Asymmetric Hydrosilylation of Olefins Catalyzed by MOP-Palladium Complexes[†]

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Axially chiral monophosphines, 2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl (MeO–MOP, **1a**) and its biphenanthryl analog **5**, were prepared starting with homochiral 2,2'-dihydroxy-1,1'-binaphthyl and 3,3'-dihydroxy-4,4'-biphenanthryl, respectively. The palladium complexes coordinated with the MOP ligands are highly effective catalysts for several types of catalytic asymmetric reaction where chelating bisphosphine ligands cannot be used because of their low catalytic activity or low selectivity towards the desired reaction pathway. Palladium-catalyzed hydrosilylation of olefins is one of the typical examples. High enantioselectivity was observed in the asymmetric hydrosilylation of alkyl-substituted terminal olefins (92–97% ee), bicyclo[2.2.1]heptene derivatives (92–96% ee), styrene derivatives (89–96% ee), and cyclic 1,3-dienes (80% ee). The hydrosilylation products were efficiently converted into optically active alcohols by oxidation of the carbon–silicon bond.

Asymmetric reactions catalyzed by transition metal complexes containing optically active phosphine ligands have attracted significant interest owing to their synthetic utility.[1] One of the most exciting and challenging subjects in the research of catalytic asymmetric synthesis is the development of a chiral ligand which will influence the reaction efficiency in terms of catalytic activity and enantioselectivity. Most of the chiral phosphine ligands prepared and used for catalytic asymmetric reactions hitherto are the bisphosphines, which in the general case are anticipated to be effective in constructing a chiral environment by chelate coordination to a metal. The representatives are BINAP[2] and ferrocenylbisphosphines.[3–5] These chelating bisphosphines have been demonstrated to be effective for several types of asymmetric reaction including rhodium- or ruthenium-catalyzed hydrogenation,[2] palladium- or nickel-catalyzed allylic substitution reactions,[4] and gold- or silver-catalyzed aldol reactions.[5] On the other hand, there have been reported only a limited number of monodentate chiral phosphine ligands, probably because they have been described as being of little practical use.[1,6] However, there exist transition-metal-catalyzed reactions where the bisphosphine–metal complexes cannot be used because of their low catalytic activity and/or low selectivity toward a desired reaction pathway and therefore chiral monodentate phosphine ligands are

required for the catalytic asymmetric synthesis to be viable. We have previously reported a nickel-catalyzed asymmetric cross-coupling forming axially chiral binaphthyls which was realized for the first time by use of a monophosphine ligand containing ferrocene planar chirality,[7] and we have continued our efforts to develop new enantioselective chiral monodentate phosphine ligands for transition-metal-catalyzed reactions where only a monodentate phosphine ligand can be used. We found that high enantioselectivity and high catalytic activity can be achieved in the palladium-catalyzed asymmetric reactions, including hydrosilylation of olefins, 1,4-hydroboration of 1,3-enynes, and reduction of allylic esters with formic acid, by use of palladium complexes coordinated with an axially chiral monodentate phosphine ligand, 2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl (MeO–MOP) or its biphenanthryl analog (MOP-phen). Here we describe the preparation of the chiral monodentate phosphine ligands (MOP ligands) and their use in palladium-catalyzed asymmetric hydrosilylation of various types of olefin.

Preparation of MOP ligands

The chiral binaphthyl skeleton was chosen as the basic structure of the monodentate phosphine ligand since 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

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literature.[1] Morgans and coworkers have reported[8] the selective monophosphinylation of 2,2'-bis(trifluoro-methanesulfonyloxy)-1,1'-binaphthyl (2) with diphenyl-phosphine oxide in the presence of a palladium catalyst giving a high yield of 2-diphenylphosphinyl-2'-trifluoro-methanesulfonyloxy-1,1'-binaphthyl (3), which 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 function-ality for the introduction of various types of functional group onto the binaphthyl.

