a**) with trichlorosilane, several chiral monophosphine ligands, (*R*)-2-diarylphosphino-1,1′-binaphthyls (**2a**−**g**), 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 (**5a**) of 98% ee after oxidation of the hydrosilylation product, 1-phenyl-1-(trichlorosilyl)ethane (**4a**). The palladium complex of **2g** also efficiently catalyzed the asymmetric hydrosilylation of substituted styrenes on the phenyl ring or at the β position to give the corresponding chiral benzylic alcohols of over 96% ee. Deuterium-labeling studies on the hydrosilylation of regiospecifically deuterated styrene revealed that β-hydrogen elimination from 1-phenylethyl(silyl)palladium intermediate is very fast compared with reductive elimination giving hydrosilylation product when ligand **2g** is used. The reaction of *o*-allylstyrene (**9**) with trichlorosilane catalyzed by (*R*)-**2g**/Pd gave (1*S*,2*R*)-1-methyl-2-(trichlorosilylmethyl)indan (**10**) (91% ee) and (*S*)-1-(2-(propenyl)phenyl)-1-trichlorosilylethanes (**11a** and **11b**) (95% ee). On the basis of their opposite configurations at the benzylic position, a rationale for the high enantioselectivity of ligand **2g** is proposed.

Introduction

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 the preparation of a series of enantiomerically pure monophosphine ligands, whose chirality is due to 1,1′-binaphthyl axial chirality,[2,3] and their use as chiral ligands for transition metal-catalyzed asymmetric reactions[4] including palladium-catalyzed asymmetric hydrosilylation of prochiral alkenes.[5,6] A representative of the axially chiral monophosphine ligands is 2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl (MeO-MOP (**1**)), which has been demonstrated to be an effective chiral ligand for the palladium-catalyzed asymmetric hydrosilylation of simple terminal alkenes such as 1-octene[2,5] with trichlorosilane and that of cyclic alkenes such as norbornene[6] giving the corresponding secondary alkyl alcohols of over 90% enantioselectivity. Recently, we found that MeO-MOP is not as effective for the asymmetric hydrosilylation of styrene derivatives as for that of simple terminal alkenes or cyclic alkenes.[7] We modified the MOP ligands by replacement of the methoxy group at the 2′-position by other substituents and found that 2-diphenylphosphino-1,1′-binaphthyl (H-MOP (**2a**)) is much more enantioselective than MeO-MOP for the reaction of styrene derivatives.[8,9] However, unfortunately, the enantioselectivity 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 catalyst coordinated with H-MOP 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.[8] We have further modified H-MOP ligand on the diphenylphosphino group and found that

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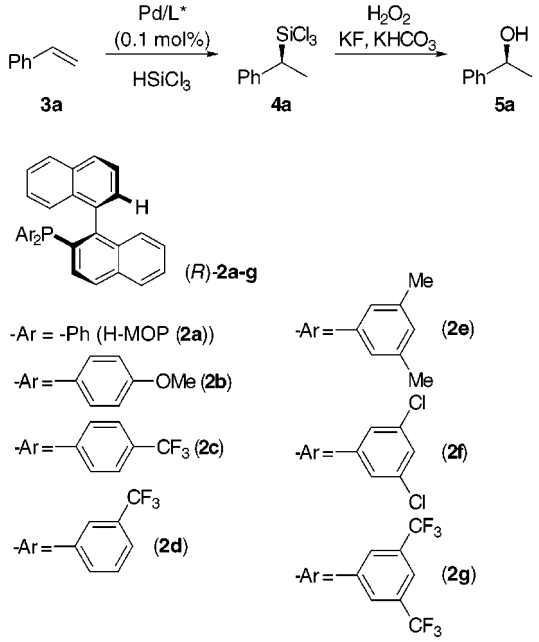
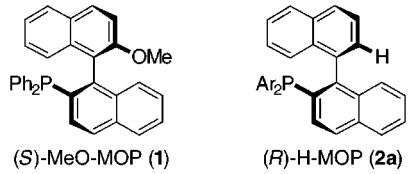
Scheme 1



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**), its use for the hydrosilylation of styrene derivatives,[10] and some mechanistic aspects of the palladium-catalyzed asymmetric hydrosilylation.



Results and Discussion

We have previously modified the MOP ligands by replacement of the methoxy group in MeO-MOP (**1**) by some substituents including hydrogen and alkyl groups.[3] In the present studies, H-MOP ligand (**2a**) was modified on the diphenylphosphino group by introduction of a methoxy group or a 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 2 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.[11] 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). On the basis of 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 the meta,meta positions. Of the three ligands, bis-trifluoromethylated ligand **2g** was found to be the 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 at 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). 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.[7−9]

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)	*T* (°C)	time (h)	yield[b] (%) of **4a**	% ee[c] (confign)[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, $[\alpha]^{22}_D$ −48.8 (*c* 1.61, dichloromethane). [e] In benzene (1.0 M solution).

The H-MOP ligands **2** that contain substituted diarylphosphino groups at the 2-position on the 1,1′-binaphthyl skeleton were prepared starting from (*R*)-2-trifluoromethanesulfonyloxy-1,1′-binaphthyl (**6**)[3] (Scheme 2). Diarylphosphinyl groups were introduced at the 2-position by the palladium-catalyzed cross-coupling type reaction,[2,3,12] and the phosphine oxide was reduced with trichlorosilane and triethylamine according to the reported procedures.[3]

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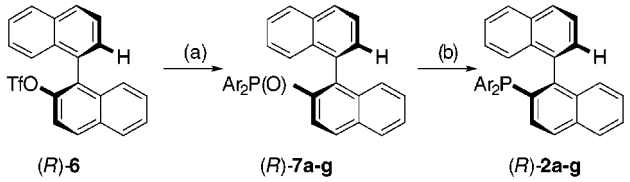
Table 2. Asymmetric Hydrosilylation of Styrenes 3 with Trichlorosilane Catalyzed by Palladium-(*R*)-2g[a]

entry		styrene ArCH=CHR **3** Ar	R	*T* (°C)	time (h)	yield[b] (%) of **4**	% ee[c] (abs confign)[d]	optical rotation value of alcohol **5**
1[e]	**3a**	Ph	H	0	1	93	97 (*S*) (93)	
2[f]	**3a**	Ph	H	−20	24	85	98 (*S*)	$[\alpha]^{22}_D$ −48.8 (*c* 1.61, CH_2Cl_2)
3	**3b**	2-MeC_6H_4	H	0	10	83	97 (*S*)	$[\alpha]^{21}_D$ −48.1 (*c* 1.76, EtOH)
4[f]	**3b**	2-MeC_6H_4	H	0	1	92	96 (*S*)	
5	**3c**	3-MeC_6H_4	H	0	4	91	97 (*S*)	$[\alpha]^{21}_D$ −36.5 (*c* 1.97, EtOH)
6	**3d**	4-MeC_6H_4	H	0	0.5	90	95 (*S*) (89)	$[\alpha]^{21}_D$ −40.8 (*c* 1.54, EtOH)
7	**3e**	2-ClC_6H_4	H	0	15	88	91 (*S*)	$[\alpha]^{20}_D$ −48.0 (*c* 1.65, $CHCl_3$)
8	**3f**	3-ClC_6H_4	H	0	4	93	96 (*S*) (95)	$[\alpha]^{20}_D$ −41.0 (*c* 1.41, $CHCl_3$)
9	**3g**	4-ClC_6H_4	H	0	4	92	98 (*S*) (94)	$[\alpha]^{21}_D$ −48.5 (*c* 2.11, Et_2O)
10[f]	**3h**	3-BrC_6H_4	H	0	6 days	90	94 (*S*)	$[\alpha]^{20}_D$ −32.2 (*c* 2.50, $CHCl_3$)
11	**3i**	4-BrC_6H_4	H	−10	15	95	97 (*S*)	$[\alpha]^{20}_D$ −35.1 (*c* 1.11, $CHCl_3$)
12	**3j**	4-$MeOC_6H_4$	H	−10	20	90	97 (*S*) (61)	$[\alpha]^{20}_D$ −41.0 (*c* 1.41, $CHCl_3$)
13	**3k**	3-$NO_2C_6H_4$	H	0	6 days	89	98 (*S*)	$[\alpha]^{20}_D$ −36.6 (*c* 1.34, $CHCl_3$)
14	**3l**	H	Me	0	48	81	98 (*S*) (89)	$[\alpha]^{20}_D$ −50.0 (*c* 1.23, $CHCl_3$)
15[f]	**3m**	H	CH_2OMe	0	30	85	97	$[\alpha]^{20}_D$ −35.8 (*c* 1.62, *c*-C_5H_{10})
16[f]	**3n**	H	CH_2OCH_2Ph	20	16	87	97 (*S*)	$[\alpha]^{20}_D$ −37.4 (*c* 1.23, $CHCl_3$)

