ELSEVIER

Journal of Organometallic Chemistry 576 (1999) 195–202

Journal of Organometallic Chemistry

Review

Catalytic asymmetric reactions via π-allylpalladium complexes coordinated with chiral monophosphine ligands☆

Tamio Hayashi *

Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan

Received 1 September 1998

Abstract

Chiral monophosphines (MOPs), whose chirality is due to biaryl axial chirality, are prepared from enantiometrically pure 2,2′-dihydroxy-1,1′-binaphthyl and 3,3′-dihydroxy-4,4′-biphenanthryl. The representatives are 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MeO–MOP and 3-(diphenylphosphino)-3′-methoxy-4,4′-biphenanthryl (MOP–phen). The palladium complexes coordinated with the MOP ligands are highly effective catalysts for catalytic asymmetric allylic substitution reactions, where chelating bisphosphine ligands cannot be used because of their low catalytic activity or low selectivity towards the desired reaction pathway. The catalytic asymmetric reactions are: (1) asymmetric reduction of allylic esters with formic acid (93% ee). (2) Regio- and enantioselective alkylation of allyl esters (87% ee).

Keywords: π-Allylpalladium; Chiral monodendrate phosphine; Catalytic asymmetric reactions; Allylic substitution; Reduction

1. Introduction

Asymmetric reactions catalyzed by transition metal complexes coordinated with enantiomerically pure chiral ligands have attracted significant interest owing to their synthetic utility [1]. Among the transition metal catalysts used for the catalytic asymmetric reactions, palladium is recognized to be the most versatile metal, which catalyzes a wide variety of asymmetric reactions [2] including cross-coupling [3], hydrosilylation of olefins [4], Heck-type reaction [1,2], Wacker-type oxidation [5], and allylic substitution reactions [3,6].

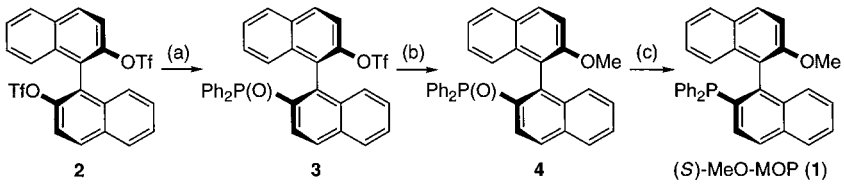
One of the most exciting and challenging subjects in the research of catalytic asymmetric synthesis is the development of a chiral ligand which will influence the reaction efficiency in terms of catalytic activity and enantioselectivity. Most of the chiral phosphine ligands prepared and used for catalytic asymmetric reactions hitherto are the bisphosphines which are, in general, anticipated to be effective in constructing a chiral environment by the chelate coordination to a metal [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 [1,7]. 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 prepared a series of monophosphine ligands, whose chirality is due to 1,1′-binaphthyl axial chirality, represented by MeO–MOP which stands for 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl and have found that high enantioselectivity and high catalytic activity can be achieved in some of the palladium-catalyzed asymmet-

☆ Dedicated to Professors J. Tsuji and R.F. Heck.

* Fax: +81-75-753-3988.

E-mail address: thayashi@kuchem.kyoto-u.ac.jp (T. Hayashi)

0022-328X/99/$ - see front matter
PII: S0022-328X(98)01058-4



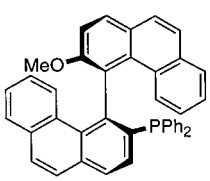
(a) Ph_2POH (2 eq), $Pd(OAc)_2$ (5 mol %), dppb (5 mol %), *i*-Pr_2NEt (4 eq), DMSO, 100 °C, 12 h (**3**, 95%). (b) (i) 3N NaOH, 1,4-dioxane, methanol. (ii) MeI (4 eq), K_2CO_3 (4 eq), acetone, reflux, 3 h (**4**, 99%). (c) Et_3N (20 eq), $HSiCl_3$ (5 eq), xylene, 120 °C, 5 h, (**1**, 97%).

Scheme 1.

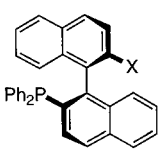
ric reactions. Here we describe the preparation of the chiral monodentate phosphine ligands (MOP ligands) and their use in the palladium-catalyzed asymmetric reactions which proceed through π-allylpalladium intermediates. The MOP-palladium catalysts have been found to be also useful for asymmetric hydrosilylation of olefins [4] and asymmetric 1,4-hydroboration of 1,3-enynes [8].

2. 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 literature [1]. Morgans and coworkers have reported [9] 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**), 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 functionality for the introduction of various types of functional groups onto the binaphthyl ring. The conversion of **3** into 2 - (diphenylphosphino) - 2′ - methoxy - 1,1′ - binaphthyl (MeO–MOP, **1**) 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*)-**4**. Reduction of the phosphine oxide with trichlorosilane and triethylamine in refluxing xylene led to (*S*)–MeO–MOP (**1**) in 97% yield. The overall yield from 2,2′-dihydroxy-1,1′-binaphthyl was about 90%.



(*R*)-MOP-phen (**5**)



X = OMe: (*S*)-MeO-MOP (**1**)

X = OCH_2Ph, OPr-*i*, Et, CN, CH_2NMe_2 COOMe, COOH, OH, H, etc.

