Pure Appl. Chem., Vol. 76, No. 3, pp. 465–475, 2004.

Rhodium-catalyzed asymmetric addition of aryl- and alkenylboron reagents to electron-deficient olefins*

Tamio Hayashi

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

Abstract: Asymmetric 1,4-arylation and -alkenylation was achieved by use of organoboronic acids or their derivatives in the presence of a rhodium catalyst coordinated with binap or its related ligands. The scope of this asymmetric addition is very broad, α,β-unsaturated ketones, esters, amides, 1-alkenylphosphonates, and 1-nitroalkenes being efficiently converted into the corresponding 1,4-addition products with over 95 % enantioselectivity. The catalytic cycle in water is proposed to involve three intermediates [aryl- or alkenyl-rhodium (oxa-π-allyl)rhodium, and hydroxo-rhodium] by NMR studies on the rhodium intermediates.

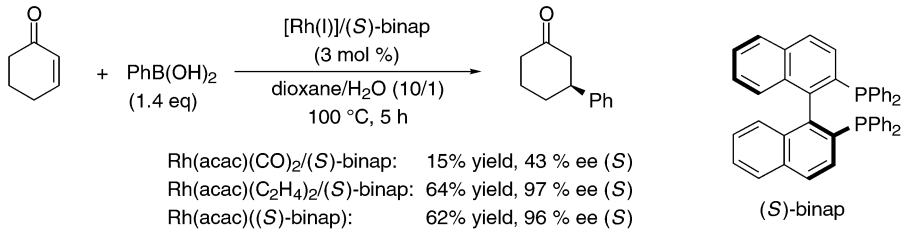
INTRODUCTION

Catalytic asymmetric synthesis is a field of great interest in its practical usefulness as well as its scientific interest [1]. Although the asymmetric reduction and oxidation have been developed so well that some of the processes are used for industrial production of enantiomerically enriched compounds, the examples of high efficiency in terms of catalytic activity and enantioselectivity are still rare in the catalytic asymmetric carbon–carbon bond-forming reactions [1]. Among the asymmetric carbon–carbon bond-forming reactions catalyzed by chiral transition-metal complexes, the asymmetric 1,4-addition is one of the most promising reactions because its non-asymmetric version is a basic synthetic reaction often used for the carbon–carbon bond formation which allows us to introduce carbon nucleophiles to the β-position of electron-deficient olefins such as α,β-unsaturated ketones and esters [2]. Recently, there have been reported two types of 1,4-addition reactions where high enantioselectivity is achieved [3]. One is the copper(I)-catalyzed addition of organozinc reagents by use of copper(I) catalysts coordinated with chiral phosphorous ligands represented by phosphoramidite ligand based on the axially chiral 1,1′-binaphthol [4]. The other is the Michael addition to α,β-unsaturated ketones catalyzed by Shibasaki's heterobimetallic catalysts consisting of chiral 1,1′-binaphthol and two kinds of metals [5]. In these two reactions, sp^3-alkyl groups and soft carbon nucleophiles, respectively, are introduced at the stereogenic carbon center at the β-position of α,β-unsaturated ketones.

Miyaura's report in 1997 describing the first example of rhodium-catalyzed 1,4-addition of aryl- and alkenyl-boronic acids to α,β-unsaturated ketones [6] stimulated the synthetic organic chemists who are interested in asymmetric catalysis to modify the reaction conditions of the rhodium-catalyzed reaction for catalytic asymmetric 1,4-addition reactions. We succeeded, for the first time, in obtaining high catalytic activity and high enantioselectivity by carrying out the reaction in dioxane and water at 100 °C in the presence of a rhodium catalyst coordinated with (*S*)-binap ligand, which was reported in 1998 [7]. As a typical example, the reaction of 2-cyclohexenone with phenylboronic acid gave (*S*)-3-phenyl-

*Plenary and invited lectures presented at the 12th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS-12), Toronto, Ontario, Canada, 6–10 July 2003. Other presentations are published in this issue, pp. 453–695.

cyclohexanone of 97 % ee (Scheme 1). After this publication, several reports appeared on the use of some other chiral phosphorus ligands for this type of rhodium-catalyzed 1,4-addition of organoboronic acids to α,β-unsaturated ketones under similar conditions to ours [8]. We have succeeded in applying the reaction to other types of electron-deficient olefins including α,β-unsaturated esters, amides phosphonates, and nitroalkenes. Here we describe the recent development of the rhodium-catalyzed asymmetric 1,4-addition of organoboron reagents recently studied in our research group [9]. It is highlighted by the mechanistic studies on the rhodium-catalyzed 1,4-addition and finding of a new catalyst system possessing higher catalytic activity.

