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Axially chiral monophosphine ligands (MOPs) and their use for palladium-catalyzed asymmetric hydrosilylation of olefins

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Abstract

The preparation of axially chiral monophosphine ligands (MOPs) is described and it is shown that the use of these ligands for the palladium-catalyzed asymmetric hydrosilylation of olefins gives rise to high catalytic activity and high enantioselectivity.

Keywords: Monophosphine ligands; Palladium catalyst; Olefins; Hydrosilylation; Asymmetric catalysis

1. Introduction

Asymmetric reactions catalyzed by transition metal complexes containing enantiomerically pure chiral ligands have attracted significant interest owing to their synthetic utility.[1] Catalytic asymmetric synthesis requires ideally only one molecule of the chiral catalyst in order to produce a large quantity of an optically active substance. Some of the catalytic asymmetric reactions have developed so well that they are practically useful for the synthesis of key intermediates for biologically active compounds. Representatives are rhodium- or ruthenium-catalyzed asymmetric hydrogenation of olefins and ketones and asymmetric epoxidation and dihydroxylation of olefins (see Footnote 1). However, other types of reactions remain not so useful in terms of enantioselectivity and catalytic activity, though attempts have been made to apply a number of catalytic reactions to asymmetric synthesis.

We have concentrated our efforts into development of an efficient chiral catalyst system for asymmetric hydrosilylation of olefins and recently found that a chiral monophosphine–palladium complex has high enantioselectivity and high catalytic activity for various types of olefins. It is well documented that the hydrosilylation of olefins is catalyzed by platinum, rhodium, and nickel complexes.[2] On the other hand, rather surprisingly, little attention has been paid to the use of palladium catalysts for hydrosilylation [8] except for the reaction of 1,3-dienes and styrene derivatives (see Footnote 2). We have found that palladium complexes coordinated with bisphosphine ligands such as 1,4-bis(diphenylphosphino)butane (dppb) did not catalyze the hydrosilylation of olefins at all, even upon elevation to a high temperature, while the hydrosilylation took place under mild conditions with monodentate phosphine ligands. It follows that efficient chiral monodentate phosphine ligands are required for the catalytic asymmetric synthesis to be viable. Although a number of chiral phosphine

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[1] For recent reviews, see [1–6].

[2] For a review, see [7].

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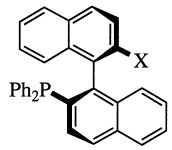
ligands have been prepared and used for the transition metal-catalyzed reactions, most of them are the bisphosphines which are, in general, anticipated to be effective in constructing a chiral environment by the chelate coordination to a metal (see Footnote 1). On the other hand, only a limited number of monodentate chiral phosphine ligands have been reported probably because they have been described as being of little practical use. We have chosen the chiral binaphthyl skeleton as the basic structure of the monodentate phosphine ligand because in the case of using axially chiral binaphthyl compounds to construct an effective chiral template for asymmetric reactions there are numerous examples documented in the literature (see Footnote 1). They are 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MeO-MOP, **1a**) and its derivatives. Here we describe the preparation of MOP ligands and their use for the palladium-catalyzed asymmetric hydrosilylation of olefins which proceeds with high enantioselectivity as well as with high catalytic activity.

2. Preparation of MOP ligands

Morgans and coworkers [9] have reported the selective monophosphinylation of 2,2′-bis-(trifluoromethanesulfonyloxy)-1,1′-binaphthyl (**2**) with diphenylphosphine oxide in the presence of a palladium catalyst giving a high yield of 2-diphenylphosphinyl-2′-trifluoromethanesulfonyloxy-1,1′-binaphthyl (**3**); this molecule attracted our attention as a versatile starting compound for the preparation of chiral monophosphine ligands. The triflate group on **3** was considered to be a convenient functionality for the introduction of various types of functional groups onto the binaphthyl



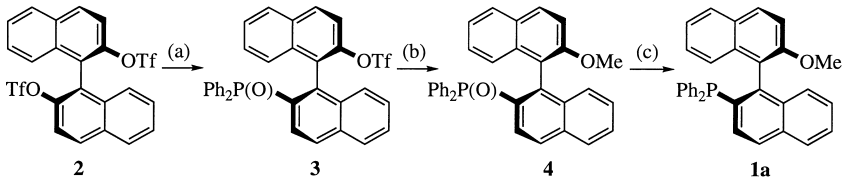
(*S*)-MOP (**1**)

1a: X = OMe
1b: X = OCH_2Ph
1c: X = OPr-*i*
1d: X = Et (*R*)
1e: X = CN
1f: X = CH_2NMe_2
1g: X = COOMe
1h: X = COOH
1i: X = OH
1j: X = H (*R*)

Fig. 1. MOP ligands prepared and used for catalytic asymmetric reactions.

ring. The conversion of **3** into 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MeO-MOP, **1a**) was achieved [10,11] in a high yield by the three-step sequence shown in Scheme 1. Thus, triflate (*S*)-**3** was hydrolyzed with aqueous sodium hydroxide to give 99% yield of alcohol and its phenolic hydroxy group was alkylated by treatment with methyl iodide in the presence of potassium carbonate in acetone to give 99% yield of methyl ether (*S*)-**4a**. Reduction of the phosphine oxide with trichlorosilane and triethylamine in refluxing xylene led to (*S*)-MeO-MOP (**1a**) in 97% yield. The overall yield from 2,2′-dihydroxy-1,1′-binaphthyl was about 90%. Similar phosphines containing a benzyl ether and an isopropyl ether, (*S*)-**1b** and (*S*)-**1c**, were also prepared by alkylation of the phenol oxygen with benzyl bromide and isopropyl iodide, respectively, followed by reduction of the phosphine oxide (Fig. 1).

