

# Catalytic asymmetric synthesis of optically active alcohols via hydrosilylation of olefins with a chiral monophosphine-palladium catalyst

Tamio Hayashi and Yasuhiro Uozumi

Catalysis Research Center and Graduate School of Pharmaceutical Science,  
Hokkaido University, Sapporo 060, Japan

**Abstract** - Axially chiral monophosphines **1**, (*S*)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl (MOP, **1a**) and its analogs substituted with isopropoxy (**1b**), benzyloxy (**1c**), and ethyl (**1d**) at 2' position, were prepared. Reaction of simple terminal alkenes **5** ( $\text{RCH}=\text{CH}_2$ ; R = *n*-C<sub>4</sub>H<sub>9</sub>, *n*-C<sub>6</sub>H<sub>13</sub>, *n*-C<sub>10</sub>H<sub>21</sub>, PhCH<sub>2</sub>CH<sub>2</sub>, *cyclo*-C<sub>6</sub>H<sub>11</sub>) with trichlorosilane at 40 °C in the presence of 0.1 or 0.01 mol % of palladium catalyst prepared in situ from [PdCl( $\pi$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub> and (*S*)-**1a** proceeded with unusual regioselectivity (up to 94%) and with high enantioselectivity to give high yields of 2-(trichlorosilyl)alkanes **6** together with a minor amount of 1-(trichlorosilyl)alkanes **6'**. Oxidation of the carbon-silicon bond gave optically active alcohols **8** ( $\text{RCH}(\text{OH})\text{CH}_3$ ), enantiomeric purity ranging between 94% and 97% ee. The high enantioselectivity was also observed in the enantioselective hydrosilylation of norbornene (**9**) and related meso bicyclic olefins catalyzed by the MOP/palladium, which gave *exo*-2-norbornanol (**11**) and related alcohols with up to 96% ee.

## INTRODUCTION

Asymmetric reactions catalyzed by transition metal complexes containing optically active phosphine ligands have attracted significant interest for their synthetic utility (ref. 1). One of the most exciting and challenging subjects in research on the catalytic asymmetric synthesis is development of the chiral ligand which will fit in with a given reaction efficiently in catalytic activity as well as in enantioselectivity. Most of the chiral phosphine ligands so far prepared and used for the catalytic asymmetric reactions are the chelating bisphosphines which are expected to construct an effective chiral environment by bidentate coordination to metal. They have been demonstrated to be effective for several types of asymmetric reactions including rhodium- or ruthenium-catalyzed hydrogenation (ref. 2), palladium- or nickel-catalyzed allylic substitution reactions (ref. 3), and gold- or silver-catalyzed aldol reactions (ref. 4). On the other hand, there exist transition metal-catalyzed reactions where the bisphosphine-metal complexes can not be used because of their low catalytic activity and/or low selectivity towards a desired reaction pathway and therefore chiral monodentate phosphine ligands are required for the realization of catalytic asymmetric synthesis (ref. 5). Unfortunately, there have been reported only a limited number of monodentate chiral phosphine ligands, which are not so useful as bisphosphine ligands with few exceptions (ref. 1). We have continued our efforts to develop new chiral monodentate phosphine ligands and found that 2-(diphenylphosphino)-2'-alkoxy-1,1'-binaphthyls (MOPs **1**) are very effective for several types of catalytic asymmetric reactions. Here we describe the preparation of the axially chiral monodentate phosphine ligands and their use for palladium-catalyzed asymmetric hydrosilylation of olefins which provides a new efficient route to optically active alcohols.