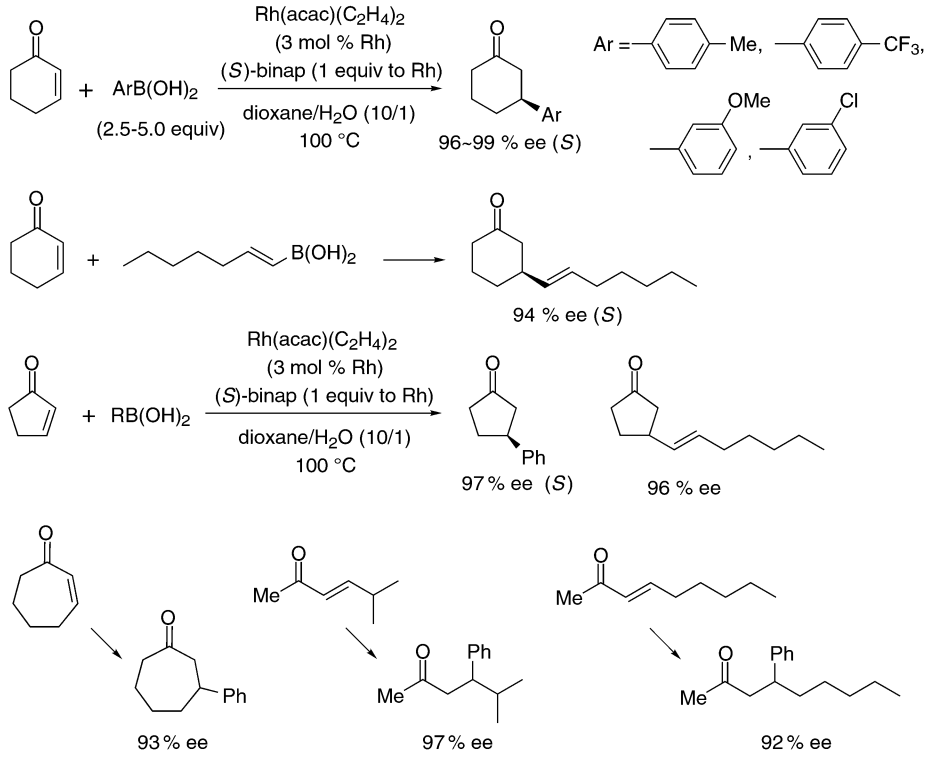


Scheme 1

RHODIUM-CATALYZED ASYMMETRIC 1,4-ADDITION OF ORGANOBORONIC ACIDS TO α,β-UNSATURATED KETONES

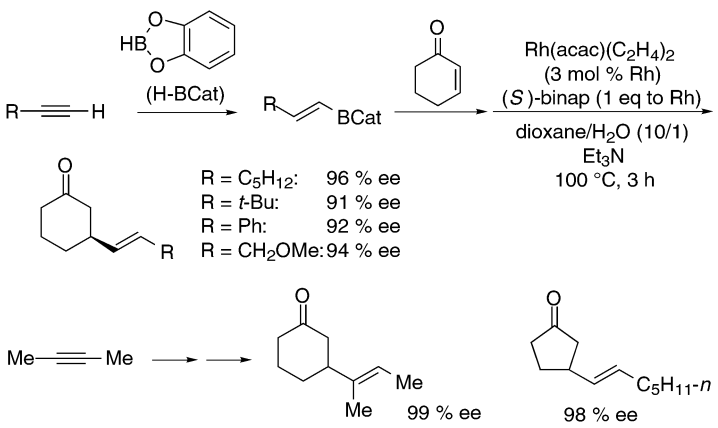
In the first report, the rhodium-catalyzed asymmetric 1,4-addition of aryl- and alkenylboronic acids proceeded with high enantioselectivity for both cyclic and linear α,β-unsaturated ketones (Scheme 1) [7]. Important points for the high catalytic activity and the high enantioselectivity at this stage are (1) the use of Rh(acac)$(C_2H_4)_2$ as a rhodium catalyst precursor, (2) binap as a chiral bisphosphine ligand, (3) high reaction temperature (100 °C), and (4) the use of a mixture of dioxane and water in a ratio of 10 to 1 as a solvent. The high reaction temperature is essential, almost no reaction taking place at 60 °C or lower. With Rh(acac)$(CO)_2$ as a catalyst precursor, the reaction is slower and the enantioselectivity is much lower. NMR studies showed that the addition of 1 equiv of binap ligand to Rh(acac)$(C_2H_4)_2$ immediately generates Rh(acac)(binap) quantitatively, while Rh(acac)$(CO)_2$ generates two kinds of unidentified rhodium complexes together with a small amount of the Rh(acac)(binap) complex.

The scope of this rhodium-catalyzed asymmetric 1,4-addition of organoboronic acids is very broad [7]. Some of the results obtained for the addition to α,β-unsaturated ketones are summarized in Scheme 2. Under standard conditions, that is, 3 mol % of Rh(acac)$(C_2H_4)_2$ and binap in dioxane/H_2O (10/1) at 100 °C, aryl groups substituted with either electron-donating or -withdrawing groups, 4-MeC_6H_4, 4-$CF_3C_6H_4$, 3-$MeOC_6H_4$, and 3-ClC_6H_4, were introduced onto 2-cyclohexenone with high enantioselectivity by the reaction with the corresponding boronic acids. Asymmetric addition of 1-alkenylboronic acids was as successful as that of arylboronic acids, the alkenylation product with 1-heptenylboronic acid being obtained with 94 % enantioselectivity. Cyclopentenone underwent the asymmetric addition of phenyl- and 1-heptenylboronic acids with high enantioselectivity under the same reaction conditions to give 3-substituted cyclopentanones with over 96 % ee in high yields. High enantioselectivity was also observed in the reaction of linear enones, 5-methyl-3-hexen-2-one and 3-nonen-2-one, which have *trans* olefin geometry. Thus, the rhodium-catalyzed asymmetric 1,4-addition proceeds with high enantioselectivity for both cyclic and linear α,β-unsaturated ketones with a variety of aryl- and alkenylboronic acids. The procedures for the preparation of (*S*)-3-phenylcyclohexanone in several grams scale has been published in *Organic Synthesis* [10]. High enantioselectivity has been recently reported by use of other chiral ligands than binap under similar reaction conditions we reported [8].