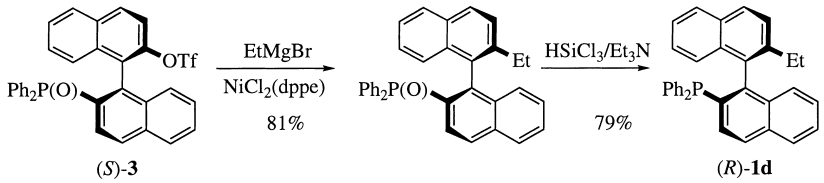
The trifluoromethanesulfonyloxy group on the 2′ position can be replaced by an alkyl group by nickel-catalyzed cross-coupling with the Grignard reagent. Introduction of an ethyl group on (*S*)-**3** with ethylmagnesium bromide followed by the reduction with trichlorosilane gave (*R*)-**1d** in 64% overall yield



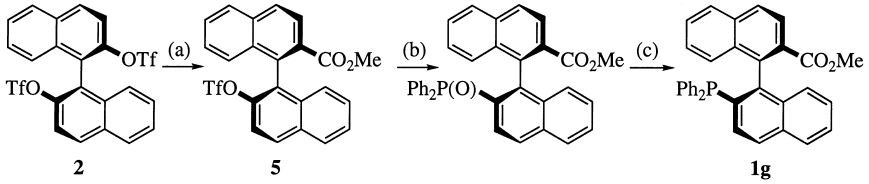
2 **3** **4** **1a**

(a) Ph_2POH (2 eq), $Pd(OAc)_2$ (5 mol %), dppb (5 mol %), *i*-Pr_2NEt (4 eq), DMSO, 100 °C, 12 h (**3**, 95%). (b) (i) 3N NaOH, 1,4-dioxane, methanol. (ii) MeI (4 eq), K_2CO_3 (4 eq), acetone, reflux, 3 h (**4a**, 99%). (c) Et_3N (20 eq), $HSiCl_3$ (5 eq), xylene, 120 °C, 5 h, (**1a**, 97%).

Scheme 1.



Scheme 2.



(a) $Pd(OAc)_2$ (10 mol %), dppp (10 mol %), CO (1 atm), *i*-Pr_2NEt (4 eq), DMSO/MeOH (54%). (b) Ph_2POH (2 eq), $Pd(OAc)_2$ (10 mol %), dppb (10 mol %), *i*-Pr_2NEt (4 eq), DMSO (52%). (c) Et_3N (30 eq), $HSiCl_3$ (10 eq), toluene (90%).

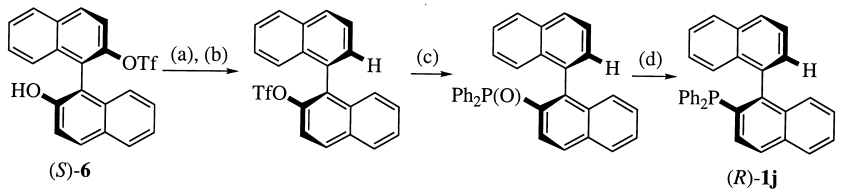
Scheme 3.

(Scheme 2). A cyano group can be also introduced at the 2′ position of **3** in a quantitative yield by the nickel-catalyzed cyanation with potassium cyanide to give **1e** after reduction of the phosphine oxide [12]. Reduction of the cyano group with diborane followed by methylation with formaldehyde/formic acid gave aminophosphine **1f**. The MOP ligand **1g** which contains an ester group was prepared through palladium-catalyzed monocarbonylation of bis(triflate) **2** giving 2-methoxycarbonyl-2′-trifluoromethanesulfonyloxy-1,1′-binaphthyl (**5**) (Scheme 3). The palladium-catalyzed carbonylation of **3** was not successful [12].

The MOP derivative (*R*)-**1j** bearing no substituent at the 2′-position, which is needed to evaluate the steric and/or electronic effects of various functional groups in other MOP derivatives, was prepared starting from (*S*)-2-hydroxy-2′ - trifluoromethanesulfonyloxy - 1,1′-binaphthyl (**5**) by a sequence of reactions including the palladium-catalyzed phosphinylation and reduction of the resulting phosphine oxide (Scheme 4) [12].

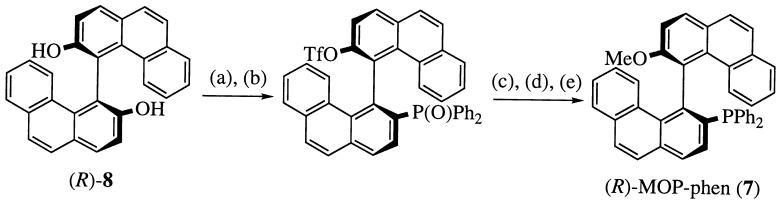
The enantiomerically pure monophosphine containing the biphenanthryl skeleton, MOP-phen (**7**), was also prepared by a sequence of reactions from 3,3′-dihydroxy-4,4′-biphenanthryl (**8**) that are essentially the same as those for the binaphthyl analog **1a** (Scheme 5) [13].

Recently we found a new catalytic method for the preparation of enantiomerically pure axially chiral biaryls. That is an enantioposition-selective substitution reaction of one of the two enantiotopic triflate



(a) H_2 (1 atm), 10% Pd-C, *i*-Pr_2NEt (2 eq) (100%). (b) Tf_2O (1.2 eq), pyridine (2.5 eq) (92%). (c) Ph_2POH (2 eq), $Pd(OAc)_2$ (5 mol %), dppb (5 mol %), *i*-Pr_2NEt (4 eq), DMSO, 100 °C, 8 h (88%). (d) Et_3N (20 eq), $HSiCl_3$ (5 eq),toluene, 100 °C, 16 h, (**1j**, 90%).