[a] The hydrosilylation was carried out in toluene (1.0 M solution) unless otherwise noted. The catalyst was generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and ligand (*R*)-**2g**. 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 esters of alcohols **5** with a chiral stationary-phase column(Sumichiral OA-4700 or 4100). The values shown in parentheses are enantiomeric purities of **5** obtained with H-MOP (**2a**). [d] Determined by measurement of the optical rotation of alcohol **5**. [e] In benzene (1.0 M solution). [f] The reaction was carried out without solvent.

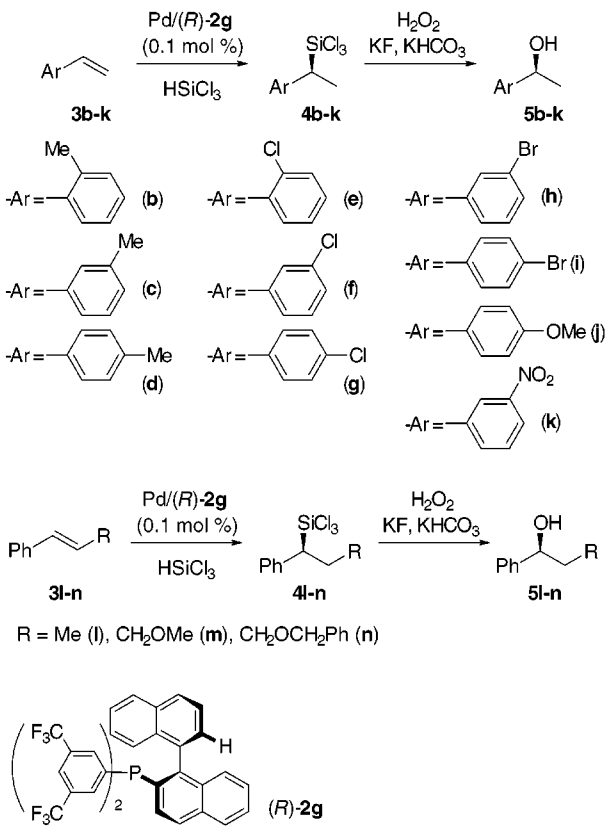
Scheme 2[a]



[a] Key: (a) $HP(O)Ar_2$, $Pd(OAc)_2$, dppb, *i*-Pr_2NEt, DMSO, 100 °C, 24 h; (b) $HSiCl_3$, Et_3N, PhMe, reflux, 15 h.

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**−**k** and *β*-alkyl-substituted styrenes **3l**−**n** (Scheme 3). The results are summarized in Table 2 which also includes some data obtained with H-MOP (**2a**) ligand for comparison. The regioselectivity in forming benzylic silanes was always perfect, as is usually observed in the palladium-catalyzed hydrosilylation of styrene derivatives.[8,9] 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 94% and 98% ee, mostly over 96% ee, except for one example (entry 7). Styrenes substituted with methyl (**3b-3d**), chloro (**3f**,**3g**), bromo (**3h,3i**), methoxy (**3j**), or nitro groups (**3k**) successfully underwent the asymmetric hydrosilylation to give the corresponding benzylic alcohols of high enantiomeric purity (entries 1−13). Although the difference in enantioselectivity between unsubstituted H-MOP (**2a**) and H-MOP(*m*,*m*-$2CF_3$) (**2g**) is not very large for the styrenes substituted with chloride on the phenyl (entries 8 and 9), the enantioselectivity was greatly improved for the styrenes substituted with electron-donating groups, methyl and methoxy (entries 6 and 12). The asymmetric hydrosilylation of *β*-alkyl-substituted styrenes, *β*-methylstyrene (**3l**) and cinnamyl ethers (**3m**, **3n**) was also successful with the (*R*)-**2g** ligand to give the corresponding benzylic alcohols of over 97% ee (entries 14−16). All the benzylic alcohols **5a**−**n** obtained here with (*R*)-**2g** have the (*S*) configuration, indicating that the addition of hydrosilane to styrenes always took place on α-*si* face of the styrene double bond irrespective of the substitution patterns on styrene.

Scheme 3



Hydrosilylation of styrene with trichlorosilane catalyzed by palladium complexes coordinated with a tertiary phosphine ligand has been shown[13] to proceed through the catalytic cycle proposed by Chalk and Harrod,[14] which involves hydropalladation of an olefin on hydrido(silyl)(olefin)palladium **B** generating alkyl(silyl)palladium species **C** and reductive elimination of the alkyl and silyl fragments from **C** forming a hydrosilylation product. Generally, intermediates **B** and **C** are in equilibrium by the reversible processes, hydropalladation (olefin inser-

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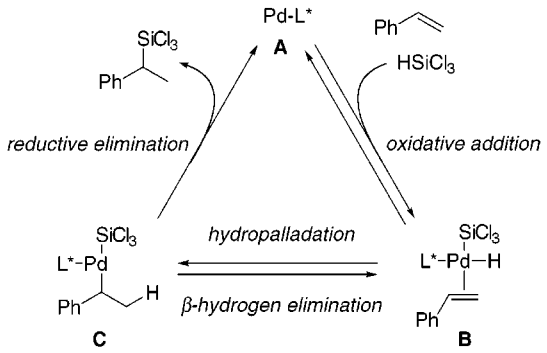
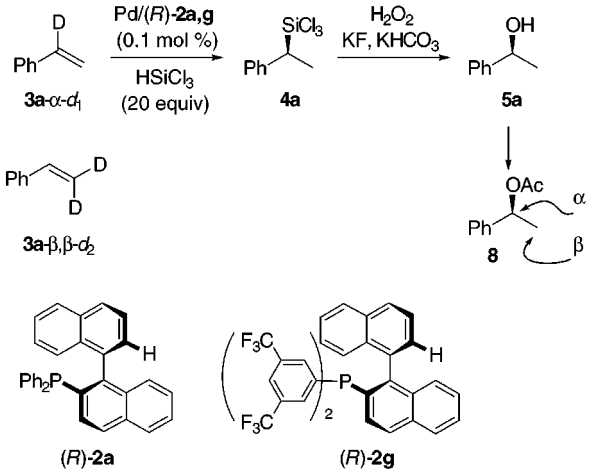
Scheme 4



Scheme 5



tion to hydridopalladium) and β-hydrogen elimination (Scheme 4). We studied the palladium-catalyzed hydrosilylation of regiospecifically deuterated styrenes (Scheme 5), which gave us significant information on the regioselectivity in forming 1-phenylethylpalladium intermediate and the relative rates of hydropalladation, β-hydrogen elimination, and reductive elimination in the catalytic cycle.