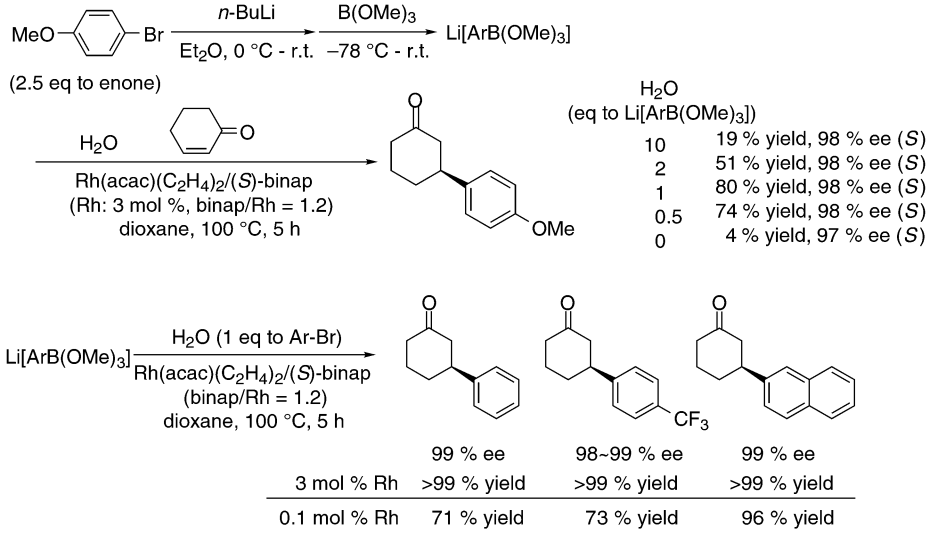
Scheme 2

Alkenylcatecholboranes obtained by the hydroboration of alkynes with catecholborane were found to be good alkenylating reagents for the asymmetric 1,4-addition [11] (Scheme 3). For the high chemical yield in this reaction, triethylamine must be added, which probably neutralizes the catechol generated under the reaction conditions. The reaction of (*E*)-1-heptenylborane, which is obtained by the hydroboration of 1-heptyne, with 2-cyclohexenone gave 92 % yield of 1,4-addition product, which is an (*S*) isomer of 96 % ee. Some other alkenylcatecholboranes were also successfully used for the catalytic asymmetric 1,4-addition. High enantioselectivity (99 % ee) was observed in the reaction starting from 2-butyne, which is an internal acetylene. One-pot synthesis of the optically active β-alkenyl ketones is possible from alkynes and catecholborane without isolation of the alkenylcatecholboranes.



Scheme 3

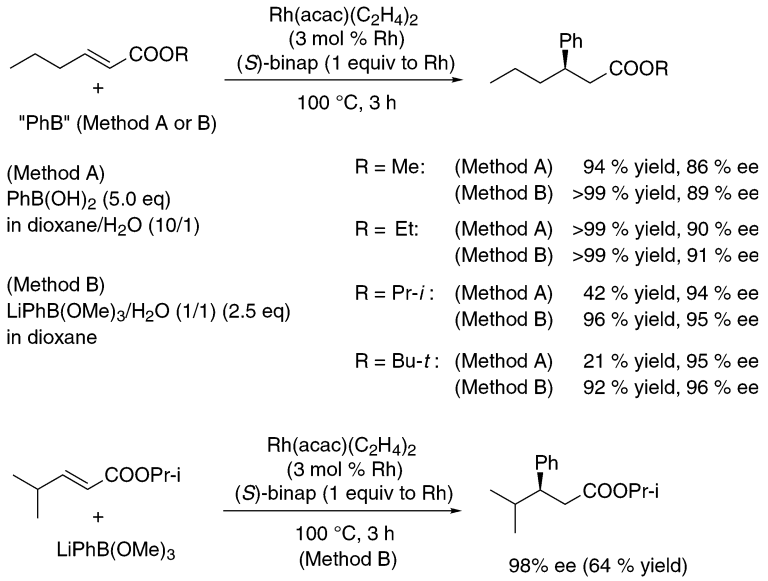
Lithium trimethyl arylborates, readily generated in situ by treatment of aryllithiums with trimethoxyborane, can be also used for the asymmetric 1,4-addition [12] (Scheme 4). This is another one-pot reaction. In general, this reaction provides higher yields than those obtained with arylboronic acids. Studies of the reaction conditions indicated that the amount of water has an effect on the yields remaining the enantioselectivity unaffected. The highest yield was obtained in the reaction carried out in the presence of 1 equiv (to arylborate) of water. The enantioselectivity was all high for the addition of several arylborate reagents. Using these in situ generated arylborate reagents, the amount of the catalyst was reduced without loss of enantioselectivity. For a typical example, in the reaction of 2-cyclohexenone with borate generated from 2-bromonaphthalene, 0.1 mol % of the catalyst gave 96 % yield of the 3-(2-naphthyl)cyclohexanone which is 99 % enantiomerically pure. In the addition to α,β-unsaturated ketones, this one-pot reaction is superior to the reaction of arylboronic acids both in higher catalytic activity resulting in higher chemical yield and in easier manipulation avoiding the isolation of arylboronic acids.