Scheme 4.



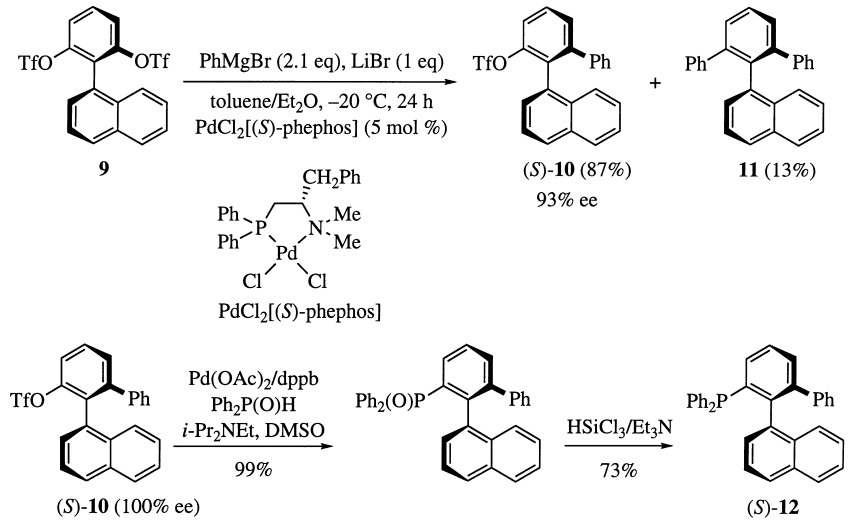
(*R*)-**8** (*R*)-MOP-phen (**7**)

(a) Tf_2O, py (100%). (b) Ph_2POH, $Pd(OAc)_2$, dppp, *i*-Pr_2NEt, DMSO (70%). (c) aq NaOH, 1,4-dioxane, methanol (99%). (d) MeI, K_2CO_3, acetone (97%). (e) Et_3N, $HSiCl_3$, toluene (91%).

Scheme 5.

groups on achiral biaryl ditriflates (Scheme 6) [14]. One of the monosubstitution products was readily converted into the enantiomerically pure monophosphine ligand. Thus, the reaction of 1-[2,6-bis[[(trifluoromethyl)sulfonyl]oxy]-phenyl]naphthalene (**9**) with phenylmagnesium bromide in the presence of 5 mol% of $PdCl_2$[(*S*)-phephos], where phephos stands for 2-(dimethylamino)-1-(diphenylphosphino)-3-phenylpropane [15], and 1 equiv of lithium bromide at −30°C for 48 h gave an 87% yield of axially chiral monophenylated biaryl (*S*)-**10** in 93% ee and a 13% yield of diphenylated biaryl **11**. The biaryl **10** is readily made enantiomerically pure with high recovery by simple recrystallization. The enantiomerically pure monotriflate (*S*)-**10** was subjected to the palladium-catalyzed diphenylphosphinylation, followed by reduction of diphenylphosphine oxide with trichlorosilane and triethylamine, giving the new axially chiral triarylmonophosphine (*S*)-**12**.

The crystal structure of *trans*-[$PdCl_2${(*R*)-MeO-MOP}$_2$] is shown in Fig. 2 [16]. The complex has a square planar geometry with two phosphorus atoms and two chlorine atoms, where the MOP ligand coordinates to palladium with the phosphorus atom as a monodentate ligand. The phosphorus atoms or chlorine atoms are *trans* to each other. It should be noted that the naphthyl ring having a methoxy group plays an important role in the construction of the chiral environment of the palladium. Thus, the naphthyl ring A (A′) points toward the vicinity of palladium



Scheme 6.

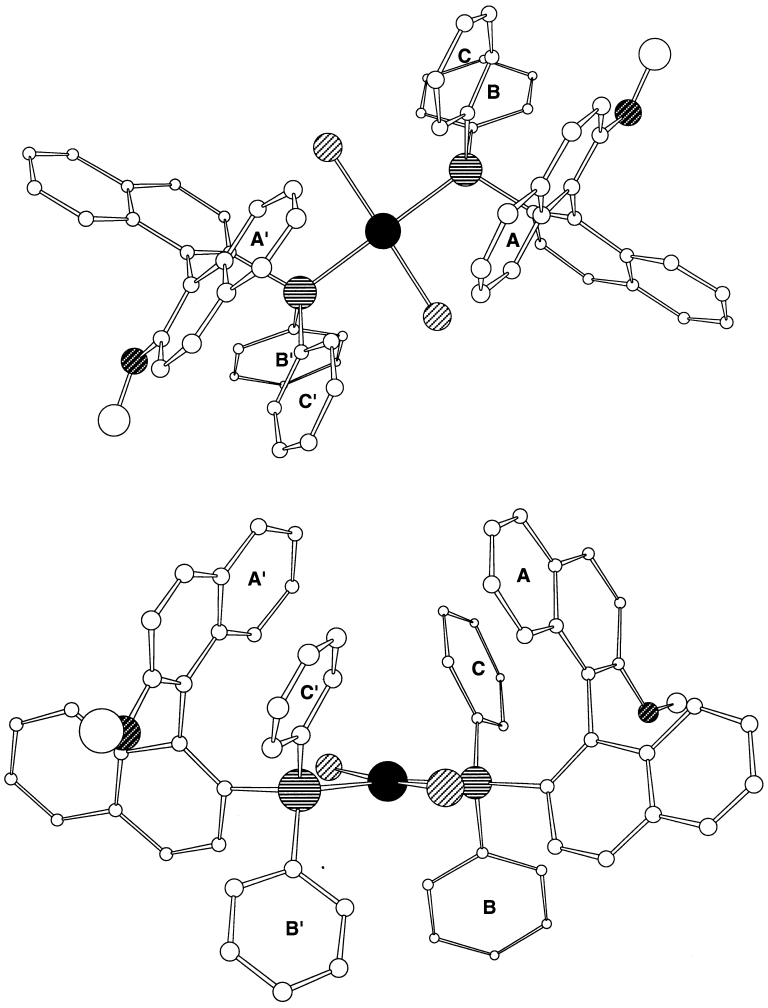


Fig. 2. Molecular structure for *trans*-$PdCl_2\{(R)$-MeO-MOP$\}_2\cdot Et_2O$. Ether molecule is omitted for simplicity.