Hydrosilylation of **3a**-α-d_1 (PhCD=CH_2) with a large excess (20 equiv) of trichlorosilane in the presence of 0.1 mol % of the palladium−**2g** catalyst gave a quantitative yield of (*S*)-1-phenyl-1-trichlorosilylethane (**4a**) (97% ee) where all deuterium remained at the original α-position (entry 1 in Table 3). The deuterium content was determined by ^{1}H and ^{2}H NMR analyses of 1-phenylethyl acetate (**8**) obtained by the oxidation of **4a** followed by acetylation of the resulting alcohol **5a**. The retention of all the deuterium in the styrene indicates that the hydrosilylation does not involve 2-phenylethylpalladium intermediate **D** in the catalytic cycle (Scheme 6). The reason 2-phenylethylsilane is not produced in the present hydrosilylation is not that the reductive elimination from **D** is slow compared with β-hydrogen elimination from **D** but that hydropalladation takes place regiospecifically in forming 1-phenylethylpalladium intermediate **C**. It has been proposed that the preferential fromation of **C** is ascribed to the contribution of a π-benzylpalladium species **C′**.[9a,g]

The hydrosilylation of **3a**-β,β-d_2 (PhCH=CD_2) brought about a considerable loss of the deuterium atoms, demonstrating that the 1-phenylethylpalladium intermediate **C** undergoes β-hydrogen elimination to some extent before the reductive elimination giving the hydrosilylation product **4a**. Thus, abstraction of β-deuterium from 1-phenyl-2,2-dideuterioethylpalladium **C1** forms silyl(deuterio)palladium **B2** where styrene lost one of the two deuterium atoms on the β-position. Substitution of deuteriosilane with hydrosilane followed by hydropalladation of β-d_1-styrene on **B2′** and reductive elimination from **C2** gives the hydrosilylation product containing only one deuterium atom. Further β-deuterium elimination from **C2** results in formation of the hydrosilylation product with no deuteriums by way of **B3**.

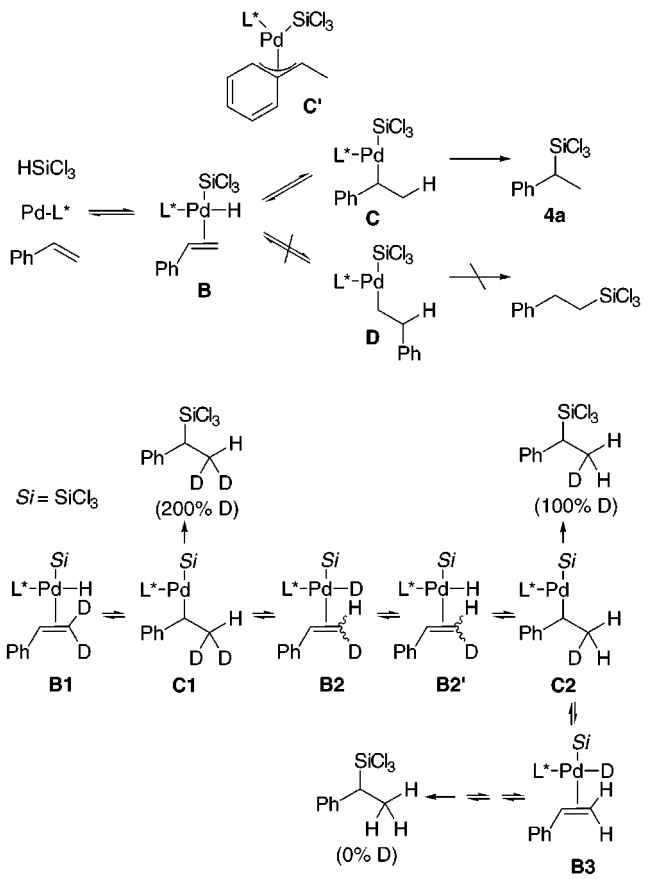
It is significant that the amount of loss of deuterium is dependent on the phosphine ligand used. In this hydrosilylation, 20 equiv (to PhCH=CD_2) of hydrosilane $HSiCl_3$ was used. It follows that the ratio of deuterium

Table 3. Asymmetric Hydrosilylation of Deuterium-Labeled Styrenes 3a-α-d_1 and 3a-β,β-d_2 with Trichlorosilane Catalyzed by Palladium Complexes of (*R*)-2a and (*R*)-2g[a]

entry	styrene	ligand	time (h)	yield (%)[b] of **4a**	D atom %[c] at α and β in **8**	% ee[d] (confign)
1	**3a**-α-d_1	(*R*)-**2g**	1	94	>99, <1	97 (*S*)
2	**3a**-β,β-d_2	(*R*)-**2g**	1	89	<1, 40	97 (*S*)
3	**3a**-β,β-d_2	(*R*)-**2a**	36	99	<1, 140	94 (*S*)

[a] The hydrosilylation was carried out at 0 °C with 20 equiv of trichlorosilane in the presence of 0.1 mol % of the palladium catalyst generated in situ by mixing [PdCl(π-C_3H_5)]$_2$ and a chiral phosphine ligand. The ratio of Pd/P is 1:2. [b] Determined by GC and NMR analyses. [c] Determined by ^{1}H and ^{2}H NMR analyses of acetate **8** which was obtained by the oxidation of **2a** followed by acetylation. Integration of α and β hydrogens relative to acetyl methyl three hydrogens was used. One deuterium atom is described as 100. [d] 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).

Scheme 6

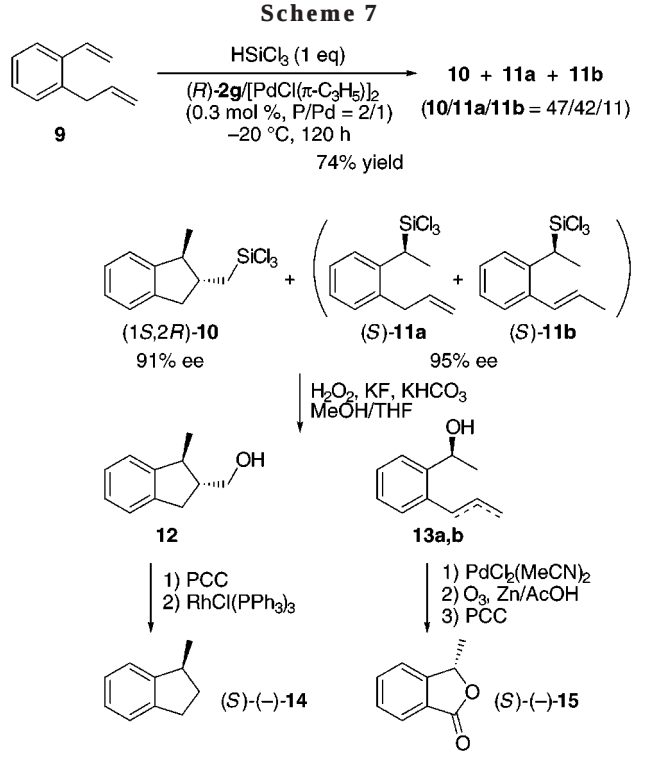


to hydrogen, which possibly participates in the hydro(deuterio)palladation and β-hydrogen (deuterium) elimination, is 2:20. Assuming that the reductive elimination takes place after complete deuterium−hydrogen scrambling, the deuterium content of the hydrosilylation product starting from $PhCH{=}CD_2$ is calculated to be 27% ($3 \times 2/(2 + 20)$). The 40% deuterium observed in **4a** with ligand **2g** (entry 2 in Table 3) is close to this value, indicating that the β-hydrogen elimination is very fast compared with the reductive elimination. In the reaction catalyzed by palladium−**2g** complex, which is the most enantioselective catalyst, the reductive elimination takes place after very fast equilibration between **B** and **C**. On the other hand, the β-hydrogen elimination is not so fast in the reaction with less enantioselective ligand **2a**, 140% (originally 200%) of deuterium remaining at the original β-position (entry 3). The much faster rate of β-hydrogen elimination than reductive elimination observed with ligand **2g** is related to the higher enantioselectivity of **2g** (vide infra). Studies on the relationship between the deuterium scrambling and enantioselectivity have been reported in nickel-catalyzed hydrocyanation of a styrene derivative, but less deuterium scrambling was observed with a catalyst of higher enantioselectivity in their system.[15]