Scheme 4

RHODIUM-CATALYZED ASYMMETRIC 1,4-ADDITION OF ORGANOBORONIC ACIDS TO OTHER ELECTRON DEFICIENT OLEFINS

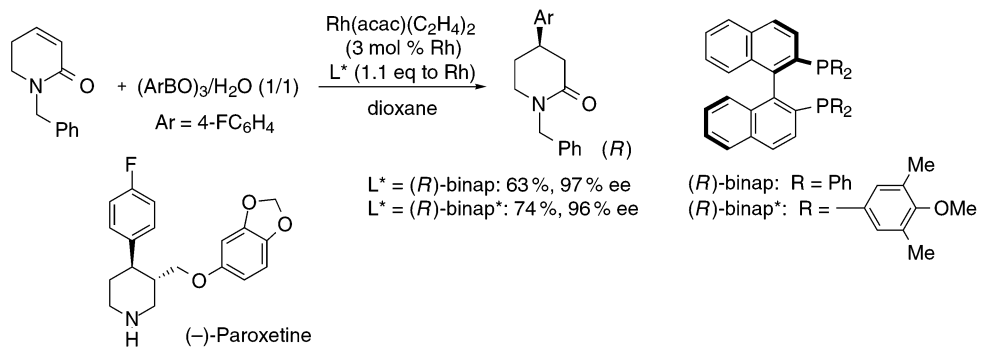
α,β-Unsaturated esters are also good substrates for the rhodium-catalyzed asymmetric addition [13]. The results obtained for the phenylation of (*E*)-hexenoate esters are shown in Scheme 5, where phenylboronic acid in dioxane/H_2O (10/1) (Method A) or phenylborate generated from phenyllithium and trimethoxyborane (Method B) was used as the phenylation reagent. In the reaction of methyl ester and ethyl ester, Method A gave high yields of the phenylation products, but in the reaction of isopropyl ester and *tert*-butyl ester the yields were much lower (<42 % yield). The yields were greatly improved by use of Method B, which gave the phenylation products in 96 and 92 % yield, respectively. Interestingly, the enantioselectivity increases as the steric bulkiness of the ester moiety increases. The enantiomeric purities of the phenylation products are 89, 91, 95, and 96 % ee for methyl, ethyl, isopropyl, and *tert*-butyl esters, respectively, in the reactions using Method B. Aryl groups, 4-ClC_6H_4, 4-MeC_6H_4, 4-$CF_3C_6H_4$, 3-$MeOC_6H_4$, and 2-naphthyl, were also introduced at the β position of isopropyl ester with enantioselectivity ranging between 93 and 97 % ee in high yields in the reactions with the corresponding lithium arylborates. Highest enantioselectivity (98 % ee) was observed in the phenylation of isopropyl 4-methyl-2-pentenoate under Method B conditions, though the yield was not high enough.



Scheme 5

Similar results for the asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated esters has been independently reported by Miyaura [14]. The asymmetric addition to α,β-unsaturated amides under similar conditions has been also reported by Miyaura [15]. The enantioselectivity is comparable to that in the addition to the corresponding esters.

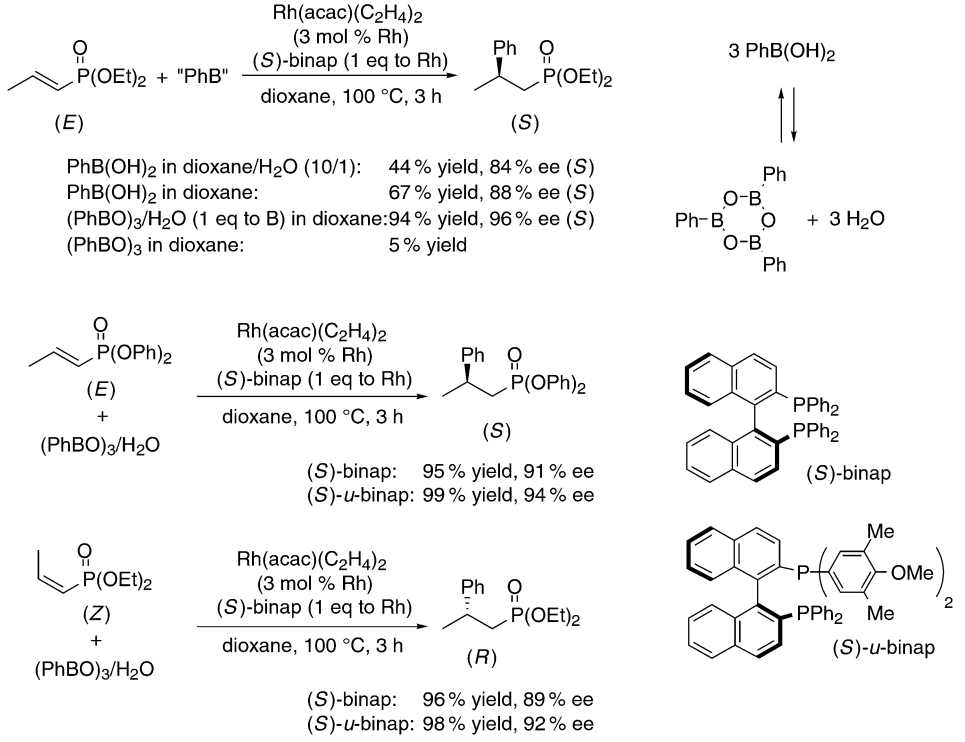
Asymmetric 1,4-addition to cyclic α,β-unsaturated amides provides a new efficient route to enantiomerically enriched 4-aryl-2-piperidinones [16] (Scheme 6). For the 1,4-addition of 4-$FC_6H_4B(OH)_2$, which is related to asymmetric synthesis of (–)-paroxetine, slightly modified conditions were required to obtain a high yield of the arylation product. The main side reaction, that is, hydrolysis of the boronic acid giving fluorobenzene, was suppressed by use of a minimum amount of the water. Thus, the reaction with 4-fluorophenylboroxine and 1 equiv (to boron) of water in the presence of Rh(acac)$(C_2H_4)_2$/(*R*)-binap catalyst in dioxane at 40 °C gave 63 % yield of (*R*)-lactam with 97 % enantioselectivity.