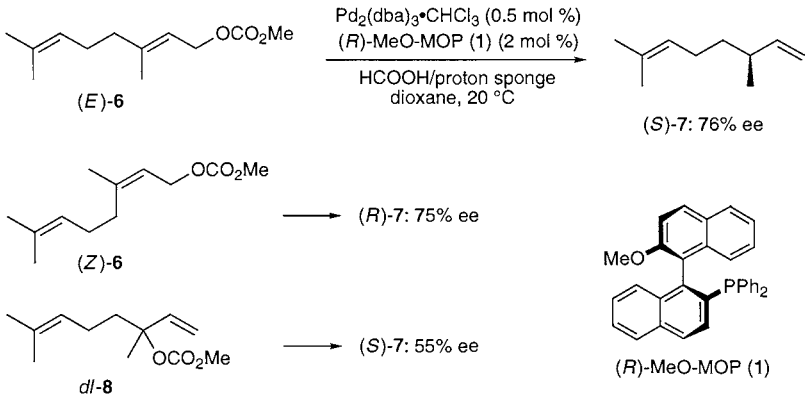
Scheme 2.

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 analog **1** [12]. Several MOP ligands containing other substituents X at 2′ position of the binaphthyl skeleton [11] were also prepared, some of which are shown in Scheme 2.

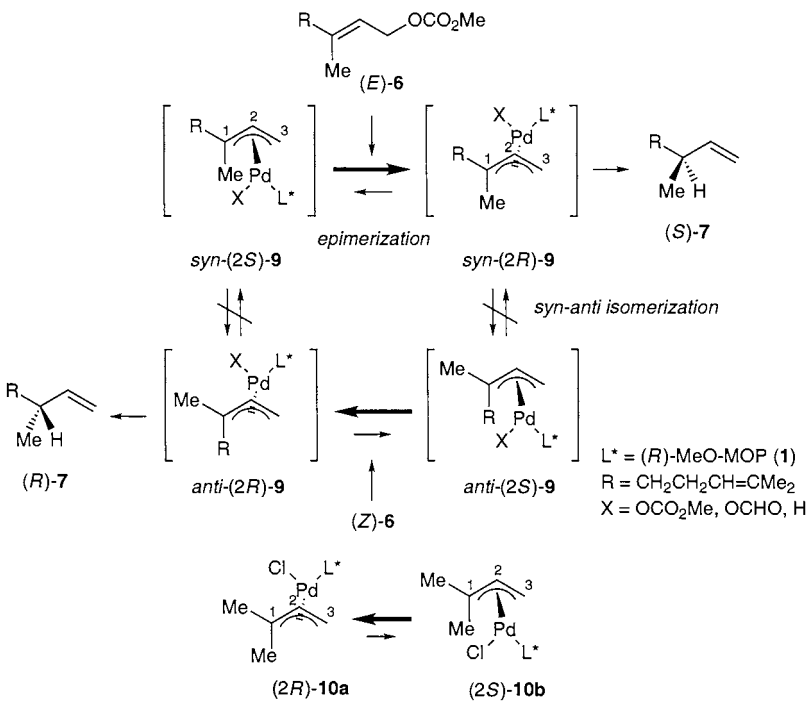
3. Asymmetric reduction of allylic esters with formic acid

Palladium-catalyzed reduction of allylic esters with formic acid, a reaction which has been developed by Tsuji and coworkers [2,13], provides a convenient method for regioselective synthesis of less-substituted olefins. Mechanistic studies [14] on the catalytic reduction have revealed that the olefin is produced by reductive elimination from the key intermediate, Pd(II)(π-allyl)(hydrido)(L), which is generated by decarboxylation of the palladium formate complex, and that the use of monodentate phosphine ligand is essential for the high regioselectivity. We found that the catalytic asymmetric reduction forming optically active olefins is attained by use of the chiral monodentate phosphine ligand, (*R*)–MeO–MOP (**1a**), and its biphenanthryl analog, (*R*)–MOP–phen (**5**) [12,15].

Reaction of geranyl methyl carbonate ((*E*)-**6**) with formic acid (2.2 equiv) and 1,8-bis(dimethylamino)naphthalene (1.2 equiv) in the presence of 1 mol.% of a palladium catalyst, generated in situ by reacting $Pd_2(dba)_3 \cdot CHCl_3$ with (*R*)–MeO–MOP (P/Pd = 2/1), in dioxane at 20°C for 16 h proceeded regioselectively to give a quantitative yield of (*S*)-3,7-dimethyl-1,6-octadiene (**7**) in 76% ee (Scheme



Scheme 3.



Scheme 4.

3). The reduction of *Z* carbonate, neryl methyl carbonate ((*Z*)-**6**), under the same reaction conditions gave the olefin (*R*)-**7** which has essentially the same enantiomeric purity (75% ee) but the opposite absolute configuration. Similarly, the reduction of racemic linalyl carbonate dl-**8** gave 82% yield of (*S*)-**7** in 55% ee. In contrast to the high catalytic activity and high regioselectivity observed with the MOP/palladium catalyst, the reduction is very slow and not regioselective with chelating bisphosphine ligands such as (*R*)-BINAP.