while the methoxy group is located in the side opposite palladium. The conformation of the naphthyl group where the C2′ substituent is well removed from the palladium center is interesting: the phenyls B (B′) and C (C′) are situated below and above the plane around the palladium atom. These structural features are very different from those commonly observed in complexes coordinated with chiral bidentate bis(phosphino) ligands such as BINAP. [3]

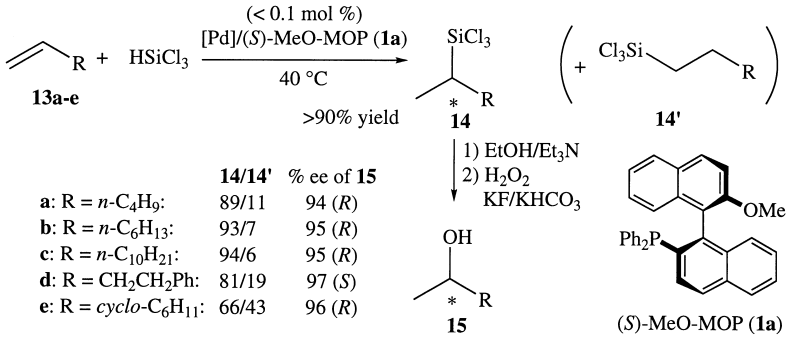
[3] For example, the structure of $PdCl_2\{(R)$-BINAP$\}$ has been reported, see [17].

3. Asymmetric hydrosilylation of simple terminal olefins

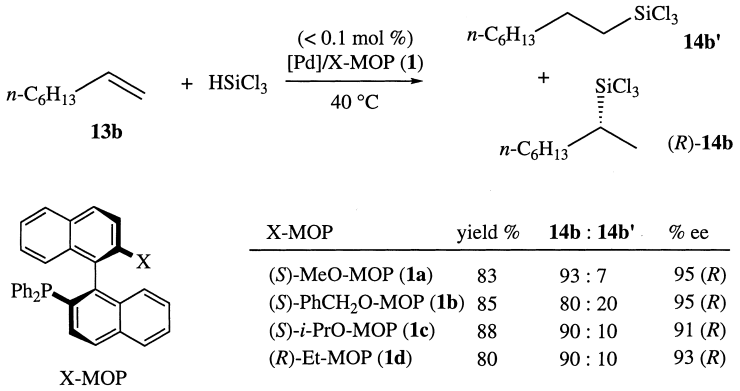
Hydrosilylation of terminal olefins catalyzed by platinum, rhodium, or nickel complexes is known to proceed with anti-Markovnikov selectivity to 1-silylalkanes (see Footnote 2). In order to develop a catalyst which possesses high catalytic activity, high regioselectivity in giving 2-silylalkanes, and high enantioselectivity in the hydrosilylation, we examined several types of phosphine–palladium catalysts for the reaction of 1-hexene (**13a**) with trichlorosilane. Palladium complexes coordinated with a chelating bis(phos-

phine), 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 upon elevation of the reaction temperature to 80°C. However, the reaction took place at 40°C with monodentate phosphine ligands, though the chemical yields in forming hexylsilanes were low. For example, the reaction in the presence of 0.1 mol% of a palladium–triphenylphosphine catalyst (P/Pd = 2/1) at 40°C for 24 h gave 12% yield of the hydrosilylation products consisting of 2-hexylsilane **14a** and its 1-isomer **14′a** in a ratio of 9/91, the hydrosilylation being accompanied by isomerization of 1-hexene into internal olefins. The regioselectivity for forming 2-silylhexane **14a** was increased to some extent by the use of sterically more bulky monophosphine ligands, pentafluorophenyl(diphenyl)phosphine and tris(2-methylphenyl)phosphine giving **14a** with 15 and 22% regioselectivity, respectively, though the low chemical yield (<20%) was still the plague of this reaction. 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 a square planar palladium(II) intermediate $PdH(SiCl_3)L(CH_2{=}CHR)$ (L = monophosphine) that offers a coordination site for the activation of the olefin while the latter cannot. Studies of the effects of monodentate phosphine ligands on the catalytic activity and the regioselective formation of 1-alkylsilanes or 2-alkylsilanes in the palladium-catalyzed hydrosilylation revealed that (*S*)-2-(diphenyl phosphino)-2′-methoxy-1,1′-binaphthyl (MeO-MOP, **1a**) is a unique ligand for the hydrosilylation, its palladium complex exhibiting both high catalytic activity and unusually high regioselectivity in forming 2-alkylsilanes and, moreover, high enantioselectivity [10,16]. The predominant formation of 2-alkylsilanes from aliphatic 1-olefins has never before been observed with any transition-metal catalysts. Mechanistic studies using deuteriated olefins suggested that the catalytic cycle includes both Pd(1-alkyl)L(silyl) and Pd(2-alkyl)L(silyl) intermediates which are in equilibrium with one another and that the MOP ligand can accelerate reductive elimination of 2-silylalkane from the 2-alkylpalladium intermediate [18].