Scheme 6

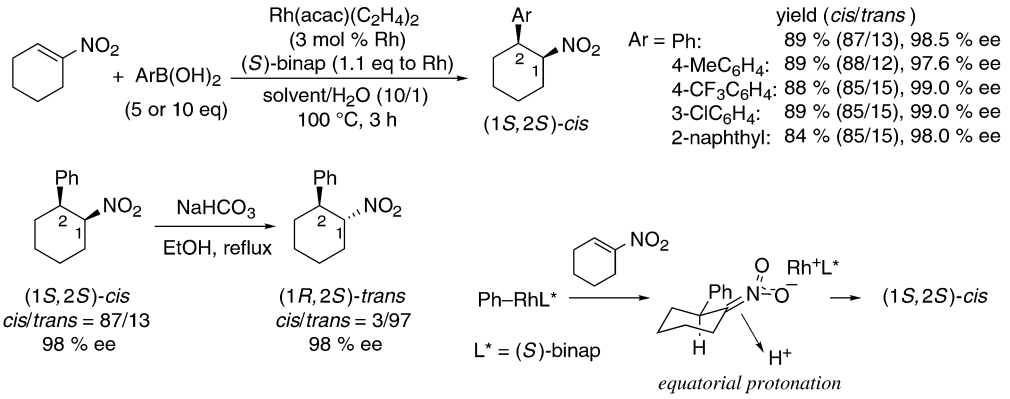
Alkenylphosphonates are less reactive toward 1,4-addition compared to α,β-unsaturated carbonyl compounds. It was found that the rhodium-catalyzed asymmetric 1,4-addition can be improved by using arylboroxines as arylating reagents instead of arylboronic acids [17] (Scheme 7). For example, the re-

action of diethyl (*E*)-propenylphosphonate with phenylboronic acid in dioxane/H_2O (10/1) under the reaction conditions used for α,β-unsaturated ketones was slow (44 % yield). The asymmetric 1,4-addition was greatly improved (94 % yield with 96 % ee) by carrying out the reaction using phenylboroxine $(PhBO)_3$ with 1 equiv of water. The addition of 1 equiv of water is essential for the high yield, almost no reaction taking place in the absence of water. A boroxine and water should be in equilibration with a boronic acid under the reaction conditions [18], and hence the use of arylboroxine in combination with 1 equiv of water for the asymmetric 1,4-addition should result in the same outcome as using the corresponding arylboronic acid with no water added. Nevertheless, the results of the catalytic reactions are better with the combination of boroxine and water. The enantioselectivities and chemical yields were slightly higher with the rhodium catalyst coordinated with unsymmetrically substituted binap ligand, (*S*)-*u*-binap, which has diphenylphosphino and bis(3,5-dimethyl-4-methoxyphenyl)phosphino groups at the 2 and 2′ positions on the 1,1′-binaphthyl skeleton. In the reaction of diphenyl (*E*)-propenylphosphonate with phenylboroxine, (*S*)-*u*-binap ligand gave 99 % yield of the 1,4-addition product with 94 % ee while the standard (*S*)-binap gave 95 % yield with 91 % ee. It is remarkable that the asymmetric phenylation of (*Z*) isomer of diethyl 1-propenylphosphonate with phenylboroxine gave *R* isomer. The optically active alkylphosphonates containing the stereogenic carbon center at β-position can be used as chiral building blocks for the synthesis of optically active alkenes by the Horner–Emmons-type reaction.