The reduction of **6** must proceed via a π-{1-(4-methyl-3-pentenyl)-1-methylallyl}palladium(II) intermediate **9** which presumably undergoes *syn–anti* isomerization (*syn*-**9**↔*anti*-**9**) and epimerization ((2*R*)-**9**↔(2*S*)-**9**) by the σ–π–σ mechanism (Scheme 4) [6]. The reversal of configuration of **7** observed for the asymmetric reduction of (*E*)-**6** and (*Z*)-**6** demonstrates that the rate of *syn–anti* isomerization of **9** is much slower than the rate of reduction in forming **7**. As a model for the key intermediate in the asymmetric reduction, the structure of PdCl(η3-1,1-dimethylallyl)((*R*)-MeO–MOP) (**10**), which is readily obtained by the reaction of [PdCl(η3-1,1-dimethylallyl)]$_2$ with (*R*)-MeO–MOP, was studied in solution and in a crystalline state.

^{1}H- and ^{31}P-NMR studies of **10** in $CDCl_3$ revealed that the π-allylpalladium **10** exists as a mixture of isomers which are in an equilibrium state between −60 and 20°C, the ratio of major isomer to minor isomer being 4.5: 1, 5.1: 1, and 6.5: 1, at 20, −20, and −60°C, respectively. Both isomers are determined by a large coupling ($^4J_{H-P}$ = ca. 9 and 5 Hz) between the methyls

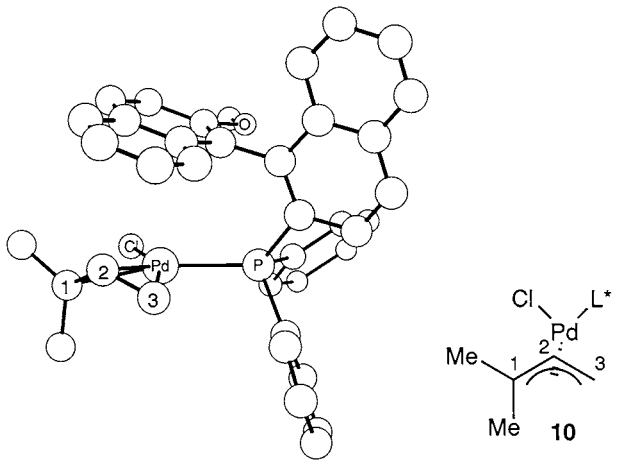
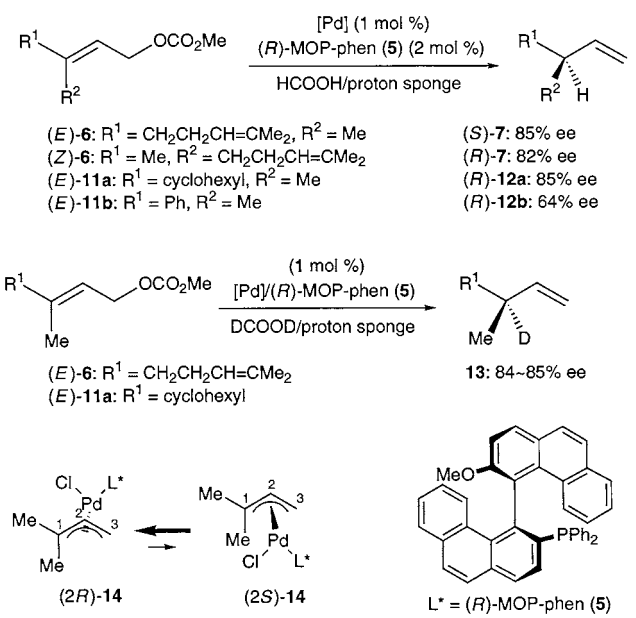


Fig. 1. Molecular structure of PdCl(η^3-1,1-dimethylallyl) ((*R*)-MOP) (**10**).

on the C-1 carbon and the phosphorus atom which is consistent with the structure **10a** and **10b** whereby the C-1 carbon on the π-allyl is trans to phosphine. One of the significant features in the ^{1}H-NMR was that the proton on the C-2 carbon of major diastereoisomer **10a** appeared at an unusually high field (2.67 ppm) compared with that of the minor isomer **10b** (4.55 ppm) and normal PdCl(π-allyl)(PR_3) complexes. The X-ray crystal structure of the palladium complex **10** (Fig. 1) obtained by recrystallization from benzene and ether shows that the C-2 proton is in close proximity to the naphthyl ring substituted with the methoxy group, which will cause the high field shift of the C-2 proton. Thus, the conformation in the X-ray crystal structure is assumed to be similar to that of the major isomer **10a** in solution. The stereochemical outcome in forming



Scheme 5.

(*S*)-**7** observed in the catalytic asymmetric reduction of (*E*)-**6** is accounted for by the reductive elimination of the hydrido and π-allyl from the intermediate *syn*-(2*R*)-**9** (X=H) after equilibration between *syn*-(2*R*)-**9** and *syn*-(2*S*)-**9**, the former possessing the same configuration for the π-allyl moiety as **10a**. Similarly, (*R*)-**7** is formed from *anti*-(2*R*)-**9** after the equilibration with *anti*-(2*S*)-**9**. An epimerization ensuing from this equilibration was demonstrated by the reduction of racemic linalyl carbonate **8** which gave nonracemic product (55% ee (*S*)).