The conversion of 3 into 2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl (MeO–MOP, 1a) was achieved[9,10] 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 a 99% yield of the 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 trichloro-silane 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 phos-phine oxide.
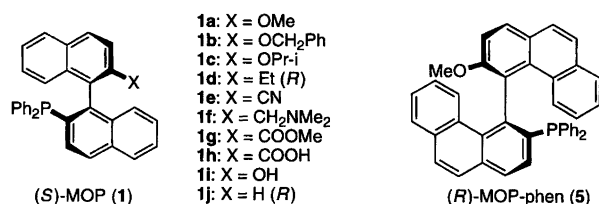
The trifluoromethanesulfonyloxy group on the 2' po-sition can be replaced by an alkyl group by nickel-cata-lyzed cross-coupling with the Grignard reagent. Introduc-tion of an ethyl group on (S)-3 with ethylmagnesium bromide followed by the reduction with trichlorosilane gave (R)-1d in 64% overall yield. A cyano group can be also introduced at the 2' position of 3 in a quantitative yield by nickel-catalyzed cyanation with potassium cyan-ide to give 1e after the reduction of the phosphine oxide.[11] The reduction of the cyano group with diborane followed

by methylation with formaldehyde/formic acid gave ami-nophosphine 1f. The MOP ligands 1g and 1h which con-tain an ester and carboxylic acid, respectively, were pre-pared through palladium-catalyzed monocarbonylation of the bis(triflate) 2 giving 2-methoxycarbonyl-2'-trifluo-romethanesulfonyloxy-1,1'-binaphthyl.[11] The MOP de-rivative (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 de-rivatives, was prepared staring with (R)-2-hydroxy-1,1'-binaphthyl by a sequence of reactions including the pal-ladium-catalyzed phosphinylation and reduction of the resulting phosphine oxide.[11] The enantiomerically pure monophosphine containing the biphenanthryl skeleton, MOP-phen (5), was also prepared by a sequence of the reactions from 3,3'-dihydroxy-4,4'-biphenanthryl which are essentially the same as those for the binaphthyl ana-log 1a.[12]

The crystal structure of trans-[PdCl₂{(R)-MeO–MOP}₂] is shown in Fig. 1.[13] 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, while the methoxy group is located in the side opposite palladium. The conformation of the naph-thyl 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 com-plexes coordinated with chiral bidentate bis(phosphino) ligands such as BINAP.[14]
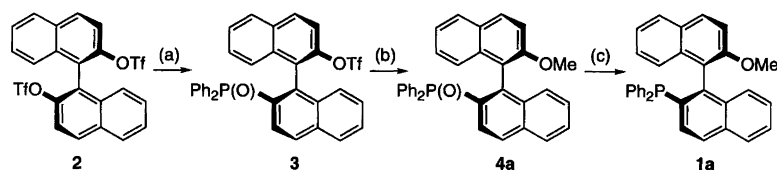
(a) Ph₂POH (2 eq), Pd(OAc)₂ (5 mol %), dppb (5 mol %), i-Pr₂NEt (4 eq), DMSO, 100 °C, 12 h (3, 95%). (b) (i) 3N NaOH, 1,4-dioxane, methanol. (ii) MeI (4 eq), K₂CO₃ (4 eq), acetone, reflux, 3 h (4a, 99%). (c) Et₃N (20 eq), HSiCl₃ (5 eq), xylene, 120 °C, 5 h, (1a, 97%).