Scheme 7

Nitroalkenes are good substrates for the rhodium-catalyzed asymmetric 1,4-addition of organoboronic acids [19]. The reaction of 1-nitrocyclohexene with phenylboronic acid in the presence of the rhodium/(*S*)-binap catalyst at 100 °C for 3 h gave 89 % yield of 2-phenyl-1-nitrocyclohexane (Scheme 8). The main phenylation product is a *cis*-isomer (*cis*/*trans* = 87/13) and both of the *cis*- and *trans*-isomers are 98 % enantiomerically pure. Treatment of the *cis*-rich mixture with sodium bicarbonate in refluxing ethanol caused *cis*/*trans* equilibration giving thermodynamically more stable *trans*-

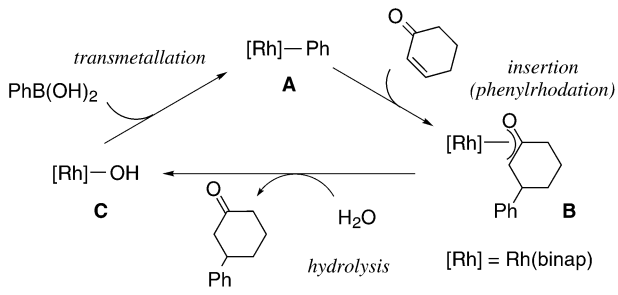


Scheme 8

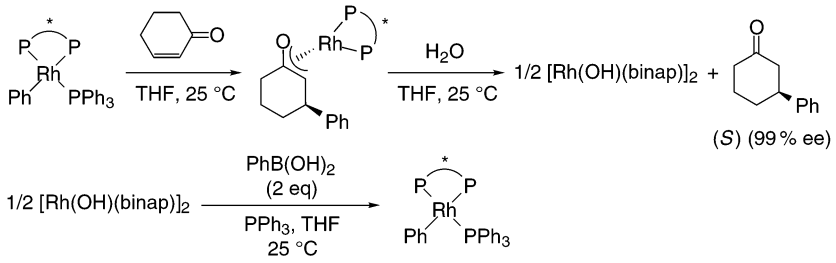
isomer (*trans*/*cis* = 97/3). It should be noted that this rhodium-catalyzed asymmetric phenylation produced thermodynamically less stable *cis*-isomer of high enantiomeric purity and it can be isomerized, if one wishes, into *trans*-isomer without loss of its enantiomeric purity. The preferential formation of *cis*-isomer in the catalytic phenylation may indicate the protonation of a rhodium nitronate intermediate in the catalytic cycle. Under similar reaction conditions, 1-nitrocyclohexene underwent asymmetric addition of some other arylboronic acids in good yields with high enantioselectivity. The corresponding *cis*-2-aryl-1-nitrocyclohexanes were produced with over 85 % *cis* selectivity and with the enantioselectivity ranging between 97.6 % and 99.0 % ee. The optically active nitroalkanes obtained here are useful chiral building blocks which can be readily converted into a wide variety of optically active compounds by taking advantages of the versatile reactivity of nitro compounds.

CATALYTIC CYCLE OF THE RHODIUM-CATALYZED 1,4-ADDITION OF ORGANOBORON REAGENTS

We succeeded in characterizing the important intermediate involved in the catalytic cycle of the rhodium-catalyzed 1,4-addition by use of $RhPh(PPh_3)(binap)$ as a key intermediate [20]. The catalytic cycle illustrated for the reaction of phenylboronic acid with 2-cyclohexenone is shown in Scheme 9. The reaction proceeds by way of three intermediates, phenylrhodium **A**, oxa-π-allylrhodium **B**, and hydroxorhodium **C** complexes. All of the intermediates and transformations between the three complexes were observed in NMR spectroscopic studies (Scheme 10). The reaction of phenylrhodium complex $RhPh(PPh_3)(binap)$ with 2-cyclohexenone gave oxa-π-allylrhodium which is formed by insertion of the carbon–carbon double bond of enone into the phenyl–rhodium bond followed by isomerization into the thermodynamically stable complex. The oxa-π-allylrhodium complex was converted immediately into hydroxorhodium complex $[Rh(OH)(binap)]_2$ on addition of water, liberating



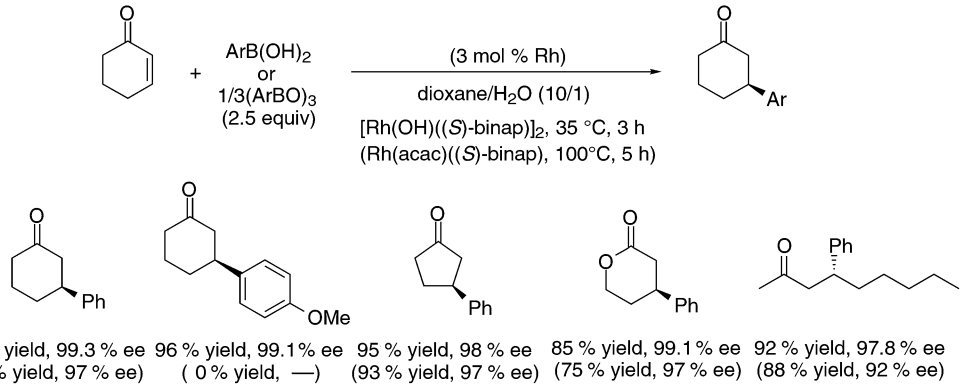
Scheme 9



Scheme 10

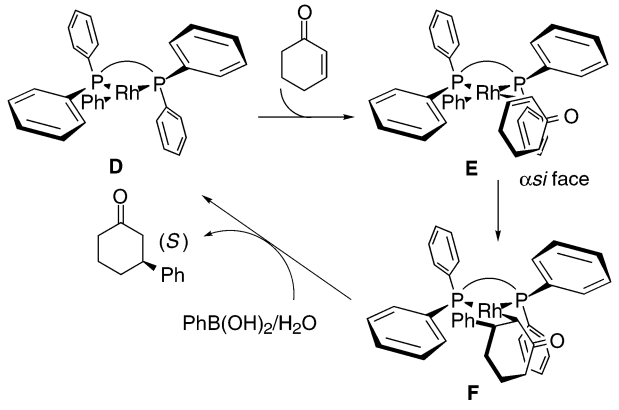
the phenylation product. Transmetallation of phenyl group from boron to rhodium takes place by addition of phenylboronic acid in the presence of triphenylphosphine to regenerate the phenylrhodium $RhPh(PPh_3)$(binap).