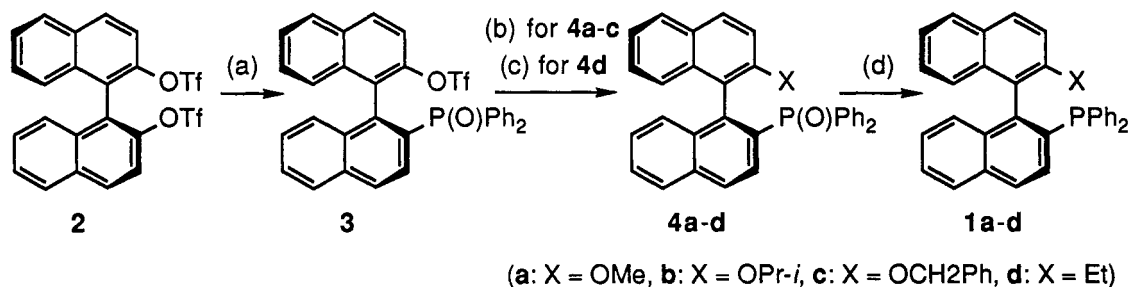
## CHIRAL MONOPHOSPHINE LIGANDS (MOPs)

Since axially chiral binaphthyl compounds have been well-documented to construct an effective chiral template for asymmetric reactions (ref. 1), we chose the chiral binaphthyl skeleton as a basic structure of monodentate phosphine ligand. We have also attached importance to introduction of a functional group into the chiral ligand that would be expected to interact attractively with a functional group in the substrate (ref. 6).

Morgans and coworkers (ref. 7) have reported the selective monophosphinylation of 2,2'-bis(trifluoromethanesulfonyloxy)-1,1'-binaphthyl (**2**) with diphenylphosphine oxide in the presence of palladium catalyst giving a high yield of 2-diphenylphosphinyl-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl (**3**), which attracted our attention as a versatile starting compound for the preparation of chiral monophosphine ligands. The trifluoromethanesulfonyloxy group on **3** must be useful for the introduction of various types of functional groups onto the binaphthyl.

The conversion of **3** into 2-(diphenylphosphino)-2'-alkoxy-1,1'-binaphthyls (MOPs **1**) was achieved (ref. 8,9) in high yields by the three step reactions shown in Scheme 1. Thus, triflate (*S*)-**3** was hydrolyzed with aqueous sodium hydroxide to give 99% yield of binaphthol, and its phenolic hydroxy group was alkylated by treatment with, for example, methyl iodide in the presence of potassium carbonate in acetone to give 99% yield of methyl ether (*S*)-**4a**. Reduction of phosphine oxide with trichlorosilane and triethylamine in refluxing xylene led to (*S*)-MeO-MOP (**1a**) in 97% yield. Similar phosphines containing benzyl ether and isopropyl ether, (*S*)-**1b** and (*S*)-**1c**, were also prepared by alkylation of the binaphthol with isopropyl iodide and benzyl bromide, respectively, followed by reduction of the phosphine oxide. The trifluoromethanesulfonyloxy group on the 2' position can be substituted with an alkyl group by the nickel-catalyzed cross-coupling with the Grignard reagent. Introduction of ethyl group on **3** followed by the reduction with trichlorosilane gave (*S*)-**1d** in 64% overall yield.

Scheme 1



(a)  $\text{Ph}_2\text{POH}$  (2 equiv),  $\text{Pd}(\text{OAc})_2$  (5 mol %), dppb (5 mol %),  $i\text{-Pr}_2\text{NEt}$  (4 equiv), DMSO, 100 °C, 12 h (**3**; 95%). (b) (i) 3N NaOH, 1,4-dioxane, methanol (ii) MeI, *i*-PrI or  $\text{PhCH}_2\text{Br}$  (3-10 equiv),  $\text{K}_2\text{CO}_3$  (2-4 mol equiv), acetone, reflux, 3-24 h (**4a**; 99%, **4b**; 92%, **4c**; 87%). (c)  $\text{EtMgBr}$  (1.1 equiv),  $\text{NiCl}_2(\text{dpppe})$  (2 mol %),  $\text{Et}_2\text{O}$ , reflux, 24 h (**4d**; 81%). (d)  $\text{Et}_3\text{N}$  (7-20 equiv),  $\text{Cl}_3\text{SiH}$  (5 equiv), xylene, 120 °C, 3-5 h (**1a**; 97%, **1b**; 84%, **1c**; 96%, **1d**; 79%).