The monodentate phosphine (*R*)-MOP–phen (**5**) that contains axially chiral biphenanthryl skeleton was found to be a more enantioselective ligand than the binaphthyl ligand MeO–MOP (**1**) for the palladium-catalyzed asymmetric reduction of allylic esters. Thus, the use of **5** for the reduction of (*E*)-**6** and (*Z*)-**6** increased the enantioselectivity to 85 and 82% ee, respectively (Scheme 5). Enantioselectivity in the reduction of (*E*)-3-cyclohexyl-2-propenyl carbonate (**11a**) and (*E*)-3-phenyl-2-propenyl carbonate (**11b**) was also increased by use of MOP–phen (**5**).

Asymmetric syntheses of optically active olefins which all bear a deuterium atom at the stereogenic center in the allylic position were also successful with the use of formic acid-d_2 (DCOOD) [12]. Thus, the reaction of (*E*)-**6** and (*E*)-**11a** with formic acid-d_2 in the presence of 1,8-bis(dimethylamino)naphthalene and the palladium–MOP–phen catalyst introduced deuterium selectively at the stereogenic center to give the corresponding deuterated olefins in 84 ~ 85% ee, the enantioselectivity being essentially the same as the reduction with HCOOH. No deuterium scrambling was observed in the reduction products.

The manner in which the MOP-phen ligand coordinates to π-allylpalladium was also studied by X-ray crystal structure analysis of the palladium complex PdCl(η3-1,1-dimethylallyl)((*R*)-MOP-phen)) (**14**) (Fig. 2) [12]. The basic structure around palladium atom in **14** is very similar to that of its binaphthyl analog **10** (see Fig. 1). Thus, the η^3-1,1-dimethylallyl group coordinates to palladium with the absolute configuration of *R* at the C-2 position, and the C-1 carbon on the π-allyl, which is substituted with two methyl groups, is *trans* to the phosphorus. ^{1}H- and ^{31}P-NMR studies of PdCl(η3-1,1-dimethylallyl)((*R*)-MOP–phen) (**14**) in $CDCl_3$ revealed that the π-allylpalladium **14** exists as a mixture of isomers which are in an equilibrium state between −60 and 20°C, the ratios of main isomer (2*R*)-**14** to minor isomer (2*S*)-**14** being 6: 1, 10: 1, and 13: 1 at 20, −20 and −60°C, respectively. The ratios are higher than those observed for the palladium–MOP complex **10** (vide supra), which is consistent with the higher enantioselectivity of MOP–phen (**5**) than MeO–MOP (**1**) for the catalytic asymmetric reduction.

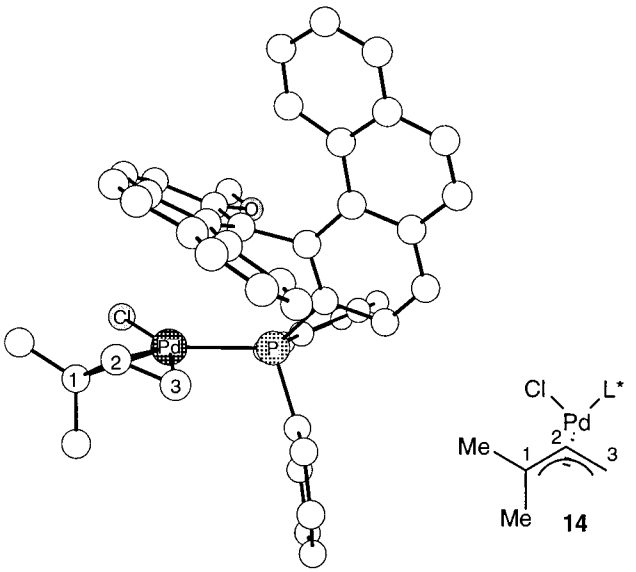
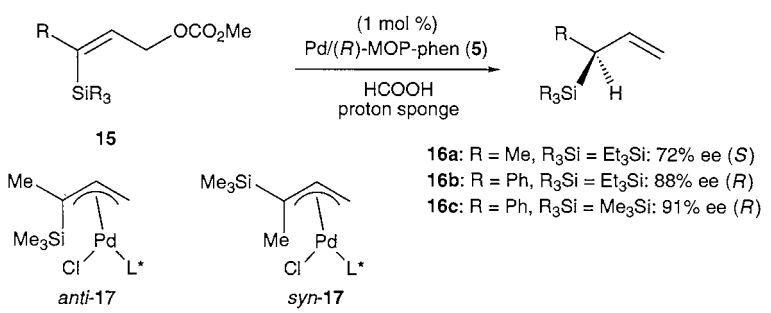


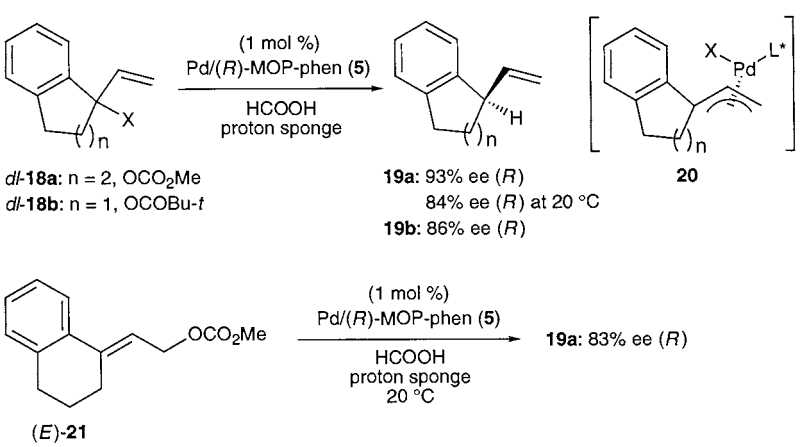
Fig. 2. Molecular structure of PdCl(η³-1,1-dimethylallyl) ((*R*)-MOP–phen) (**14**).