All three transformations in Scheme 10 were found to proceed at 25 °C, but the catalytic reaction in the presence of a rhodium catalyst generated from $Rh(acac)(C_2H_4)_2$ does not proceed at 60 °C or lower. It turned out that the acetylacetonato ligand retards the transmetallation step because of the high stability of the rhodium-acac moiety. Use of the hydroxo complex $[Rh(OH)(binap)]_2$ as a catalyst made it possible to run the reaction at lower temperature [20] (Scheme 11). Thus, the addition of phenylboronic acid or phenylboroxine to 2-cyclohexenone is catalyzed by $[Rh(OH)(binap)]_2$ at 35 °C to give a quantitative yield of 3-phenylcyclohexanone which is over 99 % enantiomerically pure. This catalyst system is also applicable to the reaction of other enones and organoboron reagents. The enantioselectivity is always higher than that in the reaction catalyzed by the rhodium-acac complex at 100 °C because the reaction temperature is lower. The chemical yields are higher and less boron reagent is used because the hydrolysis of the boronic acids, which is the main side reaction, is suppressed at the lower temperature.



Scheme 11

Scheme 12 shows the stereochemical pathway in the reaction catalyzed by the rhodium complex coordinated with (*S*)-binap [10]. According to the highly skewed structure known for transition-metal complexes coordinated with a binap ligand [21], (*S*)-binap–rhodium intermediate **D** should have an open space at the lower part of the vacant coordination site, the upper part being blocked by one of the phenyl rings of the binap ligand. The olefinic double bond of 2-cyclohexenone coordinates to rhodium with its α*si* face forming **E** rather than with its α*re* face, which undergoes migratory insertion to form a stereogenic carbon center in **F** whose absolute configuration is *S*. The absolute configurations of all the 1,4-addition products can be predicted by this type of stereocontrol model, (*S*)-binap–rhodium in-



Scheme 12

termediate attacking the α*si* face of α,β-unsaturated ketones, both cyclic and linear ones, and other electron-deficient olefins including α,β-unsaturated esters and alkenylphosphonates.

CONCLUSION

The rhodium-catalyzed asymmetric 1,4-addition reaction of organoboron reagents, which provides a highly efficient method of enantioselective transfer of aryl and alkenyl groups onto the β position of electron-deficient olefins, is complementary to the copper-catalyzed reactions where alkyl organometallic reagents are incorporated with high enantioselectivity [4]. The rhodium-catalyzed reaction involves a rhodium-aryl or -alkenyl species as an intermediate in the catalytic cycle. Considering the reactivity of the transition metal-carbon bond toward carbon–carbon or carbon-hetero atom multiple bonds, the rhodium intermediate is expected to add to some unsaturated bonds other than the electron-deficient olefins. Actually, the addition of organoboron reagents to aldehydes [22] and imines [23] has been reported to be catalyzed by a rhodium complex. The addition to aldehydes is applied to asymmetric synthesis of diarylmethanols, though the enantioselectivity is not high enough [22a]. An interesting reactions of arylboronic acids with norbornene and oxanorbornene derivatives have been reported by Miura [24] and Lautens [25], respectively, which involve the addition of rhodium-aryl bond to the norbornene double bond. In the reaction of oxanorbornene derivatives forming chiral functionalized cyclohexenes as ring-opening products, over 90 % enantioselectivity has been achieved [25]. The arylrhodium species can be also generated by transmetallation from some other organometallic agents. The addition of aryltin [26], -silicon [27], and -bismuth [28] reagents to α,β-unsaturated carbonyl compounds catalyzed by a rhodium complex is thought to proceed through a similar catalytic cycle. The addition of arylsilanes has recently been applied to the catalytic asymmetric synthesis [29]. High enantioselectivity has been achieved in the arylation of imines with arylstannanes, which is catalyzed by a rhodium complex coordinated with an axially chiral monodentate phosphine ligand (MOP) [30]. Many new catalytic reactions of synthetic value will be developed by combination of various types of organometallic reagents and unsaturated molecules, and some of them will be extended to catalytic asymmetric reactions of high enantioselectivity by proper tuning of the chiral catalyst. Our recent report on the use of aryltitanium reagents generating titanium enolates with high enantioselectivity as the 1,4-addition products is one of the examples [31].

ACKNOWLEDGMENTS

Much of the work described in this article has been supported by the Research for the Future Program, the Japan Society for the Promotion of Science, and a Grant-in-Aid for Scientific Research, the Ministry of Education, Japan.