## ASYMMETRIC HYDROSILYLATION OF OLEFINS

Catalytic asymmetric functionalization of olefins is an important goal in synthetic organic chemistry. The asymmetric synthesis of optically active alcohols from olefins has been mainly effected by asymmetric hydroboration with a stoichiometric amount of chiral hydroborating agents (ref. 10). Use of catalytic systems for the asymmetric hydroboration has not always been successful in terms of enantioselectivity or catalytic activity (ref. 11). Catalytic asymmetric hydrosilylation has been also reported to produce optically active alcohols (ref. 12), but the olefinic substrate has been limited to styrenes or 1,3-dienes and the enantioselectivity attained is not high enough.

### Enantioface selective hydrosilylation of 1-alkenes

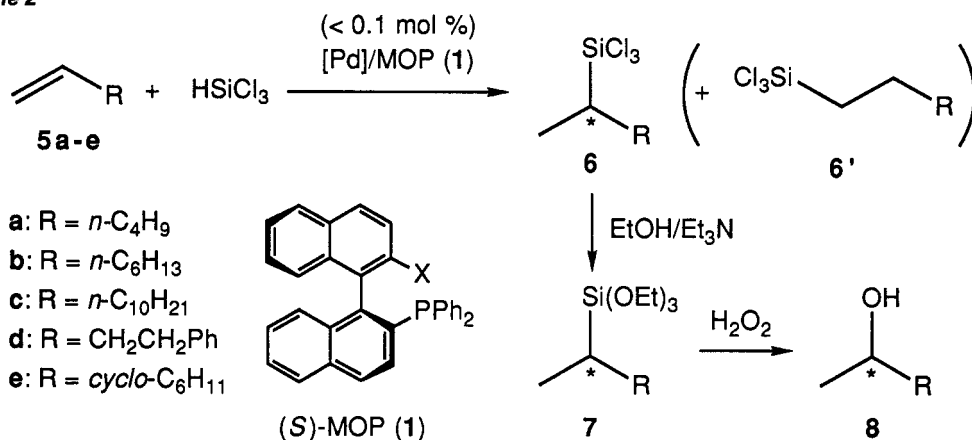
It is well-documented (ref. 13) that the hydrosilylation of terminal olefins is catalyzed by platinum, rhodium, or nickel complexes to proceed with anti-Markovnikoff selectivity leading to 1-silylalkanes. Rather surprisingly, only a little attention has been paid to the use of palladium catalysts for the hydrosilylation of 1-alkenes (ref. 14) in spite of their frequent use for the reaction of 1,3-dienes and styrenes (ref. 12,13). In order to develop a catalyst possessed of high catalytic activity, high regioselectivity giving 2-silylalkanes, and high enantioselectivity in addition, we examined several types of phosphine-palladium catalysts for the reaction of 1-hexene (**2a**) with trichlorosilane. It was found that palladium complexes coordinated with a chelating bis(phosphine), 1,4-bis(diphenylphosphino)butane (dppb), 2,3-bis(diphenylphosphino)butane (chiraphos), or 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), did not catalyze the hydrosilylation at all even at 80 °C, while the reaction took place at 40 °C with monodentate phosphine ligands. For example, the reaction in the presence of 0.1 mol % of a palladium-triphenylphosphine catalyst ( $\text{P/Pd} = 2/1$ ) at 40 °C for 24 h gave

12% yield of hexylsilanes consisting of 1- and 2-isomers in a ratio of 91/9, the hydrosilylation being accompanied by isomerization of 1-hexene into internal olefins. It is reasonable to expect that a monodentate phosphine ligand generates a palladium catalyst that is more active for the hydrosilylation than a chelating bis-(phosphine) ligand. The former can form square planar palladium(II) intermediate  $\text{PdH}(\text{SiCl}_3)\text{L}(\text{CH}_2=\text{CHR})$  ( $\text{L}$  = monophosphine), which offers a coordination site for the activation of olefin. The preferential formation of 1-alkylsilane has been reported (ref. 14) in the hydrosilylation of 1-octene catalyzed by  $\text{Pd}(\text{PPh}_3)_4$ .