The results obtained for the asymmetric hydrosilylation of 1-alkenes **13** with trichlorosilane [10,16] are summarized in Scheme 7. The hydrosilylation products, 2-alkyl(trichloro)silanes **14** were readily converted into optically active 2-alkanols **15** by treatment of **12** with $EtOH/Et_3N$ followed by oxidation of the resulting (triethoxy)silanes with hydrogen peroxide in the presence of a fluoride anion [19–24]. The terminal olefins, 1-hexene (**13a**), 1-octene (**13b**), 1-dodecene (**13c**), 4-phenyl-1-butene (**13d**), and vinylcyclohexane (**13e**) were transformed efficiently into the corresponding optically active alcohols **15** with enantioselectivities ranging between 94 and 97% ee 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 **13a–d** substituted with a primary alkyl group. Lower regioselectivity was observed with vinylcyclohexane (**13e**) which is substituted with a sterically bulky group on the double bond. Asymmetric hydrosilylation of 4-pentenyl benzoate and



Scheme 7.



X-MOP	yield %	**14b** : **14b'**	% ee
(*S*)-MeO-MOP (**1a**)	83	93 : 7	95 (*R*)
(*S*)-$PhCH_2O$-MOP (**1b**)	85	80 : 20	95 (*R*)
(*S*)-*i*-PrO-MOP (**1c**)	88	90 : 10	91 (*R*)
(*R*)-Et-MOP (**1d**)	80	90 : 10	93 (*R*)

Scheme 8.

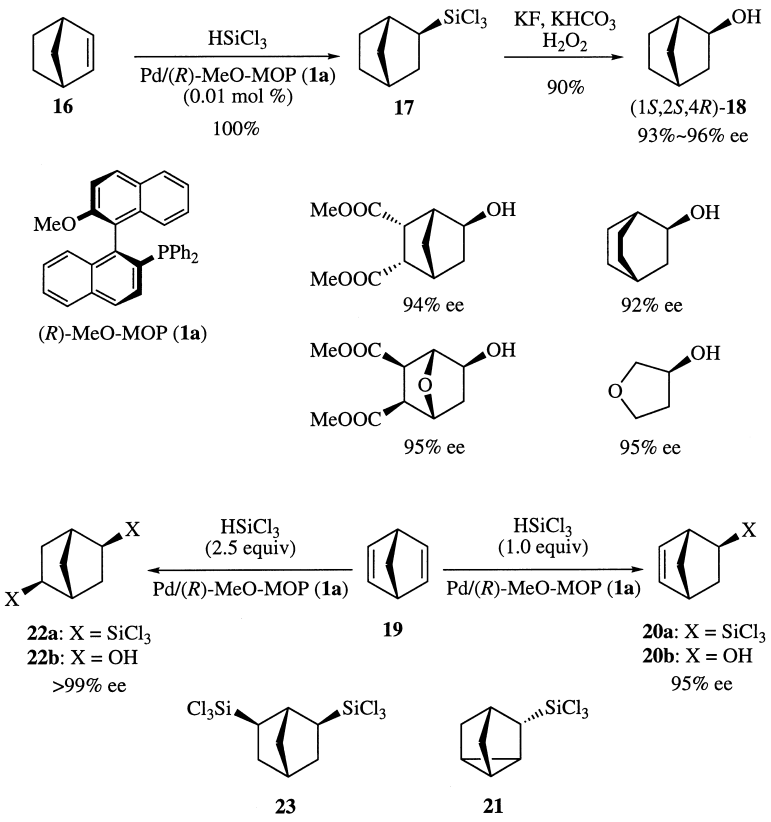
1,5-heptadiene gave corresponding 2-alkanols of 90 and 87% ee, respectively, the ester carbonyl and the internal double bond remaining intact [16]. It should be noted that the palladium–MOP complex is highly active as a catalyst, hydrosilylation taking place with a mere 0.01 mol% of the catalyst material.

The high selectivity was also observed with MOP ligands **1b**–**d**, which have other substituents than methoxy at 2′ position [16] (Scheme 8). Thus, the hydrosilylation of 1-octene (**13b**) with MOP ligands substituted with benzyloxy or isopropoxy gave over 91% enantioselectivity and over 80% branch selectivity, suggesting that the steric bulkiness of the 2′-substituents has little influence on the present asymmetric hydrosilylation. The presence of an alkoxy group at the 2′ position is not essential for the high selectivity. Replacement of the alkoxy group by an alkyl group did not affect the selectivity. The lack of influence of the 2′-substituents on the stereoselectivity is ascribed to the conformation of the ligand on palladium, where 2′-substituent is located far away from the metal (see Fig. 2).

4. Asymmetric hydrosilylation of cyclic olefins

We have applied the MOP/palladium-catalyzed hydrosilylation to the catalytic asymmetric functionalization of a meso bicyclo[2.2.1] system [25] since the optically active bicyclo[2.2.1]heptane derivatives represented by norbornanol are indispensable as versatile chiral building blocks for the synthesis of a variety of important compounds. The hydrosilylation of norbornene (**16**) with trichlorosilane took place at 0°C in the presence of 0.01 mol% of the MOP/palladium catalyst to give a quantitative yield of *exo*-2-(trichlorosilyl)-norbornane (**17**) as a single product (Scheme 9). Direct oxidation of **17** with hydrogen peroxide in the presence of a large excess of potassium fluoride and potassium bicarbonate gave *exo*-2-norbornanol (**18**) in yields greater than 90%, which was shown to be the (1*S*,2*S*,4*R*)-isomer by its optical rotation (93% ee). The hydrosilylation, carried out at −20°C, raised the enantiomeric excess to 96% ee. Bicyclo[2.2.2]octene, a diester of norbornenedicarboxylic acid, and 2,5-dihydrofuran derivatives [26] were also successfully subjected to the asymmetric hydrosilylation–oxidation under similar reaction conditions to give the corresponding optically active alcohols with the enantioselectivity being in excess of 92%.