The catalytic asymmetric reduction was applied to the synthesis of optically active allylic silanes that have a stereogenic carbon center at the α-position and thus would be considered as useful chiral reagents in organic synthesis (Scheme 6) [16]. For example, the reduction of 3-alkyl-3-trialkylsilyl-2-propenyl methyl carbonates **15** with formic acid in the presence of the palladium/MOP–phen catalyst proceeded at 20°C to give high yields (>90%) of allylsilanes **16** in up to 91% ee. The allylsilanes were treated with trimethylacetaldehyde in the presence of titanium tetrachloride to give optically active homoallyl alcohols by chirality transfer during the S'_E reaction [17]. The asymmetric reduction of the allyl carbonates bearing an *E* double bond under the same reaction conditions gave the corresponding allylsilanes with lower enantiomeric purity than those from the *Z* carbonates. The higher enantioselectivity of the reaction of *Z* carbonates was accounted for by the larger difference in thermodynamic stability between the epimeric pairs of *anti*-π-allylpalladium complex than those of the *syn* isomer, which was demonstrated by ^{1}H- and ^{31}P-NMR studies of *syn* and *anti* isomers of a model π-allylpalladium complex, PdCl(η3-1-methyl-1-(trimethylsilyl)allyl)((*R*)-MOP) (**17**).

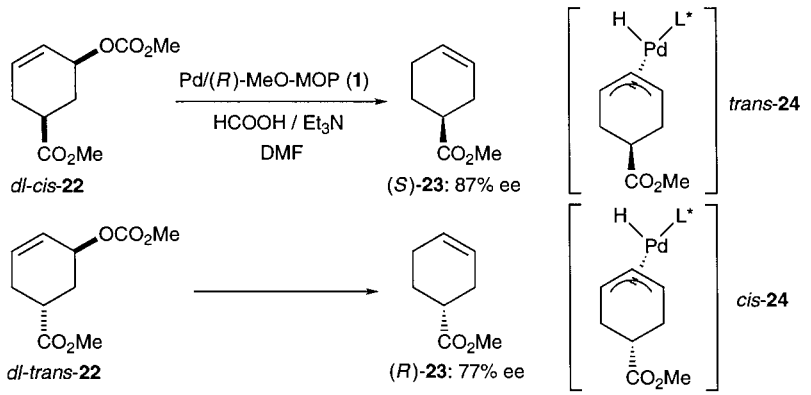
The allylic esters used for the asymmetric reduction have been limited to those with a geometrically pure *E* or *Z* double bond for high enantioselectivity, because the *E* and *Z* isomers produce the enantiomeric olefins. The reversal of configuration is exemplified by the reaction of geranyl and neryl esters (see Scheme 3). However, it was found that racemic tertiary allylic esters can also be used for asymmetric reduction if one



Scheme 6.



Scheme 7.



Scheme 8.

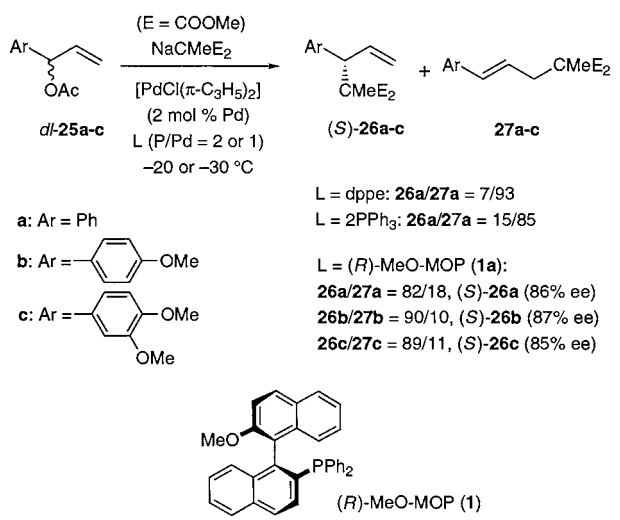
of the alkyl groups at the α position is a sterically bulky group (Scheme 7) [18]. Since the racemic tertiary allylic esters are readily obtained from a ketone and the vinyl Grignard reagent, it provides a practical method for the synthesis of optically active olefins. For example, the asymmetric reduction of racemic ester dl-**18a**, obtained from tetralone, with formic acid in the presence of the palladium catalyst coordinated with (*R*)-MOP–phen at −20°C gave an 87% yield of reduction product (*R*)-**19a** with 93% enantiomeric purity. The high enantioselectivity can be accounted for by the selective formation of the π-allylpalladium **20** that contains the more bulky group at the *syn* position. Interestingly, the reduction of dl-**18a** is much faster than that of its regioisomeric ester, 3,3-disubstituted propenyl carbonate (*E*)-**21**. The reduction of (*E*)-**21** did not take place at 0°C or lower. At 20°C it gave (*R*)-**19a** in 83% ee, the stereoselectivity being essentially the same as that for dl-**18a** at 20°C. The lower reactivity of (*E*)-**21** is ascribed to the two alkyl substituents at the 3 position of (*E*)-**21**. Steric hindrance retards the oxidative addition step in the catalytic cycle which takes place in an S'_N manner.