Studies of the effects of monodentate phosphine ligands on the catalytic activity and the regioselectivity forming 1-alkylsilane or 2-alkylsilane in the palladium-catalyzed hydrosilylation revealed that (*S*)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl (MeO-MOP, **1a**) is by far the best ligand for the hydrosilylation. Its palladium complex exhibited both high catalytic activity and high unusual regioselectivity forming 2-alkylsilanes, and high enantioselectivity in addition. The predominant formation of 2-alkylsilanes from aliphatic 1-olefins has never been observed with any transition-metal catalysts. The high catalytic activity and regioselectivity of the palladium-MOP complex may be related to the reactivity of key intermediate  $\text{Pd}(2\text{-alkyl})\text{L}(\text{silyl})$ . It seems that MOP ligand can accelerate the reductive elimination of 2-silylalkane and/or retard the  $\beta$ -hydrogen elimination forming 2-alkenes. Triphenylphosphine or tri-*o*-tolylphosphine caused the isomerization of a terminal olefin into internal olefins during the hydrosilylation while MOP did not.

The results obtained for the asymmetric hydrosilylation of 1-alkenes **5** with trichlorosilane (ref. 8) are summarized in Table I. The hydrosilylation products, 2-alkyl(trichloro)silanes **6** were readily converted into optically active 2-alkanols **8** by oxidation of (triethoxy)silane **7** with hydrogen peroxide (ref. 15) (Scheme 2). All the olefins, 1-hexene (**5a**), 1-octene (**5b**), 1-dodecene (**5c**), 4-phenyl-1-butene (**5d**), and vinylcyclohexane (**5e**) were transformed efficiently into the corresponding optically active alcohols **8** with enantioselectivity ranging between 94% and 97% ee (entries 1, 2, and 9-11) by the catalytic hydrosilylation-oxidation procedure, the selectivity being highest for the enantioface selection of simple terminal olefins. The regioselectivity forming 2-(silyl)alkanes is surprisingly high for the terminal olefins **5a-d** substituted with a primary alkyl group. Lower regioselectivity was observed with vinylcyclohexane (**5e**), which is substituted with a sterically bulky group on the double bond (entry 11). Ligands **1b-d** gave almost the same results as **1a**, indicating that the substituents at the 2' position on ligand **1** did not have significant effects on the catalytic activity or the selectivity (entries 6-8). It should be noted that the palladium-MOP complex is highly catalytically active, the hydrosilylation taking place with 0.01 mol % of the catalyst (entry 3).

Scheme 2



A practical procedure is given for the reaction of 1-octene (**5b**) (entry 3). A mixture of **5b** (2.81 g, 25 mmol), trichlorosilane (4.06 g, 30 mmol),  $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$  (0.46 mg, 0.0013 mmol, 0.01 mol % Pd), and (*S*)-(-)-MOP-OMe (**1a**, 2.34 mg, 0.005 mmol, 0.02 mol %) was kept stirred at 40 °C for 72 h. The reaction mixture was distilled (bulb-to-bulb) under reduced pressure to give 6.20 g (97% yield) of (trichlorosilyl)octane consisting of 2-silyl and 1-silyl isomers (**6b** and **6'b**, respectively) in a ratio of 87/13, which was converted quantitatively into (triethoxysilyl)octane **7b** (contaminated with regioisomer **7'b**) by treatment with ethanol (5 mL) and triethylamine (10 mL) in ether (600 mL). Oxidation of the triethoxysilane according to the procedure reported by Tamao (ref. 15) followed by removal of a small amount of 1-octanol resulting from **6'b** by the preferential complexation with calcium chloride (ref. 16) gave 2.28 g (70% from **5b**) of