1a: X = OMe
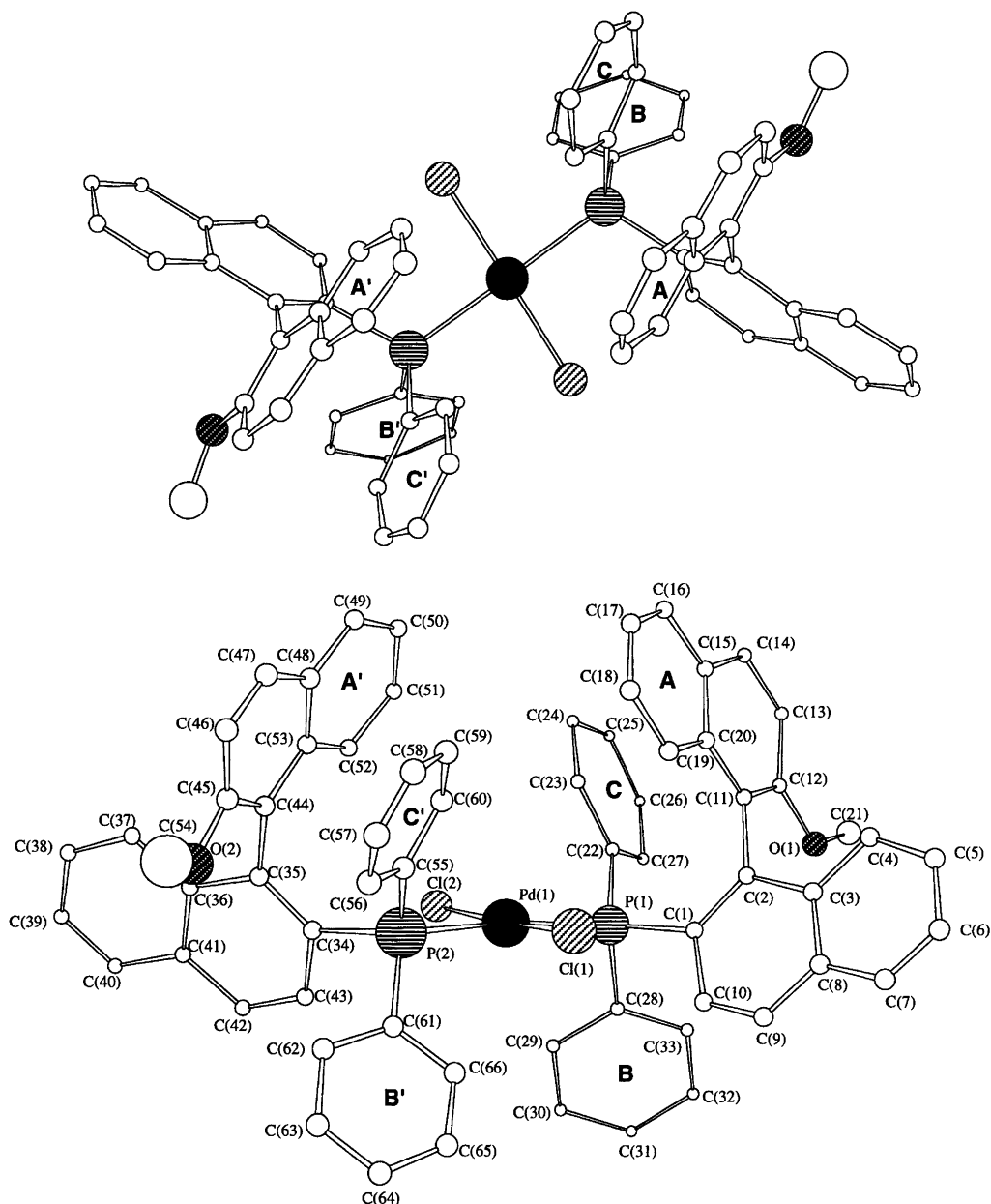1b: X = OCH₂Ph
1c: X = OPr-i
1d: X = Et (R)
1e: X = CN
1f: X = CH₂NMe₂
1g: X = COOMe
1h: X = COOH
1i: X = OH
1j: X = H (R)

(S)-MOP (1)

(R)-MOP-phen (5)

Scheme 1.

Fig. 1. Molecular structure and atom numbering scheme for *trans*-PdCl$_2$[(*R*)-MeO-MOP]$_2$. The ether molecule is omitted for simplicity.

Palladium-catalyzed 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 mainly been effected by asymmetric hydroboration with a stoichiometric amount of a chiral hydroborating agent.[15] Use of catalytic systems for asymmetric hydroboration has not always been successful in terms of enantioselectivity or catalytic activity.[16] Catalytic asymmetric hydrosilylation has been also reported to produce optically active alcohols,[17] but the reaction is typically one of low enantioselectivity.[1]