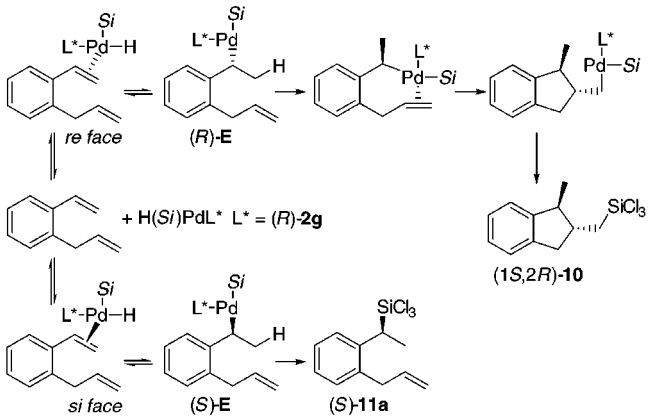
Reaction of *o*-allylstyrene (**9**) with trichlorosilane catalyzed by palladium complexes coordinated with **2a** and **2g** gave us further insight into the mechanism of the present asymmetric hydrosilylation.[16] The reaction of **9** in the presence of 0.3 mol % of the palladium-**2g** catalyst at −20 °C for 120 h gave 74% yield of the hydrosilylation product, which consists of *trans*-1-methyl-2-(trichlorosilylmethyl)indan (**10**), 1-(2-(2-propenyl)phenyl)-1-trichlorosilylethane (**11a**), and 1-(2-((*E*)-1-propenyl)phenyl)-1-trichlorosilylethane (**11b**) in a ratio of 47:42:11 (Scheme 7). Compounds **11a** and **11b** are the hydrosilylation products on the styrene double bond, isomerization of the 2-propenyl group into 1-propenyl being accompanied under the reaction conditions. The indan derivative **10** is formed by insertion of the 2-propenyl group into the palladium−carbon bond formed by the hydropalladation of styrene double bond.[13] It should be noted that **10** was not produced at all in the hydrosilylation catalyzed by a palladium complex of **2a** under otherwise the same reaction conditions, only **11** being produced.

The enantiomeric purities of hydrosilylation products **10**, **11a**, and **11b** obtained with ligand **2g** were determined to be 91%, 95%, and 95% ee, respectively, by GLC analysis using a chiral stationary phase column (Cyclodex β236M) of their trimethylsilyl derivatives prepared by treatment of the trichlorosilanes with an excess of methylmagnesium bromide. The absolute configurations were assigned by correlation with known compounds, 1-methylindan[17] (**14**) and 3-methylphthalide[18] (**15**). Thus, trichlorosilyl group in **10** was converted into hydroxy group by the hydrogen peroxide oxidation to give *trans*-1-methyl-2-(hydroxymethyl)indan (**12**). The primary alcohol was oxidized into aldehyde, and deformylation with

Scheme 7



Scheme 8



a stoichiometric amount of $RhCl(PPh_3)_3$ gave (*S*)-(−)-**14**. Oxidation of a mixture of isomers **11a** and **11b** into alcohols **13a** and **13b** followed by isomerization of olefinic double bond by treatment of the mixture of alcohols with $PdCl_2(MeCN)_2$ gave isomerically pure 1-(2-((*E*)-1-propenyl)phenyl)ethanol (**13b**). Ozonolysis of the double bond followed by oxidation of the resulting lactol gave lactone, (*S*)-(−)-**15**. Thus, the hydrosilylation products **10** and **11** were determined to have the absolute configuration of (1*S*,2*R*) and (*S*), respectively. The (*S*) configuration of **11** shows that it is formed by reductive elimination from (*S*)-alkylpalladium intermediate (*S*)-**E**, which is generated by hydropalladation of styrene double bond on its *si* face (Scheme 8). The enantioface selection is the same as that observed for the asymmetric hydrosilylation of styrene derivatives **3** including ortho-substituted styrenes **3b** and **3e** with (*R*)-**2g** ligand. Rather surprisingly, the cyclization product (1*S*,2*R*)-**10** is formed through (*R*)-alkylpalladium intermediate (*R*)-**E**, which is deduced by the (1*S*) configuration of **10**. Thus, the products **10** and **11** were formed from different diastereoisomeric intermediates coordinated with (*R*)-**2g** ligand. Consider-

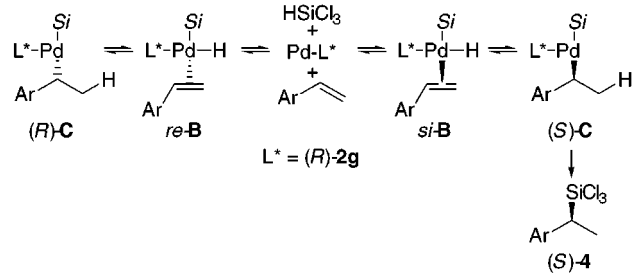
(15) Casalnuovo, L. A.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869.

(16) We have reported nonasymmetric version of the palladium-catalyzed hydrosilylation of *o*-allylstyrene (ref 13).

(17) Hansen, H.-J.; Sliwka, H.-R.; Hug, W. *Helv. Chim. Acta* **1979**, *62*, 1120.

(18) (a) Nagai, U.; Shishido, T.; Chiba, R.; Mitsuhashi, H. *Tetrahedron* **1965**, *21*, 1701. (b) Brown, H. C.; Wetherill, R. B. *Tetrahedron Lett.* **1996**, *37*, 2205.

Scheme 9



ing that the β-hydrogen elimination from alkylpalladium intermediate is fast compared to reductive elimination in the reaction with **2g** which was observed in the hydrosilylation of **3a**-β,β-d_2, two diastereomeric alkylpalladium intermediates (*S*)-**E** and (*R*)-**E** must be in a fast equilibration by way of π-olefin complexes. It is likely that one of the diastereomeric intermediates, that is (*S*)-**E**, is much more reactive than the other diastereomer (*R*)-**E** toward the reductive elimination giving **11** while (*R*)-**E** does not undergo the reductive elimination but undergoes insertion of the 2-propenyl double bond into the palladium−carbon bond giving cyclization product **10**. As mentioned above, the hydrosilylation of *o*-allylstyrene (**9**) by use of ligand **2a** does not give any cyclization product **10**. It is in good agreement with the relatively fast reductive elimination observed with ligand **2a** in the reaction of **3a**-β,β-d_2.

Conclusion

We have demonstrated that the (*R*)-H-MOP(*m*,*m*-2CF_3) (**2g**) ligand shows the highest enantioselectivity in the asymmetric hydrosilylation of styrene derivatives, and the difference between ligands **2a** and **2g** is that the β-hydrogen elimination from alkylpalladium intermediate is fast compared to reductive elimination in the reaction with **2g** and the β-hydrogen elimination is not so fast with **2a**. The higher enantioselectivity of **2g** is attributable to the fast β-hydrogen elimination from alkylpalladium intermediates coordinated with **2g** and highly selective reductive elimination from one of the diastereomeric intermediates (Scheme 9). The enantioface selectivity of styrene on coordination to the palladium bearing **2g** ligand is probably not so high as to give hydrosilylation product **4** of over 96% ee. The catalytic cycle involves both of the diastereomeric alkylpalladium intermediates (*S*)-**C** and (*R*)-**C** in a certain ratio, which are in a fast equilibrium by β-hydrogen elimination and hydropalladation processes. Reductive elimination takes place selectively from (*S*)-**C** to give hydrosilylation product (*S*)-**4**, and (*R*)-**C**, which is much less reactive toward reductive elimination, undergoes β-hydrogen elimination to turn back to (*S*)-**C** resulting in the formation of (*S*)-**4**. Questions why bistrifluoromethylated H-MOP ligand **2g** causes the fast β-hydrogen elimination resulting in high enantioselectivity and which characteristics of **2g** are responsible for it, electronic or steric, remain to be answered. We are currently trying to disclose the structure of palladium complexes coordinated with the H-MOP ligands.

Experimental Section

General Methods. All manipulations were carried out under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on JEOL JNM-AL400 spectorometer (400 MHz for ^{1}H NMR) or JEOL JNM LA500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C and 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^{1}H NMR, and to an external 85% H_3PO_4 standard for ^{31}P NMR. Residual chloroform (δ 77.0 for ^{13}C) was used as internal reference for ^{13}C NMR. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted.

Materials. (*R*)-2-(Trifluoromethanesulfonyloxy)-1,1′-binaphthyl (**6**) was prepared from (*R*)-(+)-2-hydroxy-1,1′-binaphthyl[19] by treatment with trifluoromethanesulfonic anhydride and pyridine in 1,2-dichloroethane according to the reported procedures.[3] Deuterated styrenes, **3a**-α-d_1 and **3a**-β,β-d_2,[20] [PdCl(π-C_3H_5)]$_2$,[21] and *o*-allylstyrene[22] (**9**) were prepared according to the reported procedures.