**Table I.** Asymmetric Synthesis of 2-Alkanols through Catalytic Asymmetric Hydrosilylation of 1-Alkenes<sup>a</sup>

entry	ligand (X in 1)	1-alkene (5)	reaction conditions	yield <sup>b</sup> of 6 (%)	ratio <sup>c</sup> of 6/6'	yield <sup>d</sup> of 8 (%)	% ee <sup>e</sup> (config)
1	1a (OMe)	<i>n</i> -C <sub>4</sub> H <sub>9</sub> CH=CH <sub>2</sub> (5a)	40 °C 24 h	91	89/11	70	94 ( <i>R</i> )
2	1a (OMe)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CH=CH <sub>2</sub> (5b)	40 °C 24 h	83	93/7	71	95 ( <i>R</i> )
3 <sup>f</sup>	1a (OMe)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CH=CH <sub>2</sub> (5b)	40 °C 72 h	97	87/13	70	94 ( <i>R</i> )
4 <sup>g</sup>	1a (OMe)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CH=CH <sub>2</sub> (5b)	40 °C 24 h	97	88/12		91 ( <i>R</i> )
5	1a (OMe)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CH=CH <sub>2</sub> (5b)	60 °C 16 h	93	89/11		86 ( <i>R</i> )
6	1b (OPr- <i>i</i> )	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CH=CH <sub>2</sub> (5b)	40 °C 24 h	88	90/10		91 ( <i>R</i> )
7	1c (OCH <sub>2</sub> Ph)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CH=CH <sub>2</sub> (5b)	40 °C 24 h	85	80/20		95 ( <i>R</i> )
8	1d (Et)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> CH=CH <sub>2</sub> (5b)	40 °C 24 h	80	90/10		93 ( <i>R</i> )
9	1a (OMe)	<i>n</i> -C <sub>10</sub> H <sub>21</sub> CH=CH <sub>2</sub> (5c)	40 °C 72 h	90	94/6	75	95 ( <i>R</i> )
10	1a (OMe)	PhCH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> (5d)	40 °C 24 h	90	81/19	68	97 ( <i>S</i> )
11	1a (OMe)	<i>cyclo</i> -C <sub>6</sub> H <sub>11</sub> CH=CH <sub>2</sub> (5e)	40 °C 24 h	100	66/34	45 <sup>h</sup>	96 ( <i>R</i> )

<sup>a</sup> All reactions were run without solvent in the presence of palladium catalyst prepared in situ by mixing [PdCl( $\pi$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub> and ligand (*S*)-MOP (1). The ratio of 5/HSiCl<sub>3</sub>/Pd/1 is 1.0/1.2/0.001/0.002 unless otherwise noted. <sup>b</sup> Isolated yield of a mixture of 6 and 6' by distillation. <sup>c</sup> Determined by GLC or <sup>1</sup>H NMR analysis of 6 (and 6') or 7 (and 7'). <sup>d</sup> Isolated yield (overall from 5) of regioisomerically pure alcohol 8. <sup>e</sup> Determined by HPLC analysis of (3,5-dinitrophenyl)carbamate with a chiral column (see text). <sup>f</sup> Reaction with 0.01 mol % of the catalyst. <sup>g</sup> Ratio of P/Pd is 1/1. <sup>h</sup> Contaminated with 5% of 2-cyclohexylethanol.

isomerically pure (*R*)-2-octanol (8b) ([ $\alpha$ ]<sub>D</sub><sup>25</sup> -10.3° (*c* 5.59, ethanol)). HPLC analysis of the (3,5-dinitrophenyl)carbamate of 8b (ArNCO/pyridine/toluene) using chiral stationary phase column (Sumichiral OA-1100, hexane/dichloroethane/ethanol = 100/20/1) demonstrated the enantiomeric purity to be 94%.