Asymmetric hydrosilylation of simple terminal olefins

It is well documented[18] that the hydrosilylation of terminal olefins is catalyzed by platinum, rhodium, or nickel complexes to proceed with anti-Markovnikov selectivity leading to 1-silylalkanes. Rather surprisingly, little attention has been paid to the use of palladium catalysts for the hydrosilylation of 1-alkenes[19] in spite of their frequent use for the reaction of 1,3-dienes and styrenes.[17,18] In order to develop a catalyst which possesses high catalytic activity, is highly regioselective in giving 2-silylalkanes, and is highly enantioselective in the hydrosilylation, we examined several types of phosphine-palladium catalyst
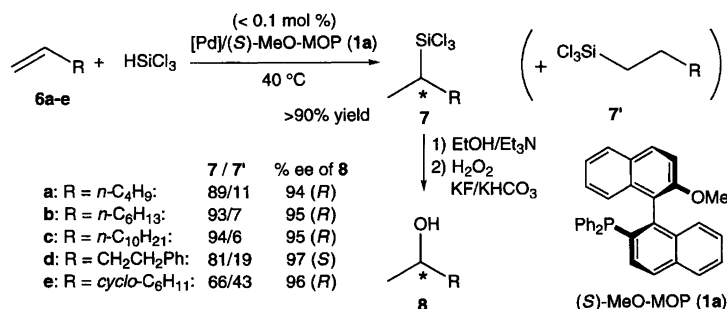
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for the reaction of 1-hexene (**6a**) with trichlorosilane. It was found that palladium complexes coordinated with a chelating bis(phosphine), 1,4-bis(diphenylphosphino)butane (dppb), 2,3-bis(diphenylphosphino)butane (chiraphos), or 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), did not catalyze the hydrosilylation at all even upon elevation 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 **7a** and its 1-isomer **7'a** in a ratio of 9/91, the hydrosilylation being accompanied by isomerization of 1-hexene into internal olefins. The regioselectivity forming 2-silylhexane **7a** was increased to some extent by use of sterically more bulky monophosphine ligands, pentafluorophenyl(diphenyl)phosphine and tris(2-methylphenyl)phosphine giving **7a** 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 regioselectivity forming 1-alkylsilanes or 2-alkylsilanes in the palladium-catalyzed hydrosilylation revealed that (S)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl (MeO–MOP, **1a**) is a unique ligand for the hydrosilylation, its palladium complex exhibiting both high catalytic activity and high unusual regioselectivity in forming 2-alkylsilanes, and moreover high enantioselectivity.[9] 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.[20]

The results obtained for the asymmetric hydrosilylation of 1-alkenes **6** with trichlorosilane[9] are summarized in Scheme 2. The hydrosilylation products, 2-alkyl(trichloro)silanes **7** were readily converted into optically active 2-alkanols **8** by treatment of **7** with EtOH–Et$_3$N followed by oxidation of the resulting (triethoxy)silanes with hydrogen peroxide in the presence of a fluoride anion.[21] The terminal olefins, 1-hexene (**6a**), 1-octene (**6b**), 1-dodecene (**6c**), 4-phenyl-1-butene (**6d**), and vinylcyclohexane (**6e**) were transformed efficiently into the corresponding optically active alcohols **8** 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 **6a–d** substituted with a primary alkyl group. Lower regioselectivity was observed with vinylcyclohexane (**6e**), which is substituted with a sterically bulky group on the double bond. It should be noted that the palladium–MOP complex is highly active as a catalyst, the hydrosilylation taking place with a mere 0.01 mol% of the catalyst material.
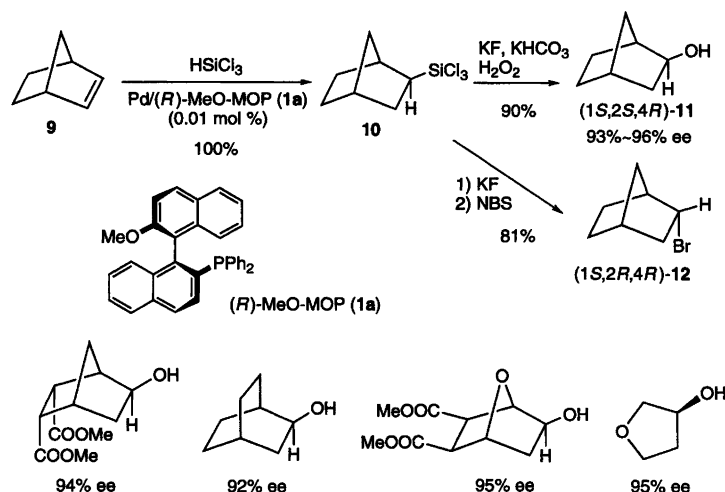
Asymmetric hydrosilylation of cyclic olefins