It is remarkable that the monofunctionalization of norbornadiene (**19**) giving *exo*-5-trichlorosilyl-2-norbornene (**20a**) is effected by the palladium–MOP catalyst with high chemo and enantioselectivity [25]. This is in striking contrast to the reaction catalyzed by chloroplatinic acid or palladium–triphenylphosphine which gives nortricyclene **21** as a major product. Thus, the reaction of **19** with 1 equiv of trichlorosilane and the palladium–MOP catalyst (0.1 mol%) followed by the hydrogen peroxide oxidation gave (1*R*,4*R*,5*S*)-*exo*-5-hydroxy-2-norbornene (**20b**) with 95% ee. Reacting **19** with 2.5 equiv of trichlorosilane induced enantioselective hydrosilylation in both double bonds, thus giving a 78% yield of chiral disilyl-



Scheme 9.

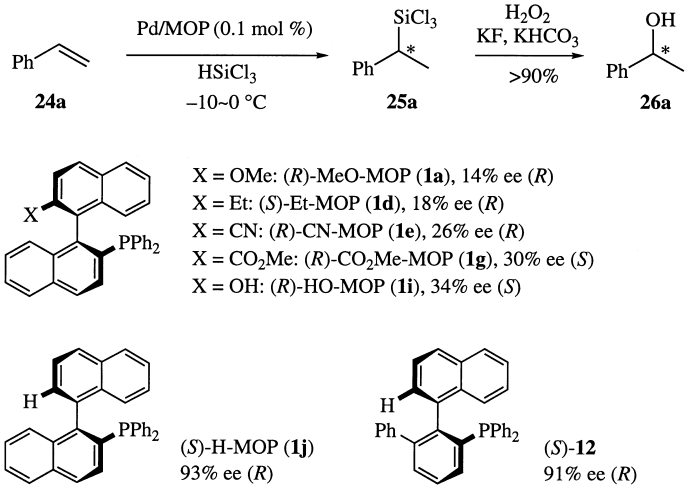
norbornane **22a** and the meso isomer **23** in a ratio of 18:1. The oxidation of **22a** gave the diol (1*R*,2*S*,4*R*,5*S*)-**22b** with >99% ee, the high purity attained was due to the expected double stereoselection.

5. Asymmetric hydrosilylation of styrenes

Although simple terminal olefins such as 1-octene and cyclic olefins such as norbornene have been converted efficiently into the corresponding secondary alcohols with over 90% enantioselectivity by use of the palladium catalyst coordinated with MeO-MOP (**1a**); such high selectivity has not been observed in the hydrosilylation of styrene derivatives.[4] Thus, the palladium-catalyzed hydrosilylation of styrene (**24a**) with trichlorosilane in the presence of MeO-MOP (**1a**) ligand under standard conditions (without solvent), followed by oxidation, gave 1-phenylethanol (**26a**) of only 14% ee. Use of benzene as solvent for the hydrosilylation improved the enantioselectivity to 71%. Although this value is the highest for the hydrosilylation of styrene at this moment, it is still low compared with the selectivity observed in the reaction of simple terminal olefins [31].

We have examined MOP ligands, where the methoxy group at the 2′ position in MeO-MOP is replaced by several groups, for their enantioselectivity in the palladium-catalyzed asymmetric hydrosilylation of styrene (**24a**) (Scheme 10). The enantiomeric purities and absolute configuration of alcohol **26a** obtained with Et-MOP (**1d**), CN-MOP (**1e**), CO_2Me-MOP (**1g**), and HO-MOP (**1i**) are 18% ee (*R*), 26% ee (*R*), 30% ee (*S*), and 34% ee (*S*), respectively. These results suggest that the electronic nature of

[4] For the asymmetric hydrosilylation of styrene with other chiral ligands, see [27–30].

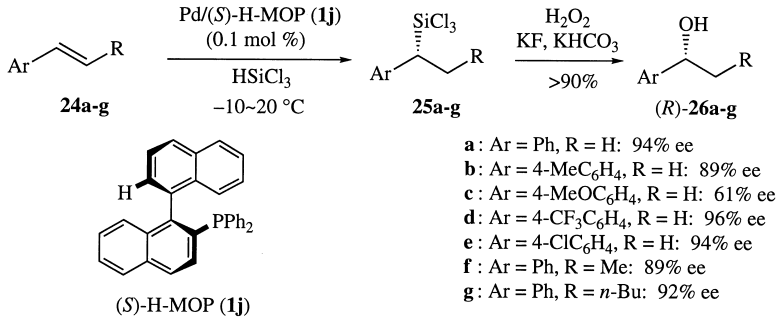


Scheme 10.