The palladium–MOP catalyst is also effective for the asymmetric reduction of racemic 5-carbomethoxy-2-cyclohexenyl methyl carbonates **22** which proceeds through palladium intermediates **24** that have *meso*-type π-allyl. The reduction of *cis*-**22** and *trans*-**22** gave (*S*)-4-carbomethoxycyclohexene (**23**) (87% ee) and (*R*)-**23** (77% ee), respectively (Scheme 8) [15].

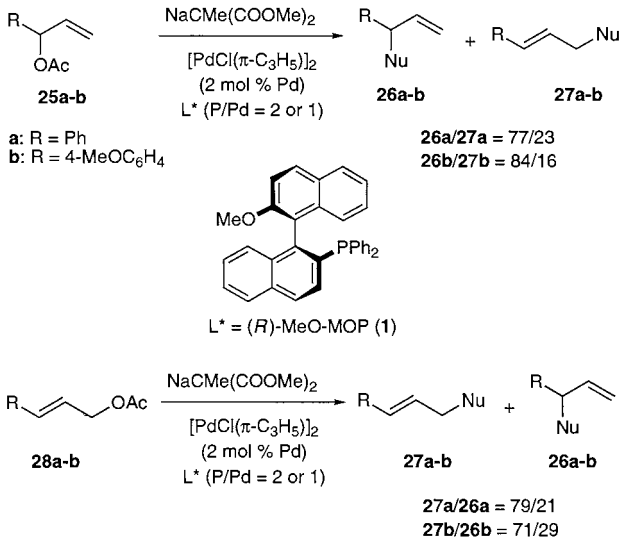
4. Regio- and enantioselective alkylation of allylic esters

One of the major problems in developing catalytic asymmetric allylic alkylation is undesirable regiochemistry which limits the substitution patterns of allylic substrates [6]. As a typical example, the substitution with soft carbon nucleophiles that proceeds through π-allylpalladium intermediates containing one substituent at C-1 position produces linear isomer rather than branch isomer. It follows that the reaction cannot be extended to asymmetric synthesis because the linear isomer lacks the chiral carbon center. The regioselectivity in forming a branch isomer is usually very low except when methyl is the substituent [19]. We found that the use of MeO–MOP (**1**), which is a sterically bulky chiral monophosphine ligand, for the allylic alkylation of 1-aryl-2-propenyl acetates **25** reversed the regiochemistry to give branch isomers **26** with high selectivity, and asymmetric synthesis was realized in this new allylic alkylation system [20].

The results obtained for allylic substitution of racemic 1-aryl-2-propenyl acetates dl-**25** in the presence of palladium–phosphine complexes are summarized in Scheme 9. The reaction of dl-1-phenyl-2-propenyl acetate (**25a**) with the sodium salt of dimethyl methylmalonate in THF at −20°C in the presence of 2 mol.% of palladium catalyst generated from $[PdCl(\pi\text{-}C_3H_5)]_2$ and 1,2-bis(diphenylphosphino)ethane (dppe) gave linear isomer (*E*)-**27a** with 93% regioselectivity. The linear-selectivity (85% regioselectivity) was also observed



Scheme 9.



Scheme 10.

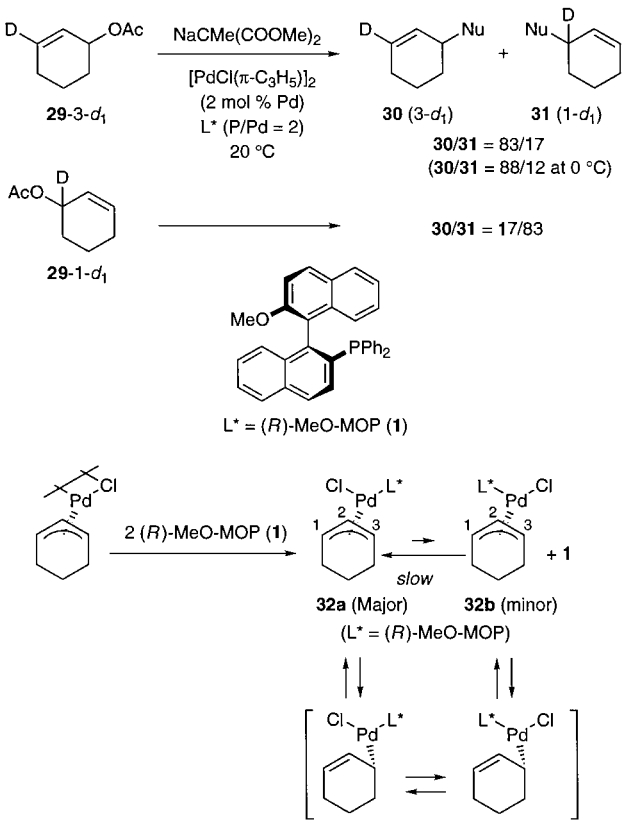
in the reaction with a palladium catalyst coordinated with triphenylphosphine. It is noteworthy that the reaction catalyzed by palladium–PPh_3 requires two equivalents of triphenylphosphine (to Pd) for the allylic substitution to proceed smoothly. With one equivalent of triphenylphosphine, the reaction stops at about 60% conversion. The opposite regioselectivity was observed in the same substitution reaction of **25a** by use of MeO–MOP as a ligand, which gave branch isomer **26a** with 82% regioselectivity at −30°C. The branch product **26a** was 86% enantiomerically pure. With the palladium–MeO–MOP catalyst, the ratio of phosphine to palladium did not affect either catalytic activity or regioselectivity. Higher regioselectivity in forming the branch isomer was observed in the reaction of 1-aryl-2-propenyl acetates **25b** and **25c** that contain methoxy group(s) on the aromatic ring. At the reaction temperature of −30°C, 1-(4-methoxyphenyl)-2-propenyl acetate (**25b**) gave branch isomer (*S*)-**26b** (87% ee) with 90% regioselectivity. Here again the palladium catalyst containing dppe or triphenylphosphine gave linear isomer **27b** preferentially. The reaction of allylic acetate **25c** in the presence of MeO–MOP at −30°C also gave the corresponding alkylation product **26c** in 85% ee with high branch-selectivity (89%). Thus, MeO–MOP (**1**) is playing a key role on the high branch-selectivity in the catalytic allylic alkylation of 1-aryl-2-propenyl acetates. This type of asymmetric alkylation is considered to be difficult with chelating bisphosphine ligands used so far mostly for asymmetric allylic alkylation which proceeds by way of palladium intermediates containing 1,3-disubstituted π-allyl such as 1,3-diphenyl [6,21].