Preparation of H-MOP Ligands (*R*)-2a−g. (*R*)-2-Diphenylphosphino-1,1′-binaphthyl (**2a**) was prepared by the palladium-catalyzed diphenylphosphinylation[3,12] of (*R*)-2-(trifluoromethanesulfonyloxy)-1,1′-binaphthyl (**6**) with diphenylphosphine oxides followed by reduction of the resulting phosphine oxide (*R*)-**7a** with trichlorosilane and triethylamine according to the reported procedures.[3] In a similar manner, other H-MOP Ligands (*R*)-**2b**−**g** were prepared by use of the corresponding diarylphosphine oxides. A typical procedure shown below is for the preparation of (*R*)-2-bis(3,5-bis(trifluoromethyl)phenyl)-phosphino-1,1′-binaphthyl (**2g**).

(*R*)-2-Bis(3,5-bis(trifluoromethyl)phenyl)phosphino-1,1′-binaphthyl (2g). To a mixture of (*R*)-2-(trifluoromethanesulfonyloxy)-1,1′-binaphthyl (**6**) (365 mg, 0.908 mmol), bis(3,5-bis(trifluoromethyl)phenyl)phosphine oxide (879 mg, 1.85 mmol), palladium diacetate (104 mg, 0.464 mmol), and 1,4-bis(diphenylphosphino)butane (dppb, 195 mg, 0.458 mmol) were added dimethyl sulfoxide (4.2 mL) and *N*,*N*-diisopropylethylamine (0.80 mL), and the mixture was heated with stirring at 100 °C for 2.5 h. After being cooled to 50 °C, the mixture was concentrated under reduced pressure (0.1−0.2 mmHg). The residue was diluted with ethyl acetate, and the solution was washed with water (three times), dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/ethyl acetate =1/1) to give 497 mg (75% yield) of (*R*)-2-bis(3,5-bis(trifluoromethyl)phenyl)phosphinyl-1,1′-binaphthyl (**7g**) as white powder. (*R*)-**7g**: $[\alpha]^{20}_D$ +24.3 (*c* 1.15, $CHCl_3$); ^{1}H NMR δ 6.88 (d, J = 8.6 Hz, 1), 7.1−7.4 (m, 5H), 7.5−7.8 (m, 8H), 7.8−8.1 (m, 3H), 8.21 (d, J = 10.9 Hz, 2H); ^{13}C{^{1}H} NMR δ 122.4 (q, J_{C-F} = 273 Hz, CF_3), 122.7 (q, J_{C-F} = 273 Hz, CF_3), 124.4−145.9; ^{31}P{^{1}H} NMR δ 22.6 (s). Anal. Calcd for $C_{36}H_{19}OF_{12}P$: C, 59.50; H, 2.64. Found: C, 59.77; H, 2.91.

To a mixture of (*R*)-**7g** (253 mg, 0.348 mmol) and triethylamine (1.20 mL, 8.6 mmol) in toluene (6.0 mL) was added trichlorosilane (0.40 mL, 4.0 mmol) at 0 °C. The reaction mixture was stirred at 100 °C for 5 days. After being cooled to room temperature, the mixture was diluted with ether and a small amount of saturated aqueous sodium bicarbonate was added. The resulting suspension was filtered through Celite. The filtrate was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Chromatography on silica gel (hexane/ethyl acetate = 10/1) gave (178 mg, 72% yield) of (*R*)-**2g** as white powder: $[\alpha]^{20}_D$ −22.2 (*c* 0.77, $CHCl_3$); ^{1}H NMR δ 6.90 (d, J = 8.3 Hz, 1H), 7.12 (t, J = 8.3 Hz, 1H), 7.2−7.6 (m, 8H), 7.63 (d, J = 5.9 Hz, 2H), 7.70 (s, 1H), 7.9−8.0 (m, 6H); ^{13}C{^{1}H} NMR δ 122.9 (q, J_{C-F} = 273 Hz, CF_3), 123.0 (q, J_{C-F} = 273 Hz, CF_3), 122.9−146.7; ^{31}P{^{1}H} NMR δ −11.2 (s). Anal. Calcd for $C_{36}H_{19}F_{12}P$: C, 60.84; H, 2.70. Found: C, 60.86; H, 2.92.

(19) (a) Sasaki, H.; Irie, R.; Katsuki, T. *Synlett* **1993**, 3000. (b) Tamai, Y.; Nakano, T.; Koike, S.; Kawahara, K.; Miyano, S. *Chem. Lett.* **1989**, 1135. (c) Meyers, A. I.; Lutomski, K. A. *J. Am. Chem. Soc.* **1982**, *104*, 879.

(20) Schubert, W. M.; Lamm, B. *J. Am. Chem. Soc.* **1966**, *88*, 120.

(21) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B.*J. Am. Chem. Soc.* **1985**, *107*, 2033.

(22) (a) Garratt, P. J.; Vollhardt, K. P. C. *Synthesis* **1971**, 423. (b) Bestmann, H. J.; Kratzer, O. *Chem. Ber.* **1963**, *96*, 1899.

For phosphine oxides **7b**−**f** and phosphines **2b**−**f**, spectral and analytical data are shown below:

(*R*)-2-Bis(4-methoxyphenyl)phosphinyl-1,1′-binaphthyl (7b): 61% yield; $[\alpha]^{20}_D$ −54.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR δ 3.68 (s, 3H), 3.73 (s, 3H), 6.49 (d, J = 6.9 Hz, 2H), 6.56 (d, J = 6.9 Hz, 2H), 6.84 (d, J = 8.4 Hz 1H), 7.0−7.7 (m, 13H), 7.93 (d, J = 8.3 Hz, 1H), 7.99 (d, J = 7.8 Hz, 2H); ^{13}C{^{1}H} NMR δ 54.37, 55.49, 112.52, 113.59, 123.1−134.8, 143.39, 161.21; ^{31}P-{^{1}H} NMR δ 28.9 (s). Anal. Calcd for $C_{34}H_{27}O_3P$: C, 79.36; H, 5.29. Found: C, 79.16; H, 5.57.

(*R*)-2-Bis(4-trifluoromethylphenyl)phosphinyl-1,1′-binaphthyl (7c): 65% yield; $[\alpha]^{20}_D$ −3.8 (*c* 1.01, $CHCl_3$); ^{1}H NMR δ 6.91 (d, J = 8.3 Hz, 1H), 7.06 (d, J = 6.4 Hz, 2H), 7.12 (dd, J = 6.9, 8.3 Hz, 1H), 7.20 (d, J = 8.3 Hz, 1H), 7.2−7.8 (m, 14H), 7.95 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H); ^{13}C-{^{1}H} NMR δ 122.1−136.9, 144.59, 171.01; ^{31}P{^{1}H} NMR δ 26.2 (s). Anal. Calcd for $C_{34}H_{21}F_6OP$: C, 69.16; H, 3.58. Found: C, 69.46; H, 3.79.

(*R*)-2-Bis(3-trifluoromethylphenyl)phosphinyl-1,1′-binaphthyl (7d): 79% yield; $[\alpha]^{20}_D$ +8.98 (*c* 1.00, $CHCl_3$); ^{1}H NMR δ 6.87 (d, J = 8.9 Hz, 2H), 7.1−7.8 (m, 15H), 7.9−8.0 (m, 4H); ^{31}P{^{1}H} NMR δ 25.5 (s). Anal. Calcd for $C_{34}H_{21}OF_6P$: C, 69.14; H,3.59. Found: C, 68.89; H, 3.36.

(*R*)-2-Bis(3,5-dimethylphenyl)phosphinyl-1,1′-binaphthyl (7e): 97% yield; $[\alpha]^{20}_D$ −12.1 (*c* 1.01, $CHCl_3$); ^{1}H NMR δ 1.90 (s, 6H), 2.08 (s, 6H), 6.47 (s, 1H), 6.7−7.6 (m, 15H), 7.8−7.9 (m, 3H); ^{13}C{^{1}H} NMR δ 20.52, 21.14, 21.77, 123.8−133.3, 134.44, 134.54, 136.62, 136.71, 137.13, 137.26, 143.85; ^{31}P{^{1}H} NMR δ 28.5 (s). Anal. Calcd for $C_{36}H_{31}OP$: C, 84.68; H, 6.12. Found: C, 84.41; H, 6.47.