Asymmetric synthesis through selective monofunctionalization of enantiotopic positions is contended as being one of the most attractive strategies for one-step construction of multiple chiral carbon centers.[22] In spite of the impressive development of enantioface selective asymmetric reactions catalyzed by transition metal complexes, the enantioposition selective approach is yet to be developed.[1] We have applied the MOP–palladium-catalyzed hydrosilylation to the catalytic asymmetric functionalization of a *meso*-bicyclo[2.2.1] system,[23] because 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 (**9**) 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 (**10**) as a single product (Scheme 3). Direct oxidation of **10** with hydrogen

	7 / 7'	% ee of 8
a: R = *n*-C$_4$H$_9$:	89/11	94 (*R*)
b: R = *n*-C$_6$H$_{13}$:	93/7	95 (*R*)
c: R = *n*-C$_{10}$H$_{21}$:	94/6	95 (*R*)
d: R = CH$_2$CH$_2$Ph:	81/19	97 (*S*)
e: R = *cyclo*-C$_6$H$_{11}$:	66/43	96 (*R*)

Scheme 2.

Scheme 3.

peroxide in the presence of a large excess of potassium fluoride and potassium bicarbonate gave exo-2-norbornanol (11) in yields greater than 90%, which was shown to be the 1S,2S,4R isomer by its optical rotation (93% ee). The hydrosilylation carried out at − 20°C raised the enantiomeric excess to 96% ee. The trichlorosilane 10 can be also converted into (1S,2R,4R)-endo-2-bromonorbornane (12) by treatment with an excess of potassium fluoride followed by bromination of the resulting pentafluorosilicate with N-bromosuccinimide.[24] Bicyclo[2.2.2]octene, a diester of norbornenedicarboxylic acid, and 2,5-dihydrofuran derivatives[25] 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%.
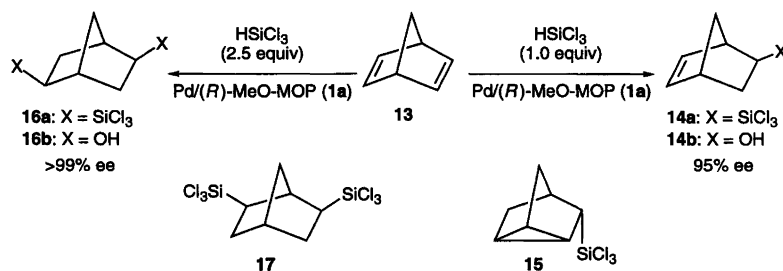
It is remarkable that the monofunctionalization of norbornadiene (13) giving exo-5-trichlorosilyl-2-norbornene (14a) is effected by the palladium–MOP catalyst with high chemo- and enantio-selectivity (Scheme 4).[23] It is in striking contrast with the reaction catalyzed by chloroplatinic acid or palladium–triphenylphosphine which gives nortricyclene 15 as a major product. Thus, the reaction of 13 with 1.0 equiv. of trichlorosilane and the palladium–MOP catalyst (0.1 mol%) followed by hydrogen peroxide oxidation gave (1R,4R,5S)-exo-5-hydroxy-

2-norbornene (14b) with 95% ee. Reacting 13 with 2.5 equiv. of trichlorosilane induced enantioselective hydrosilylation in both double bonds thus giving a 78% yield of chiral disilylnorbornane 16a and the meso isomer 17 in a ratio of 18:1. The oxidation of 16a gave the diol (1R,2S,4R,5S)-16b with >99% ee; the high purity attained was due to the expected double stereoselection.
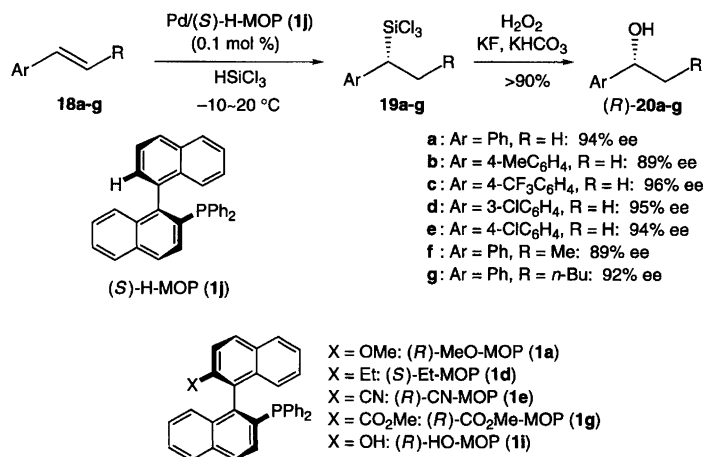
Asymmetric hydrosilylation of styrenes