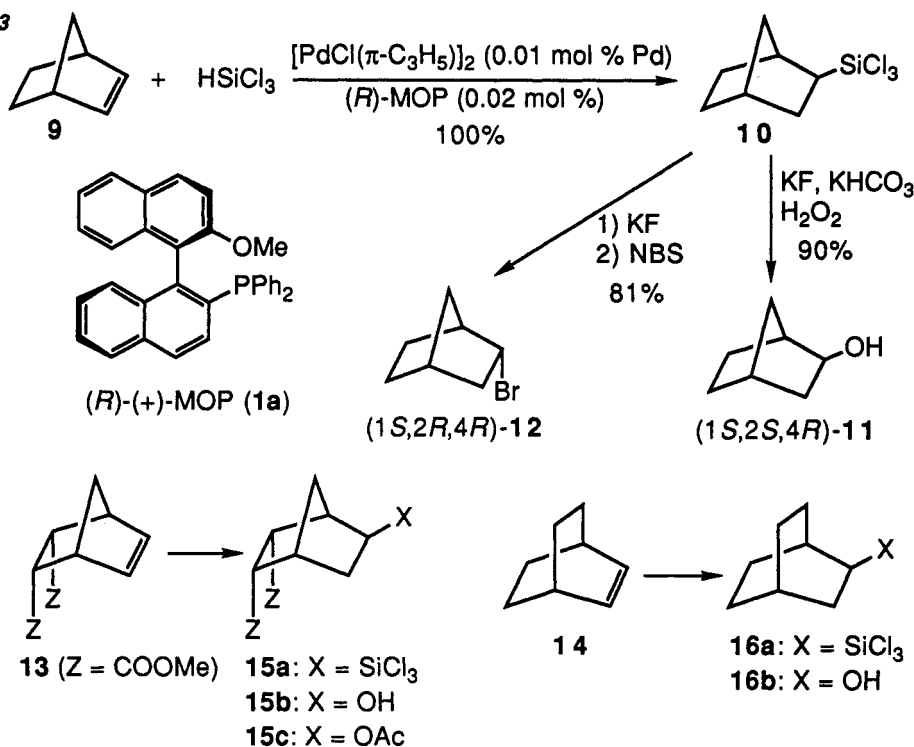
#### Enantioposition selective hydrosilylation of meso olefins

Asymmetric synthesis through a selective monofunctionalization of enantiotopic positions is one of the most attractive strategies for one-step construction of multiple chiral carbon centers (ref. 17). In spite of the impressive development of enantioface selective asymmetric reactions catalyzed by transition metal complexes, the enantioposition selective approach still remains to be developed (ref. 1). We have applied the MOP/palladium-catalyzed hydrosilylation to the catalytic asymmetric functionalization of meso bicyclo[2.2.1] system (ref. 18), because the optically active bicyclo[2.2.1]heptane derivatives represented by norbornanol are of great value as versatile chiral building blocks for the synthesis of a variety of important compounds.

A typical procedure for the asymmetric synthesis of *exo*-2-norbornanol (11) from norbornene (9) (Scheme 3) is as follows: A mixture of norbornene (9, 15.0 g, 0.16 mol), trichlorosilane (20.0 mL, 0.20 mol), [PdCl( $\pi$ -C<sub>3</sub>H<sub>5</sub>)]<sub>2</sub> (2.9 mg, 0.01 mol % Pd) and (*R*)-MOP (1a, 14.8 mg, 2 equiv to Pd) was stirred at 0 °C for 24 h. Removal of excess silane followed by distillation (65 °C/3.5 mm Hg) gave 100% yield (36.5 g) of *exo*-2-trichlorosilylnorbornane (10) as a single product. Direct oxidation of 10 with hydrogen peroxide in the presence of a large excess of potassium fluoride and potassium bicarbonate gave *exo*-2-norbornanol (11) in over 90% yield. Sublimation in vacuo gave 13.3 g (74% yield) of analytically pure (1*S*,2*S*,4*R*)-11 with 93% ee. The absolute configuration was assigned on the basis of the optical rotation (11: [ $\alpha$ ]<sub>D</sub><sup>25</sup> -2.94° (*c* 10.55, CHCl<sub>3</sub>)) and the enantiomeric excess was determined by HPLC analysis of the carbamate ester obtained by treatment with 3,5-dinitrophenyl isocyanate. The hydrosilylation carried out at -20 °C for 3 days (99% yield) raised the enantiomeric excess to 96% ee (entries 1 and 2 in Table II).