(*R*)-2-Bis(3,5-dichlorophenyl)phosphinyl-1,1′-binaphthyl (7f): 64% yield; $[\alpha]^{20}_D$ +26.5 (*c* 0.45, $CHCl_3$); ^{1}H NMR δ 6.84 (s, 2H), 6.90 (d, J = 8.6 Hz, 1H), 6.95 (dd, J = 2.0, 12.2 Hz, 1H), 7.2−7.8 (m, 13H), 7.98 (d, J = 8.3 Hz, 1H), 8.04 (dd, J = 2.6, 8.6 Hz, 1H); ^{31}P{^{1}H}NMR δ 23.8 (s). Anal. Calcd for $C_{32}H_{19}Cl_4PO$: C, 65.09; H, 3.25. Found: C, 64.84; H, 3.16.

(*R*)-2-Bis(4-methoxyphenyl)phosphino-1,1′-binaphthyl (2b); 91% yield; $[\alpha]^{20}_D$ −91.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR δ 3.72 (s, 3H), 3.77 (s, 3H), 6.72 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 6.8 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 7.1−7.4 (m, 13H), 7.84 (t, J = 8.8 Hz, 2H), 7.89 (dd, J = 7.3, 7.9 Hz, 2H); ^{13}C{^{1}H} NMR δ 55.13, 55.16 (OMe), 113.92, 123.9−137.4, 144.36, 159.87; ^{31}P{^{1}H} NMR δ −16.3(s). Anal. Calcd for $C_{34}H_{27}O_2P$: C, 81.91; H, 5.46. Found: C, 81.64; H, 5.70.

(*R*)-2-Bis(4-trifluoromethylphenyl)phosphino-1,1′-binaphthyl (2c): 80% yield; $[\alpha]^{20}_D$ −69.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR δ 6.97 (d, J = 8.6 Hz, 1H), 7.0−7.5 (m, 16H), 7.8−7.9 (m, 4H); ^{13}C{^{1}H} NMR δ 122.9−133.8, 136.9, 142.3, 146.1; ^{31}P-{^{1}H} NMR δ −13.3(s). Anal. Calcd for $C_{34}H_{21}F_6P$: C, 71.08; H, 3.68. Found: C, 70.87; H, 3.95.

(*R*)-2-Bis(3-trifluoromethylphenyl)phosphino-1,1′-binaphthyl (2d): 93% yield; $[\alpha]^{20}_D$ −53.6 (*c* 1.10, $CHCl_3$); ^{1}H NMR δ 7.04 (d, J = 8.3 Hz, 1H), 7.1−7.6 (m, 16H), 7.92 (d, J = 8.6 Hz, 3H), 7.96 (d, J = 8.6 Hz, 1H); ^{31}P{^{1}H} NMR δ −12.66 (s). Anal. Calcd for $C_{34}H_{21}F_6P$: C, 71.06; H, 3.69. Found: C, 70.84; H, 3.68.

(*R*)-2-Bis(3,5-dimethylphenyl)phosphino-1,1′-binaphthyl (2e): 90% yield; $[\alpha]^{20}_D$ −52.7 (*c* 1.01, $CHCl_3$); ^{1}H NMR δ 2.13 (s, 6H), 2.21 (s, 6H), 6.71 (d, J = 7.8 Hz, 2H), 6.78 (s, 1H), 6.86 (d, J = 7.8 Hz, 2H), 6.91 (s, 1H), 7.1−7.4 (m, 9H), 7.8−7.9 (m, 4H); ^{13}C{^{1}H} NMR δ 21.19, 21.31, 124.9−137.6, 144.72, 144.94; ^{31}P{^{1}H} NMR δ −12.7 (s). Anal. Calcd for $C_{36}H_{31}P$: C, 87.42; H, 6.32. Found: C, 87.14; H, 6.31.

(*R*)-2-Bis(3,5-dichlorophenyl)phosphino-1,1′-binaphthyl (2f): 74% yield; $[\alpha]^{20}_D$ −38.3 (*c* 0.88, $CHCl_3$); ^{1}H NMR δ 6.86 (dd, J = 2.0, 6.9 Hz, 2H), 7.04 (d, J = 6.6 Hz, 2H), 7.2−7.6 (m, 11H), 7.9−8.0 (m, 4H); ^{31}P{^{1}H} NMR δ −10.4 (s). Anal. Calcd for $C_{32}H_{19}Cl_4P$: C, 66.90; H, 3.34. Found: C, 66.82; H, 3.61.

Asymmetric Hydrosilylation of Styrenes. Typical Procedure. To a mixture of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.37 mg, 2.0 μmol Pd), (*R*)-H-MOP (**2a**) (1.77 mg, 4.0 μmol), and styrene (**3a**) (2144 mg, 2.05 mmol) was added trichlorosilane (0.25 mL, 2.5 mmol) at 0 °C. The mixture was stirred at 0 °C for 12 h. GC analysis and ^{1}H NMR study of the reaction mixture indicated that 1-phenyl-1-(trichlorosilyl)ethane (**4a**) was formed quantitatively. The crude mixture was purified by bulb-to-bulb distillation under reduced pressure to give 520 mg (100% yield) of 1-phenyl-1-(trichlorosilyl)ethane (**4a**).

The results obtained for the asymmetric hydrosilylation of styrenes **3a**−**n** are summarized in Tables 1 and 2. ^{1}H NMR data for the hydrosilylation products are shown below:

1-Phenyl-1-(trichlorosilyl)ethane (4a): ^{1}H NMR δ 1.64 (d, J = 7.6 Hz, 3H), 2.89 (q, J = 7.6 Hz, 1H), 7.20−7.38 (m, 5H).

1-(2-Methylphenyl)-1-(trichlorosilyl)ethane (4b): ^{1}H NMR δ 1.60 (d, J = 7.3 Hz, 3H), 2.36 (s, 3H), 3.16 (q, J = 7.3 Hz, 1H), 7.05−7.33 (m, 4H).

1-(3-Methylphenyl)-1-(trichlorosilyl)ethane (4c): ^{1}H NMR δ 1.60 (d, J = 7.4 Hz, 3H), 2.35 (s, 3H), 2.85 (q, J = 7.4 Hz, 1H), 7.0−7.1 (m, 3H), 7.21 (t, J = 7.8 Hz, 1H).

1-(4-Methylphenyl)-1-(trichlorosilyl)ethane (4d): ^{1}H NMR δ 1.60 (d, J = 7.6 Hz, 3H), 2.33 (s, 3H), 2.85 (q, J = 7.6 Hz, 1H), 7.13 (s, 4H).

1-(2-Chlorophenyl)-1-(trichlorosilyl)ethane (4e): ^{1}H NMR δ 1.60 (d, J = 7.6 Hz, 3H), 3.62 (q, J = 7.6 Hz, 1H), 7.14−7.46 (m, 4H).

1-(3-Chlorophenyl)-1-(trichlorosilyl)ethane (4f): ^{1}H NMR δ 1.61 (d, J = 7.6 Hz, 3H), 2.87 (q, J = 7.6 Hz, 1H), 7.09−7.30 (m, 4H).

1-(4-Chlorophenyl)-1-(trichlorosilyl)ethane (4g): ^{1}H NMR δ 1.60 (d, J = 7.6 Hz, 3H), 2.87 (q, J = 7.6 Hz, 1H), 7.17 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H).

1-(3-Bromophenyl)-1-(trichlorosilyl)ethane (4h): ^{1}H NMR δ 1.60 (d, J = 7.3 Hz, 3H), 2.85 (q, J = 7.3 Hz, 1H), 7.16−7.22 (m, 2H), 7.38−7.41 (m, 2H).

1-(4-Bromophenyl)-1-(trichlorosilyl)ethane (4i): ^{1}H NMR δ 1.60 (d, J = 7.4 Hz, 3H), 2.86 (q, J = 7.4 Hz, 1H), 7.11 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H).