Although simple terminal olefins such as 1-octene and cyclic olefins such as norbornene have been efficiently converted into the corresponding secondary alkyl 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.[17,26,27] It was found that H–MOP (1j), which has the same basic skeleton as MeO–MOP but lacks the methoxy group, is particularly effective for the palladium-catalyzed hydrosilylation of styrenes to give the corresponding benzylic alcohols with high enantiomeric purity, the enantioselectivity ranging from 89% to 96% ee (Scheme 5).[28]

Hydrosilylation of styrene (18a) with trichlorosilane in the presence of 0.1 mol% of H–MOP-palladium catalyst,

Scheme 4.

Pd/(S)-H-MOP (1j)
(0.1 mol %)

Ar ⌇⌇⌇ R ——————————→ Ar ⌇⌇⌇ R ——————————→ Ar ⌇⌇⌇ R
18a-g   HSiCl₃   19a-g   >90%   (R)-20a-g
             −10~20 °C

SiCl₃   H₂O₂
             KF, KHCO₃

OH

(S)-H-MOP (1j)

a : Ar = Ph, R = H: 94% ee
b : Ar = 4-MeC₆H₄, R = H: 89% ee
c : Ar = 4-CF₃C₆H₄, R = H: 96% ee
d : Ar = 3-ClC₆H₄, R = H: 95% ee
e : Ar = 4-ClC₆H₄, R = H: 94% ee
f : Ar = Ph, R = Me: 89% ee
g : Ar = Ph, R = n-Bu: 92% ee

X = OMe: (R)-MeO-MOP (1a)
X = Et: (S)-Et-MOP (1d)
X = CN: (R)-CN-MOP (1e)
X = CO₂Me: (R)-CO₂Me-MOP (1g)
X = OH: (R)-HO-MOP (1i)

Scheme 5.

generated *in situ* by mixing [PdCl(π-C₃H₅)]₂ and (S)-H–MOP (1j), at 0°C for 12 h gave a quantitative yield of 1-phenyl-1-trichlorosilylethane (19a) as a single regioisomer, which was converted into (R)-1-phenylethanol (20a) in 97% yield by oxidative cleavage[21] 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 slightly raised the enantiomeric excess to 94% ee.

Rather surprisingly, MeO–MOP (1a), which is substituted with a methoxy group at the 2′-position on H–MOP and has been used successfully for the asymmetric hydrosilylation of other types of olefin as shown above, is much less effective than H–MOP for the asymmetric hydrosilylation of styrene. Thus, the hydrosilylation of 18a in the presence of MeO–MOP–palladium catalyst under the same reaction conditions gave (R)-20a with only 14% ee. Several MOP derivatives containing other substituents at the 2′-position were also examined for their enantioselectivity in the hydrosilylation of styrene (18a). The enantiomeric purities and absolute configuration of alcohol 20a obtained with Et–MOP (1d), CN–MOP (1e), CO₂Me–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 the substituent is not a decisive factor in the enantioselection, all of the MOPs substituted with methoxy, hydroxy, methoxycarbonyl, cyano, and ethyl groups showing low enantioselectivity irrespective of their electron-withdrawing or electron-donating character. It follows that the small size of the hydrogen at the 2′-position in H–MOP (1j) is important for the 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 18b–e and β-alkyl-substituted styrenes 18f and 18g to give the corresponding benzylic

alcohols (R)-20b–g of over 89% ee. Interestingly, MeO–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.