the substituent is not a decisive factor in the enantioselection since all of the MOPs substituted with methoxy, hydroxy, methoxycarbonyl, cyano, and ethyl groups show low enantioselectivity, irrespective of their electron-withdrawing or electron-donating character. It turned out that H-MOP (**1j**), which has the same 1,1′-binaphthyl skeleton as MeO-MOP but lacks the methoxy group, is particularly effective for the palladium-catalyzed hydrosilylation of styrene [32]. Hydrosilylation of styrene (**24a**) with trichlorosilane in the presence of 0.1 mol% of H-MOP–palladium catalyst, generated in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and (*S*)-H-MOP (**1j**), at 0°C for 12 h gave a quantitative yield of 1-phenyl-1-trichlorosilylethane (**25a**) as a single regioisomer, which was converted into (*R*)-1-phenylethanol (**26a**) in 97% yield by the oxidative cleavage of the carbon–silicon bond. The enantiomeric excess determined by HPLC analysis with a chiral stationary phase column was 93% ee. The hydrosilylation carried out at −10°C raised the enantiomeric excess slightly to 94% ee. The monophosphine (*S*)-**12** which was prepared through the catalytic asymmetric cross-coupling was as effective as (*S*)-H-MOP (**1j**) for the hydrosilylation of styrene giving (*R*)-**26a** of 91% ee [14]. Neither of the ligands (*S*)-**1j** or (*S*)-**12** has any substituent at the 2′ position. It follows that the small size of the hydrogen at the 2′ position in H-MOP (**1j**) is important for high enantioselectivity. The dihedral angle between the two naphthyl rings in the binaphthyl skeleton, which is controlled by the steric bulkiness of the 2′-substituent, is presumably related to the enantioselectivity.

The H-MOP–palladium complex also catalyzed the asymmetric hydrosilylation of styrene derivatives substituted on the phenyl ring **24b–e** and β-alkyl-substituted styrenes **24f** and **g** to give the corresponding benzylic alcohols (*R*)-**26b–g** [32] (Scheme 11). The enantioselectivity is high for the styrenes containing electron-withdrawing groups on the phenyl, *p*-chlorostyrene and *p*-trifluoromethylstyrene giving the corresponding alcohols in over 94% ee; however, unfortunately, the enantioselectivity is not so high for those containing electron-donating groups on the phenyl ring. The reaction of β-substituted styrenes proceeded with perfect regioselectivity to give the corresponding benzylic alcohols of around 90% ee. Interestingly, H-MOP–palladium catalyst was less enantioselective and/or less active than MeO-MOP–palladium for the hydrosilylation of non-styrene type olefins such as 1-octene and norbornene.

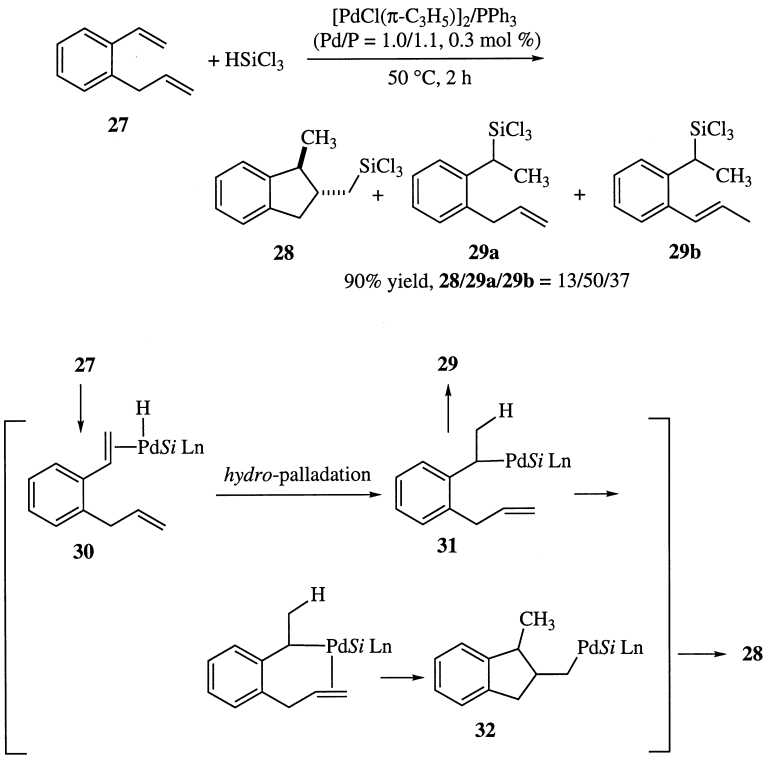
Palladium-catalyzed hydrosilylation of styrene has been demonstrated to proceed with the hydro-palladation mechanism (not silyl-palladation) in the hydrosilylation of *o*-allylstyrene (**27**) with trichlorosilane [33]. In the presence of 0.3 mol% of a palladium catalyst bearing triphenylphosphine at 50°C, *o*-allylstyrene (**27**) gave *trans*-1-methyl-2-(trichlorosilylmethyl)-indan (**28**) together with the simple hydro-



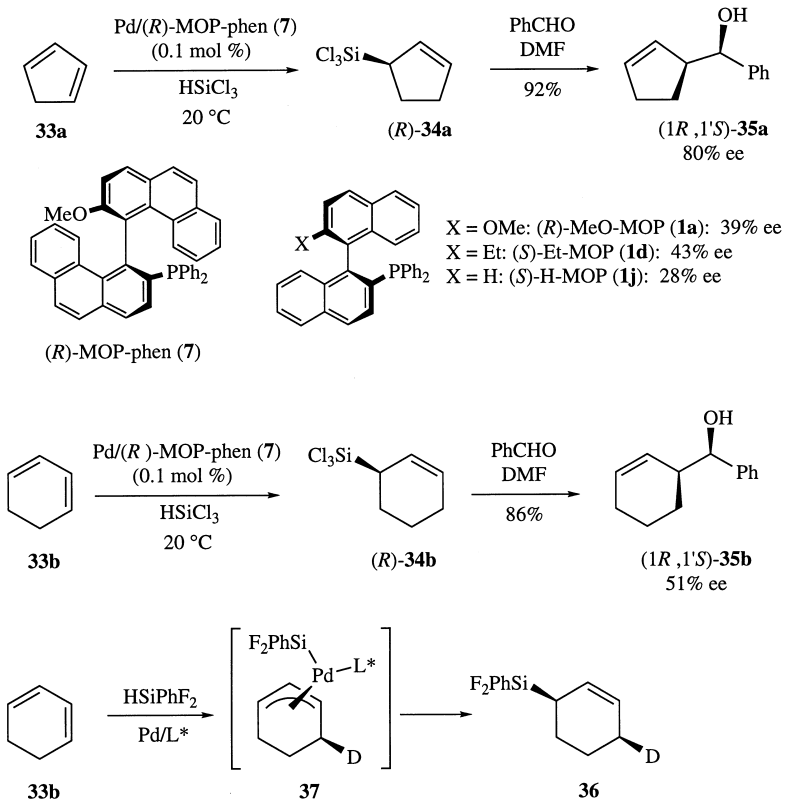
Scheme 11.