1-(4-Methoxyphenyl)-1-(trichlorosilyl)ethane (4j): ^{1}H NMR δ 1.59 (d, J = 7.6 Hz, 3H), 2.84 (q, J = 7.6 Hz, 1H), 3.80 (s, 3H), 6.87 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H).

1-(3-Nitrophenyl)-1-(trichlorosilyl)ethane (4k): ^{1}H NMR δ 1.68 (d, J = 7.4 Hz, 3H), 3.04 (q, J = 7.4 Hz, 1H), 7.52 (t, J = 8.3 Hz, 1H), 7.59 (d, J = 7.9 Hz, 1H), 8.10−8.15 (m, 2H).

1-Phenyl-1-(trichlorosilyl)propane (4l): ^{1}H NMR δ 0.93 (t, J = 7.3 Hz, 3H), 1.89−2.29 (m, 2H), 2.62 (dd, J = 11.6, 4.0 Hz, 1H), 7.14−7.43 (m, 5H).

1-Phenyl-3-methoxy-1-(trichlorosilyl)propane (4m): ^{1}H NMR δ 2.05−2.22 (m, 1H), 2.29−2.46 (m, 1H), 3.00 (dd, J = 11.9, 3.6 Hz, 1H), 3.13−3.23 (m, 1H), 3.25 (s, 3H), 3.33−3.43 (m, 1H), 7.16−7.43 (m, 5H).

1-Phenyl-3-benzyloxy-1-(trichlorosilyl)propane (4n): ^{1}H NMR δ 2.09−2.24 (m, 1H), 2.36−2.52 (m, 1H), 3.05 (dd, J = 11.9, 3.7 Hz, 1H), 3.22−3.35 (m, 1H), 3.44−3.55 (m, 1H), 4.34 (d, J = 11.9 Hz, 1H), 4.43 (d, J = 11.9 Hz, 1H), 7.14−7.46 (m, 10H).

Oxidation of Hydrosilylation Products 4a−**n. Typical Procedure.** To a suspension of potassium fluoride (690 mg, 11.9 mmol) and potassium bicarbonate (1.76 g, 17.6 mmol) in 100 mL of THF/MeOH (1/1) was added 1-phenyl-1-(trichlorosilyl)ethane (**4a**) (460 mg, 1.90 mmol). To the suspension was added 2.0 mL of 30% hydrogen peroxide at ambient temperature, and the reaction mixture was vigorously stirred for 11 h. To the reaction mixture was added 10 mL of saturated $Na_2S_2O_3$ solution, and then the entire mixture was stirred for 1 h. The mixture was filtered through a Celite plug, and the filter cake was rinsed with ether. The filtrate was concentrated in vacuo, and the resulting residue was extracted with ether. After the residue was dried over anhydrous magnesium sulfate, the solvent was removed in vacuo and the resulting crude mixture was chromatographed on silica gel (hexane/ethyl acetate = 5/1) to give 225 mg (97% yield) of 1-phenylethanol (**5a**):

Specific rotations of alcohols **5a**−**n** obtained by the asymmetric hydrosilylation are shown in Table 2. The reported specific rotation values for the alcohols **5a**−**l** are as follows.

(*S*)-**5a**:[23] $[\alpha]^{22}_D$ −52.5 (*c* 1.3, dichloromethane). (*S*)-**5b** of 95% ee:[24] $[\alpha]^{20}_D$ −58.6 (*c* 0.0665, ethanol). (*S*)-**5c**:[25] $[\alpha]^{25}_D$ −39.8 (*c* 0.944, ethanol). (*R*)-**5d** of 94% ee:[26] $[\alpha]^{20}_D$ +51.6 (*c* 1.0, chloroform). (*R*)-**5e** of 72% ee:[26] $[\alpha]^{20}_D$ +22.4 (*c* 1.1, chloroform). (*R*)-**5f** of 85% ee:[26] $[\alpha]^{20}_D$ +36.7 (*c* 1.0, chloroform). (*R*)-**5g**:[27] $[\alpha]_D$[21] +49.9 (*c* 2.0, Et_2O). (*S*)-**5h**:[25] $[\alpha]^{26}_D$ −28.6 (*c* 1.78, ethanol). (*S*)-**5i** of 96% ee:[24] $[\alpha]_D$ −37.5 (*c* 0.0666, chloroform). (*R*)-**5j** of 89% ee:[26] $[\alpha]^{20}_D$ +47.2 (*c* 1.0, chloroform). (*S*)-**5k** of 45% ee:[28] $[\alpha]^{27}_D$ −17.2 (*c* 2.03, methanol). (*S*)-**5l**:[29] $[\alpha]_D$ −45.45 (*c* 5.15, chloroform).

The absolute configuration of **5n** was assigned to be (*S*)-(−) by ^1H and ^{19}F NMR studies of its (*R*)-MTPA ester.[30] Major isomer: ^{19}F NMR ($CDCl_3$, reference = CF_3COOH) δ 6.31; ^1H NMR δ 2.08 (−CH_2CH_2O−), 2.28 (−CH_2CH_2O−), 4.47 (−OCH_2-Ph). Minor isomer: ^{19}F NMR ($CDCl_3$, reference = CF_3COOH) δ 6.49; ^1H NMR δ 2.05 (−CH_2CH_2O−), 2.25 (−CH_2CH_2O−), 4.41 (−OCH_2Ph).

Palladium-Catalyzed Asymmetric Hydrosilylation of Deuterated Styrenes (3a-α-*d*$_1$ and 3a-*β*,*β*-*d*$_2$). The reaction conditions and results are summarized in Table 3. The reaction was carried out with 20 equiv (to styrene) of trichlorosilane. After oxidation of the hydrosilylation product, 1-phenylethanol was converted into acetate ester **8** by treatment with acetic anhydride and triethylamine. The deuterium and hydrogen content was determined by ^1H and ^2H NMR analyses of acetate **8**. (*R*)-**8** (entry 1 in Table 3, **3a**-α-*d*$_1$ and **2g**): ^1H NMR (C_6D_6) δ 1.33 (s, 3.0H), 1.64 (s, 3.0H, $CH_3C(O)$), 7.03−7.26 (m, 5H); ^2H NMR ($CHCl_3/CDCl_3$) δ 5.88 (br s). (*R*)-**8** (entry 2 in Table 3, **3a**-*β*,*β*-*d*$_2$ and **2g**): ^1H NMR (C_6D_6) δ 1.33 (d, J = 6.6 Hz, 2.6H), 1.64 (s, 3.0H, $CH_3C(O)$), 5.94 (q, J = 6.6 Hz, 1.0H), 7.03−7.26 (m, 5H); ^2H NMR ($CHCl_3/CDCl_3$) δ 1.53 (br s). (*R*)-**8** (entry 3 in Table 3, **3a**-*β*,*β*-*d*$_2$ and **2a**): ^1H NMR (C_6D_6) δ 1.28−1.35 (m, 1.6H), 1.64 (s, 3.0H, $CH_3C(O)$), 5.90−5.97 (m, 1.0H), 7.03−7.26 (m, 5H); ^2H NMR ($CHCl_3/CDCl_3$) δ 1.52 (br s).