It has been generally accepted that, in the allylic substitution which proceeds through 1,3-unsymmetrically substituted π-allylpalladium(II) intermediate, the regiochemistry of starting allylic ester is lost at the formation of the π-allylpalladium(II) intermediate and the regiochemistry in the substitution product is determined at the attack of nucleophile on the π-allylpalladium. Recently we found a new type of palladium-catalyzed allylic alkylation reactions where selective substitution at the position originally substituted with acetate takes place by use of MeO–MOP (**1**) which is a sterically bulky monodentate phosphine ligand (Scheme 10) [22].

The reaction of 1-phenyl-2-propenyl acetates (**25a**) with sodium salt of dimethyl methylmalonate in the presence of a palladium catalyst generated by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ with one or two equivalents of MeO–MOP (**1**) gave a regioisomeric mixture of allylic alkylation products consisting of branch isomer **26a** and linear isomer **27a** in a ratio of 77 to 23. On the other hand, the allylic alkylation of (*E*)-3-phenyl-2-propenyl acetate (**28a**) under the same conditions gave branch isomer **26a** and linear isomer **27a** in a ratio of 21 to 79. Thus, the nucleophile attacked the position originally substituted with acetate. The retention of regiochemistry observed here is quite unusual in the palladium-catalyzed allylic substitution reactions. With other phosphine ligands such as triphenylphosphine and 1,2-bis(diphenylphosphino)ethane (dppe), the ratio of branch isomer **26a** and linear isomer **27a** is the same irrespective of the regiochemistry of the starting allylic esters.

The substitution at the carbon originally substituted with acetate was also observed in the reaction of specifically deuterated cyclohexenyl acetates **29**. The alkylation of 3-deuterated acetate **29**-3-d_1 and 1-deuterated acetate **29**-1-d_1 with sodium salt of dimethyl methylmalonate in the presence of palladium/MeO–MOP catalyst took place with high selectivity (83% at 20°C) at the position originally substituted with acetate, giving **30** and **31**, respectively (Scheme 11). The reaction carried out at 0°C in the presence of 0.5 equivalents of lithium chloride increased the regioselectivity up to 88%. Here again use of dppe or triphenylphosphine ligand in place of MeO–MOP gave a 1/1 mixture of **30** and **31**, starting with either **29**-3-d_1 or **29**-1-d_1, indicating that the regiochemical integrity of cyclohexenyl acetates **29**-3-d_1 and **29**-1-d_1 is lost before the nucleophilic attack in the case of dppe or PPh_3 as a ligand.

Studies of the structure of π-allylpalladium complexes generated by mixing $[PdCl(\pi\text{-cyclohexenyl})]_2$ with one or two equivalents of MeO–MOP (**1**) revealed that cationic bisphosphine complex $[Pd(\mathbf{1})_2(\pi\text{-cyclohexenyl})]^+Cl^-$ is not formed even in the presence of excess ligand but neutral monophosphine complex PdCl(**1**)(π-cyclohexenyl) (**32**) is formed leaving excess ligand free and that the exchange of the coordination site of Cl and **1** in **32** is much slower than that in the corresponding triphenylphosphine complex $PdCl(PPh_3)(\pi\text{-cyclohex-}$



Scheme 11.

enyl). The slow exchange can rationalize the retention of regiochemistry in the allylic alkylation catalyzed by palladium/MeO–MOP complex.

References

[1] For reviews: (a) H. Brunner, Synthesis (1988) 645. (b) H. Brunner, Top. Stereochem. 18 (1988) 129. (c) R. Noyori, M. Kitamura, in: R. Scheffold (Ed.), Modern synthetic methods, vol. 5, Springer-Verlag, New York, 1989, p 115. (d) I. Ojima, N. Clos, C. Bastos, Tetrahedron 45 (1989) 6901. (e) I. Ojima, Catalytic asymmetric synthesis, VCH, New York, 1993. (f) R. Noyori, Asymmetric catalysis in organic synthesis, Wiley, New York, 1994.