Trichlorosilane 10 can be converted into (1*S*,2*R*,4*R*)-*endo*-2-bromonorbornane (12) in 81% yield by treatment with excess potassium fluoride followed by bromination of the resulting pentafluorosilicate with *N*-bromosuccinimide (ref. 19). Dimethyl ester derivative 13 and bicyclo[2.2.2]octene 14 were also successfully subjected to the asymmetric hydrosilylation-oxidation under the similar reaction conditions to give the corresponding alcohols, (1*R*,2*S*,4*R*,5*S*,6*R*)-15b (94% ee) and (2*S*)-16b (92% ee), respectively (entries 3 and 4).

Scheme 3

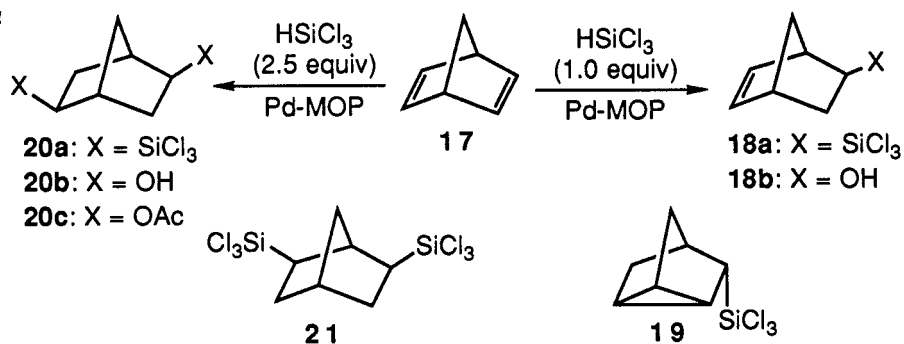
Table II. Asymmetric Hydrosilylation Catalyzed by Palladium-MOP<sup>a</sup>

entry	olefin	conditions	product	yield <sup>b</sup> % ( <i>exo</i> : <i>endo</i> ) <sup>c</sup>	yield <sup>b</sup> % of alcohol	% ee
1	9	0 °C, 24 h	10	100 (100 : 0)	90 (11)	93 <sup>d</sup>
2	9	-20 °C, 3 d	10	99 (100 : 0)		96 <sup>d</sup>
3	13	0 °C, 24 h	15a	100 (100 : 0)	96 (15b)	94 <sup>e</sup>
4	14	0 °C, 24 h	16a	85 (—)	90 (16b)	92 <sup>d</sup>
5	17	0 °C, 24 h	18a	85 <sup>f</sup> (100 : 0)	89 (18b)	95 <sup>d</sup>

<sup>a</sup> All reactions were run without solvent in the presence of palladium catalyst prepared in situ by mixing  $[\text{PdCl}(\pi\text{-C}_3\text{H}_5)]_2$  (0.01–0.1 mol % Pd) and (R)-MOP (2 equiv to Pd). The ratio of olefin/ $\text{HSiCl}_3$  is 1/1.20–1.25. <sup>b</sup> Isolated yield. <sup>c</sup> Determined by GLC and  $^1\text{H}$  NMR analysis. <sup>d</sup> Determined by HPLC analysis of (3,5-dinitrophenyl)carbamate of the alcohol with Sumichiral OA-4500 (n-hexane/dichloroethane/ethanol = 50/10/1). <sup>e</sup> Determined by  $^1\text{H}$  NMR analysis of acetate **15c** using  $\text{Eu}(\text{hfc})_3$ . <sup>f</sup> Nortricyclene **19** was also formed in 14%.