Palladium-Catalyzed Asymmetric Hydrosilylation of *o*-Allylstyrene (9). To a mixture of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.69 mg, 1.9 μmol), (*R*)-2-bis(3,5-bis(trifluoromethyl)phenyl)phosphino-1,1′-binaphthyl (**2g**) (5.3 mg, 3.8 μmol), and *o*-allylstyrene (**9**) (174 mg, 1.2 mmol) was added trichlorosilane (165 mg, 1.2 mmol) at −78 °C, and the reaction mixture was stirred at −20 °C for 120 h. The reaction progress was monitored by GLC analysis. GLC and ^1H NMR study on the whole crude mixture indicated that the ratio of 1-methyl-2-(trichlorosilylmethyl)-indan (**10**)/1-(2-(2-propenyl)phenyl)-1-trichlorosilylethane (**11a**)/1-(2-((*E*)-1-propenyl)phenyl)-1-trichlorosilylethane (**11b**) was 47/42/11. The mixture was distilled (bulb-to-bulb) under reduced pressure to give 249 mg (74% yield) of the mixture of **10**, **11a**, and **11b**. The mixture was treated with an excess of methylmagnesium bromide in ether according to the reported procedures[13] to give a mixture of 1-methyl-2-(trimethylsilylmethyl)indan (**10′**), 1-(2-(2-propenyl)phenyl)-1-trimethylsilylethane (**11a′**), and 1-(2-((*E*)-1-propenyl)phenyl)-1-trimethylsilylethane (**11b′**) as colorless oil. The mixture was analyzed by GLC using a chiral stationary phase column (Cyclodex *β*236M) to determine their enantiomeric purities, **10′**, **11a′**, and **11b′** being 91% ee, 95% ee and 95% ee, respectively. Their absolute configuration was assigned by correlation with known compounds, (*S*)-(−)-1-methylindan[17] (**14**) and (*S*)-(−)-3-methylphthalide[18] (**15**), which are shown below.

Oxidation of 10 and 11. To a suspension of potassium fluoride (3.83 g, 63.6 mmol) and potassium bicarbonate (9.92 g, 95.4 mmol) in 400 mL of THF/MeOH (1/1) was added a mixture of **10** and **11** (2.98 g, 10.6 mmol) which contained **10** (85% ee) and **11** (83% ee) in a ratio of 55:45. To the suspension was added 12.5 mL of 30% hydrogen peroxide at ambient temperature, and the reaction mixture was vigorously stirred for 10 h. To the reaction mixture was added 50 mL of saturated $Na_2S_2O_3$ solution and then entire mixture was stirred for 1 h. The mixture was filtered through a Celite plug, and the filter cake was rinsed with ether. The filtrate was concentrated in vacuo and the resulting residue was extracted with ether. After drying over anhydrous magnesium sulfate, the solvent was removed in vacuo and the resulting crude mixture was chromatographed on silica gel (hexane/ethyl acetate = 5/1) to give 646 mg of 1-methyl-2-(hydroxymethyl)indan[13] (**12**) (68%) and 748 mg of a mixture of 1-(2-(2-propenyl)phenyl)ethanol[13] (**13a**) 1-(2-((*E*)-1-propenyl)phenyl)ethanol[13] (**13b**) (96%) as colorless oil. **12** (85% ee): $[\alpha]^{20}_D$ −28.0 (*c* 1.12, $CHCl_3$). A mixture of **13a** and **13b**: (83% ee) $[\alpha]^{20}_D$ −48.1 (*c* 1.40, $CHCl_3$).

(*S*)-(−)-1-Methylindan (14). To a suspension of pyridinium chlorochromate (PCC) (2.16 g, 10.0 mmol) and powdered 4A molecular sieves (1.62 g) in dichloromethane (15 mL) was added a solution of 1-methyl-2-(hydroxymethyl)indan (**12**) (81% ee) in dichloromethane (5 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h, diluted with ether, and filtered through a Celite plug. The filter cake was rinsed with dichloromethane. The combined filtrates were concentrated in vacuo and the residue was chromatographed on silica gel (hexane/ethyl acetate = 5:1) to give (1*S*,2*R*)-1-methyl-2-formylindan as colorless oil (253 mg, 1.58 mmol, 81%): ^1H NMR δ 1.41 (d, J = 6.8 Hz, 3H), 2.87 (dddd, J = 2.4, 7.3, 8.3, 8.3 Hz, 1H), 3.15 (dd, J = 8.3, 16.1 Hz, 1H), 3.21 (dd, J = 8.3, 16.1 Hz, 1H), 3.53 (dq, J = 7.3, 6.8 Hz, 1H), 7.13−7.36 (m, 4H), 9.83 (d, J = 2.4 Hz, 1H).

To a solution of $RhCl(PPh_3)_3$ (1.48 g, 1.60 mmol) in acetonitrile (15 mL) was added a solution of (1*S*,2*R*)-1-methyl-2-formylindan (253 mg, 1.58 mmol) in acetonitrile (10 mL) at room temperature. The reaction mixture was refluxed for 26 h, cooled to ambient temperature, and filtered. The filtrate was extracted with pentane (three times). The pentane phase was separated and concentrated. The residue was chromatographed on silica gel (pentane) to give **14** as colorless oil. The oil was distilled by bulb-to-bulb distillation (32 mmHg, 120 °C) to give pure **14** (86.0 mg, 0.651 mmol, 41%): $[\alpha]^{20}_D$ −8.05 (*c* 1.47, benzene) (lit.[17] for (*R*)-(+) $[\alpha]^{20}_D$ +10.0 (*c* 0.014, benzene)); ^1H NMR δ 1.29 (d, J = 6.8 Hz, 3H), 1.60 (dddd, J = 8.3, 8.3, 8.8, 12.2 Hz, 1H), 2.30 (dddd, J = 3.9, 7.8, 8.3, 12.2 Hz, 1H), 2.83 (ddd, J = 8.3, 8.3, 16.6 Hz, 1H), 2.91 (ddd, J = 3.9, 8.3, 16.6 Hz, 1H), 3.18 (ddq, J = 7.8, 8.8, 6.8 Hz, 1H), 7.12−7.25 (m, 4H).

(*S*)-1-(2-((*E*)-1-Propenyl)phenyl)ethanol (13b). To a solution of $PdCl_2(CH_3CN)_2$ (25.9 mg, 10.0 mmol) in benzene (4 mL) was added a mixture of 1-(2-(2-propenyl)phenyl)ethanol (**13a**) 1-(2-((*E*)-1-propenyl)phenyl)ethanol (**13b**) (324 mg, 2.00 mmol) (**13a**/**13b** = 4/1) at room temperature. The reaction mixture was refluxed for 5 min and concentrated in vacuo. The residue was chromatographed on silica gel (hexane/ethyl acetate = 10/1 to 5/1) to give isomerically pure **13b** (265 mg, 1.64 mmol, 82%): ^1H NMR δ 1.48 (d, J = 6.3 Hz, 3H), 1.77 (br s, 1H), 1.91 (dd, J = 1.5, 6.8 Hz, 3H), 5.22 (q, J = 6.3 Hz, 1H), 6.08 (dq, J = 15.6, 6.8 Hz, 1H), 6.69 (dd, J = 1.5, 15.6 Hz, 1H), 7.14−7.57 (m, 4H).

(*S*)-(−)-3-Methylphthalide (15). To a solution of **13b** (80.0 mg, 0.493 mmol) in dichloromethane (5 mL) was bubbled O_3 at −78 °C for 1 h. Excess ozone was purged from the solution with nitrogen (5 min). To the reaction mixture were added zinc powder (200 mg) and acetic acid (0.4 mL) at the same temperature, and the mixture was allowed to warm to 0 °C. After being stirred for 2 h under nitrogen atmosphere, the reaction mixture was filtered and washed with dichloromethane. The combined filtrates were washed with saturated sodium bicarbonate, water, and brine (once each). The organic

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phase was dried over anhydrous sodium sulfate and concentrated in vacuo. The crude lactol (60.8 mg) obtained was subjected to the oxidation without further purification.

To a suspension of PCC (437 mg, 2.03 mmol) and powdered 4A molecular sieves (600 mg) in dichloromethane (2 mL) was added a solution of crude lactol in dichloromethane (2 mL) at room temperature. The reaction mixture was stirred at room temperature for 1.5 h, diluted with ether, and filtered through a Celite plug, and the filter cake was rinsed with dichloromethane. The combined filtrates were concentrated in vacuo and the residue was chromatographed on silica gel (hexane/ethyl acetate = 5/1) to give **15** as colorless oil (26.0 mg, two steps, 36%): $[\alpha]^{22}_{D}$ −25.6 (*c* 0.675, MeOH) (lit.[18] for 97% ee of (*S*)-(−) $[\alpha]^{22}_{D}$ −27.85 (*c* 1.3, MeOH)); ^{1}H NMR δ 1.65 (d, J = 6.8 Hz, 3H), 5.57 (q, J = 6.8 Hz, 1H), 7.44−7.91 (m, 4H).

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