[2] For a review: J. Tsuji, Palladium reagents and catalysts, Wiley, Chichester, 1995.

[3] T. Hayashi, in: I. Ojima (Ed.), Catalytic asymmetric synthesis, VCH, NY, 1993, p. 325.

[4] T. Hayashi, Acta Chem. Scand. 50 (1996) 259, and references cited therein.

[5] (a) Y. Uozumi, K. Kato, T. Hayashi, J. Am. Chem. Soc. 119 (1997) 5063. (b) Y. Uozumi, K. Kato, T. Hayashi, J. Org. Chem. 63 (1998) 5071.

[6] For reviews on catalytic asymmetric allylic substitutions: (a) B.M. Trost, D.L. Van Vranken, Chem. Rev. 96 (1996) 395. (b) G. Consiglio, R.M. Waymouth, Chem. Rev. 89 (1989) 257. (c) C.G. Frost, J. Howarth, J.M.J. Williams, Tetrahedron Asymmetry 3 (1992) 1089.

[7] Examples of optically active monophosphine ligands: (a) (*S*)-(*o*-Methoxyphenyl)cyclohexylmethylphosphine ((*S*)-CAMP): W.S. Knowles, M.J. Sabacky, B.D. Vineyard, J. Chem. Soc. Chem. Commun. (1972) 10. (b) Neomentyldiphenylphosphine: J.D. Morrison, R.E. Burnett, A.M. Aguiar, C.J. Morrow, C. Phillips, J. Am. Chem. Soc. 93 (1971) 1301. (c) Ferrocenylmonophosphines: T. Hayashi, in: A. Togni, T. Hayashi (Eds.), Ferrocenes, VCH, Weinheim, 1995, p. 105.

[8] Y. Matsumoto, M. Naito, Y. Uozumi, T. Hayashi, J. Chem. Soc., Chem. Commun. (1993) 1468.

[9] L. Kurz, G. Lee, D. Morgans Jr, M.J. Waldyke, T. Ward, Tetrahedron Lett. 31 (1990) 6321.

[10] Y. Uozumi, T. Hayashi, J. Am. Chem. Soc. 113 (1991) 9887.

[11] (a) Y. Uozumi, A. Tanahashi, S.-Y. Lee, T. Hayashi, J. Org. Chem. 58 (1993) 1945. (b) Y. Uozumi, N. Suzuki, A. Ogiwara, T. Hayashi, Tetrahedron 50 (1994) 4293.

[12] T. Hayashi, H. Iwamura, Y. Uozumi, Y. Matsumoto, F. Ozawa, Synthesis (1994) 526.

[13] (a) J. Tsuji, T. Yamakawa, Tetrahedron Lett. (1979) 613. (b) J. Tsuji, I. Shimizu, I. Minami, Chem. Lett. (1984) 1017. (c) J. Tsuji, I. Minami, I. Shimizu, Synthesis (1986) 623. (d) T. Mandai, T. Matsumoto, M. Kawada, J. Tsuji, J. Org. Chem. 57 (1992) 1326.

[14] M. Oshima, I. Shimizu, A. Yamamoto, F. Ozawa, Organometallics 10 (1991) 1221.

[15] T. Hayashi, H. Iwamura, M. Naito, Y. Matsumoto, Y. Uozumi, M. Miki, K. Yanagi, J. Am. Chem. Soc. 116 (1994) 775.

[16] T. Hayashi, H. Iwamura, Y. Uozumi, Tetrahedron Lett. 35 (1994) 4813.

[17] (a) T. Hayashi, M. Konishi, H. Ito, M. Kumada, J. Am. Chem. Soc. 104 (1982) 4962. (b) T. Hayashi, M. Konishi, M. Kumada, J. Org. Chem. 48 (1983) 281. (c) T. Hayashi, M. Konishi, Y. Okamoto, K. Kabeta, M. Kumada, J. Org. Chem. 51 (1986) 3772.

[18] T. Hayashi, M. Kawatsura, H. Iwamura, Y. Yamaura, Y. Uozumi, J. Chem. Soc. Chem. Commun. (1996) 1767.

[19] For examples: (a) T. Hayashi, K. Kishi, A. Yamamoto, Y. Ito, Tetrahedron Lett. 31 (1990) 1743. (b) B.M. Trost, M.J. Krische, R. Radinov, G. Zanoni, J. Am. Chem. Soc. 118 (1996) 6297.

[20] T. Hayashi, M. Kawatsura, Y. Uozumi, J. Chem. Soc. Chem. Commun. (1997) 561.

[21] For recent examples: (a) B.M. Trost, R.C. Bunt, Angew. Chem. Int. Ed. Engl. 35 (1996) 99. (b) G. Zhu, M. Terry, X. Zhang, Tetrahedron Lett. 37 (1996) 4475. (c) W. Zhang, T. Kida, Y. Nakatsuji, I. Ikeda, Tetrahedron Lett. 37 (1996) 7995. (d) N. Nomura, Y.C. Mermet-Bouvier, T.V. RajanBabu, Synlett (1996) 745. (e) H.C.L. Abbenhuis, U. Burckhardt, V. Gramlich, C. Kollner, P.S. Pregosin, R. Salzmann, A. Togni, Organometallics 14 (1995) 759.

[22] T. Hayashi, M. Kawatsura, Y. Uozumi, J. Am. Chem. Soc. 120 (1998) 1681.