silylation products on the styrene double bond, 1-(2-(2-propenyl)phenyl)-1-trichlorosilylethane (**29a**), and 1-(2-((*E*)-1-propenyl)phenyl)-1-trichlorosilylethane (**29b**) (Scheme 12). Under similar reaction conditions, the reaction of styrene with trichlorosilane gave a quantitative yield of 1-phenyl-1-(trichlorosilyl)ethane while allylbenzene did not give silylation products.

The formation of indan derivative **28** is accounted for by the hydro-palladation mechanism. Hydro-palladation of the double bond of vinyl group forming **31** followed by insertion of the double bond of the allyl group into the alkyl-palladium bond forms five-membered-ring intermediate **32** which undergoes reductive elimination leading to **28**.



Scheme 12.



Scheme 13.

6. Asymmetric hydrosilylation of 1,3-dienes

Palladium-catalyzed hydrosilylation of 1,3-dienes is one of the important synthetic methods for allylic silanes, and considerable attention has been paid to their asymmetric synthesis by this catalytic method. Unfortunately, the binaphthyl monophosphine, MeO-MOP (**1a**) or H-MOP (**1j**), is not as effective as a chiral ligand for the asymmetric hydrosilylation of 1,3-dienes as it is for other types of prochiral olefins shown above, where over 90% enantioselectivity is usually observed. We found that MOP-phen (**7**), which is the 4,4′-biphenanthryl analog of MeO-MOP, shows higher enantioselectivity than others in the hydrosilylation of cyclic 1,3-dienes to give optically active allylic silanes (Scheme 13) [34]. [5]

The reaction of cyclopentadiene (**33a**) with trichlorosilane in the presence of MOP-phen–palladium catalyst proceeded at 20°C in a 1,4-fashion to give a quantitative yield of (*R*)-3-(trichlorosilyl)cyclopentene (**34a**). The enantiomeric purity was determined to be 80% ee by HPLC analysis of (cyclopent-2-enyl)(phenyl)methanol (**35a**), which was obtained in 92% yield by treatment of the allylsilane **28a** with benzaldehyde in DMF according to Kobayashi's [39] procedure. Much lower enantioselectivity was observed in the hydrosilylation of **33a** with MOP ligands whose basic structure is the binaphthyl skeleton. Thus, MeO-MOP (**1a**), Et-MOP (**1d**), and H-MOP (**1j**) gave the allylsilane **34a** in 39, 43, and 28% ee, respectively. In the asymmetric hydrosilylation of 1,3-cyclohexadiene (**33b**), MOP-phen (**7**) also exhibited higher enantioselectivity than MeO-MOP (**1a**). The $S_{E'}$ allylation of benzaldehyde was demonstrated to proceed through a six-membered cyclic transition state by the stereochemical outcome in the reaction of

[5] For the asymmetric hydrosilylation of 1,3-dienes with other chiral ligands, see also [35–38].

the allylsilane (*R*)-**34b** forming the homoallyl alcohol (1*R*,1′*S*)-**35b**. The use of phenyldifluorosilane in place of trichlorosilane did not improve the enantioselectivity; however, the reaction with deuterium-labeled silane, $DSiF_2Ph$, gave us significant insight into the mechanism of palladium-catalyzed hydrosilylation of 1,3-dienes. The reaction of 1,3-cyclohexadiene (**33b**) with $DSiF_2Ph$ gave *cis*-3-(phenyldifluorosilyl)-6-deuteriocyclohexene (**36**) as a single isomer without any diastereo- or regioisomers, demonstrating that 1,4-*cis*-addition is an exclusive pathway. The π-allylpalladium intermediate **37**, which is formed by the addition of palladium-hydride on a PdH(Si)L* species to the diene and has the silyl group located at the *trans* position to the π-allyl carbon next to the deuterated carbon, rapidly undergoes reductive elimination forming **36** before *trans–cis* isomerization of the intermediate **37** can occur. It follows that the stereochemical outcome is determined in the enantioselective addition of palladium-hydride to the diene.

7. Concluding remarks

The axially chiral MeO-MOP ligand was also found to be very useful for several other asymmetric reactions where chelating bisphosphine–metal complexes cannot be used because of their low catalytic activity or low selectivity towards a desired reaction pathway. Examples are: (i) palladium-catalyzed asymmetric 1,4-hydroboration of 1,3-enynes with catecholborane forming axially chiral allenylboranes [40,41]; (ii) palladium-catalyzed asymmetric reduction of allylic esters with formic acid which proceeds with high regioselectivity giving less-substituted olefins as well as with high enantioselectivity [42–48]; and (iii) palladium-catalyzed alkylation of allylic esters with soft carbon nucleophiles which produces allylic alkylation products with high enantioselectivity [49,50].

The MOP ligands can be modified on the side chain in the 2′ position as well as on the biaryl skeleton according to the demand of the reaction type and they are expected to find great utility in other types of catalytic asymmetric reactions, where the use of monodentate phosphine ligands is essential or favorable for steric and/or electronic reasons.

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