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 so effective as a chiral ligand for the asymmetric hydrosilylation of 1,3-dienes as for that of other types of prochiral olefin shown above, where over 90% enantioselectivity is usually observed. We found that MOP–phen (5), which is 4,4′-biphenanthryl analog of MeO–MOP, shows higher enantioselectivity than others in the hydrosilylation of cyclic 1,3-dienes giving optically active allylic silanes (Scheme 6).[27,29,30]

The reaction of cyclopentadiene (21a) 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 (22a). The enantiomeric purity was determined to be 80% ee by HPLC analysis of (cyclopent-2-enyl)(phenyl)methanol (23a), which was obtained in 92% yield by treatment of the allylsilane 22a with benzaldehyde in DMF according to Kobayashi's procedure.[31] Much lower enantioselectivity was observed in the hydrosilylation of 21a with MOP ligands whose basic structure is the binaphthyl skeleton. Thus, MeO–MOP (1a), Et–MOP (1d), and H–MOP (1j) gave the allylsilane 22a in 39% ee, 43% ee, and 28% ee, respectively. In the asymmetric hydrosilylation of 1,3-cyclohexadiene (21b), MOP–phen (5) also exhibited higher enantioselectivity than MeO–MOP (1a). The S_E′ allylation of benzaldehyde was demonstrated to proceed through six-membered cyclic transition state by
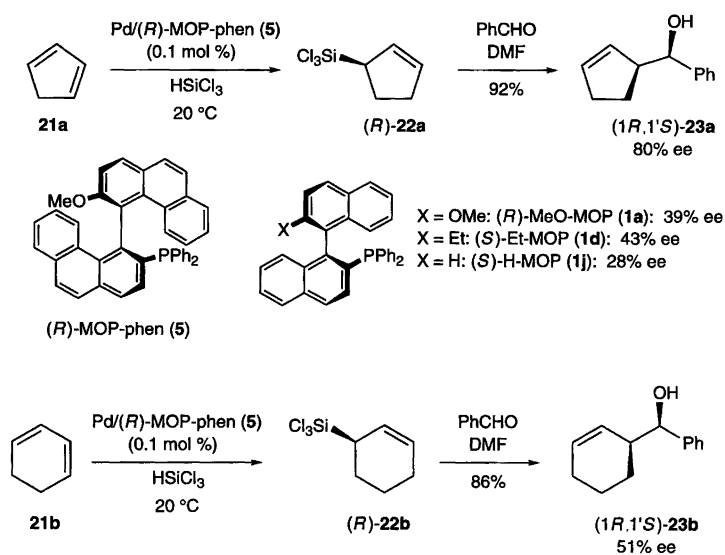
Scheme 6.

the stereochemical outcome in the reaction of the allylsilane (*R*)-*22b* forming the homoallyl alcohol (1*R*,1'*S*)-*23b*.

Other catalytic asymmetric reactions with MOP ligands

The MeO–MOP ligand was also found to be very useful for palladium-catalyzed asymmetric 1,4-hydroboration of 1,3-enynes with catechol–borane forming axially chiral allenylboranes. The use of a monodentate phosphine ligand for catalytic hydroboration is essential for the formation of allenylboranes by 1,4-addition, exclusive 1,2-addition on the triple bond that forms 1,3-dienylboranes taking place in the presence of bisphosphine ligands.[32] The allenylborane of not less than 61% ee was obtained in the reaction of 1-buten-3-yne with catechol–borane in the presence of palladium catalyst coordinated with MeO–MOP (**1a**).[33]

Palladium-catalyzed reduction of allylic esters with formic acid is another reaction where the use of a monodentate phosphine ligand is essential for high catalytic activity and for high regioselectivity giving less-substituted olefins.[34] Catalytic asymmetric reduction of 3,3-disubstituted 2-propenyl carbonate esters was achieved by use of MeO–MOP (**1a**) or MOP–phen (**5**) as a chiral phosphine ligand.[12,35] For example, the reduction of geranyl methyl carbonate with formic acid and 1,8-bis(dimethylamino)naphthalene in the presence of MOP–phen–palladium catalyst gave (*S*)-3,7-dimethyl-1,6-octadiene (**2a**) of 85% ee. A mechanism for the asymmetric induction is proposed on the basis of structural studies of PdCl(η³-1,1-dimethylallyl)[(*R*)-MOP] in solution and in the crystalline state. The MOP–phen–palladium catalyst is also effective for the asymmetric reduction of 3-alkyl-3-trialkylsilyl-2-propenyl methyl car-

bonates which gave optically active allylsilanes in up to 91% ee.[36]

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