It is remarkable that the monofunctionalization of norbornadiene (**17**) forming *exo*-2-trichlorosilyl-5-norbornene (**18a**) is effected by the palladium-MOP catalyst with high chemo- and enantioselectivity (Scheme 4). It is in striking contrast to the reaction catalyzed by chloroplatinic acid (ref. 13) or palladium-triphenylphosphine which gives nortricyclene **19** as a major product. Thus, the reaction of **17** with 1.0 equiv of trichlorosilane and the palladium-MOP catalyst (0.1 mol %) followed by the hydrogen peroxide oxidation gave (1*R*,2*S*,4*R*)-*exo*-2-hydroxy-5-norbornene (**18b**) with 95% ee (entry 5). The enantioselective hydrosilylation took place two times on the double bonds of **17** in the reaction with 2.5 equiv of trichlorosilane, which gave 78% yield of chiral disilylnorbornane **20a** and meso isomer **21** in a ratio of 18 : 1. The oxidation of **20a** followed by acetylation of diol **20b** gave diacetate (1*R*,2*S*,4*R*,5*S*)-**20c** with >99% ee, the high purity being as expected in the double stereoselection.

Scheme 4



## CONCLUSION

New monodentate phosphine ligands (MOPs), which have binaphthyl axial chirality, are highly effective for palladium-catalyzed asymmetric hydrosilylation of olefins. High stereoselectivity (~95% ee) has been observed in both enantioface-selective reaction of alkyl-substituted terminal olefins and enantio-position-selective reaction of bicyclo[2.2.1]heptane derivatives. The catalytic asymmetric hydrosilylation provides the most efficient and practical route to optically active alcohols. The chiral MOP ligands are expected to be also useful for other types of catalytic asymmetric reactions where monodentate phosphine ligands are favorable for steric and/or electronic reasons.

## REFERENCES

- For recent reviews: (a) Brunner, H. *Synthesis* **1988**, 645. (b) Brunner, H. *Top. Stereochem.* **1988**, *18*, 129. (c) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257. (d) Noyori, R.; Kitamura, M. *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: New York, 1989; Vol. 5, p 115. (e) Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901.
- For example: Noyori, R.; Ikeda, T.; Ohkuma, T.; Widhalm, M.; Kitamura, M.; Takaya, H.; Akutagawa, S.; Sayo, S.; Saito, T.; Taketomi, T.; Kumobayashi, H. *J. Am. Chem. Soc.* **1989**, *111*, 9134.
- For example: Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301.
- For example: Hayashi, T.; Sawamura, M.; Ito, Y. *Tetrahedron* **1992**, *48*, 1999.
- For example: Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153.
- Hayashi, T. *Pure Appl. Chem.* **1988**, *60*, 7.
- Kurz, L.; Lee, G.; Morgans, D., Jr.; Waldyke, M. J.; Ward, T. *Tetrahedron Lett.* **1990**, *31*, 6321.
- Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887.
- Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. to be submitted.
- Pelter, A.; Smith, K.; Brown, H. C. *Borane reagents*; Academic Press: New York, 1988.
- (a) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Tetrahedron Asymmetry* **1991**, *2*, 601 and references cited therein. (b) Burgess, K.; van der Donk, W. A.; Ohlmeyer, M. J. *Tetrahedron Asymmetry* **1991**, *2*, 613.
- Hayashi, T.; Kabeta, K. *Tetrahedron Lett.* **1985**, *26*, 3023 and references cited therein.
- For a review: Ojima, I. In *The Chemistry of Organic Silicon Compounds*, Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; p 1479.
- Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1974**, *30*, 2143.
- (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. (b) Tamao, K.; Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C37. (c) Tamao, K.; Nakajo, E.; Ito, Y. *J. Org. Chem.* **1987**, *52*, 4412. (d) Tamao, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985; p 231.
- Sharpless, K. B.; Chong, A. O.; Scott, J. A. *J. Org. Chem.* **1975**, *40*, 1252.
- For reviews: (a) Morrison, J. D., Ed. *Asymmetric Synthesis*; Academic Press: London, 1983–1985; Vol. 1–5. (b) N6grádi, M. *Stereoselective Synthesis*; Weinheim: New York, 1987.
- Uozumi, Y.; Lee, S.-Y.; Hayashi, T. submitted for publication.
- Tamao, K.; Yoshida, J.; Murata, M.; Kumada, M. *J. Am. Chem. Soc.* **1980**, *102*, 3267.