REFERENCES AND NOTES

1. (a) I. Ojima. *Catalytic Asymmetric Synthesis II,* Wiley-VCH, New York (2000); (b) E. N. Jacobsen, A. Pfaltz, H. Yamamoto. *Comprehensive Asymmetric Catalysis*, Vols. 1–3, Springer, Berlin (1999); (c) R. Noyori. *Asymmetric Catalysis in Organic Synthesis*, John Wiley, New York (1994).
2. For reviews on 1,4-addition reactions: (a) P. Perlmutter. *Conjugate Addition Reactions in Organic Synthesis*, Pergamon, Oxford (1992); (b) H.-G. Schmalz. In *Comprehensive Organic Synthesis*, B. M. Trost and I. Fleming, (Eds.), Vol. 4, Chap. 1.5, Pergamon, Oxford (1991); (c) B. E. Rossiter and N. M. Swingle. *Chem. Rev*. **92**, 771 (1992).
3. For recent reviews on catalytic asymmetric 1,4-addition: (a) N. Krause and A. Hoffmann-Röder. *Synthesis* 171 (2001); (b) M. P. Sibi and S. Manyem. *Tetrahedron* **56**, 8033 (2000); (c) K. Tomioka and Y. Nagaoka. In *Comprehensive Asymmetric Catalysis*, E. N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Vol. 3, Chap. 31.1, Springer, Berlin (1999); (d) M. Kanai and M. Shibasaki. In *Catalytic Asymmetric Synthesis*, 2nd ed., I. Ojima (Ed.), pp. 569–592, John Wiley, New York (2000).
4. As examples of the copper-catalyzed asymmetric 1,4-addition of organozinc reagents generating zinc enolates: (a) H. Mizutani, S. J. Degrado, A. H. Hoveyda. *J. Am. Chem. Soc*. **124**, 779 (2002); (b) A. Alexakis, C. Benhaim, S. Rosset, M. Humam. *J. Am. Chem. Soc*. **124**, 5262 (2002); (c) L. A. Arnold, R. Naasz, A. J. Minnaard, B. L. Feringa. *J. Am. Chem. Soc*. **123**, 5841 (2001); (d) A. Alexakis, G. P. Trevitt, G. Bernardinelli. *J. Am. Chem. Soc.* **123**, 4358 (2001); (e) S. J. Degrado, H. Mizutani, A. H. Hoveyda. *J. Am. Chem. Soc.* **123**, 755 (2001); (f) I. H. Escher and A. Pfaltz. *Tetrahedron* **56**, 2879 (2000); (g) M. Yan and A. S. C. Chan. *Tetrahedron Lett*. **40**, 6645 (1999).
5. For examples for catalytic asymmetric Michael addition of malonate esters, see: (a) M. Yamaguchi, T. Shiraishi, M. Hirama. *J. Org. Chem.* **61**, 3520 (1996); (b) T. Arai, H. Sasai, K. Aoe, K. Okamura, T. Date, M. Shibasaki. *Angew. Chem., Int. Ed. Engl*. **35**, 104 (1996); (c) M. Shibasaki, H. Sasai, T. Arai. *Angew. Chem., Int. Ed. Engl.* **36**, 1236 (1997); (d) Y. S. Kim, S. Matsunaga, J. Das, A. Sekine, T. Ohshima, M. Shibasaki. *J. Am. Chem. Soc*. **122**, 6506 (2000), and references cited therein.
6. M. Sakai, H. Hayashi, N. Miyaura. *Organometallics* **16**, 4229 (1997).
7. Y. Takaya, M. Ogasawara, T. Hayashi, M. Sakai, N. Miyaura. *J. Am. Chem. Soc.* **120**, 5579 (1998).
8. (a) M. Kuriyama, K. Nagai, K. Yamada, Y. Miwa, T. Taga, K. Tomioka. *J. Am. Chem. Soc.* **124**, 8932 (2002); (b) M. T. Reetz, D. Moulin, A. Gosberg. *Org. Lett.* **3**, 4083 (2001); (c) R. Amengual, V. Michelet, J.-P. Genêt. *Synlett* 1791 (2002); (d) J.-G. Boiteau, R. Imbos, A. J. Minnaard, B. L. Feringa. *Org. Lett.* **5**, 681 (2003).
9. For reviews concerned with the rhodium-catalyzed asymmetric addition: (a) K. Fagnou and M. Lautens. *Chem. Rev*. **103**, 169 (2003); (b) T. Hayashi and K. Yamasaki. *Chem. Rev*. **103**, 2829 (2003); (c) C. Bolm, J. P. Hildebrand, K. Muniz, N. Hermanns. *Angew. Chem., Int. Ed. Engl.* **40**, 3284 (2001); (d) T. Hayashi. *Synlett* 879 (2001).
10. T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara. *Org. Synth*. **79**, 84 (2002).
11. Y. Takaya, M. Ogasawara, T. Hayashi. *Tetrahedron Lett*. **39**, 8479 (1998).
12. Y. Takaya, M. Ogasawara, T. Hayashi. *Tetrahedron Lett*. **40**, 6957 (1999).

13. Y. Takaya, T. Senda, H. Kurushima, M. Ogasawara, T. Hayashi. *Tetrahedron: Asymmetry* **10**, 4047 (1999).
14. S. Sakuma, M. Sakai, R. Itooka, N. Miyaura. *J. Org. Chem.* **65**, 5951 (2000).
15. S. Sakuma and N. Miyaura. *J. Org. Chem.* **66**, 8944 (2001).
16. T. Senda, M. Ogasawara, T. Hayashi. *J. Org. Chem*. **66**, 6852 (2001).
17. T. Hayashi, T. Senda, Y. Takaya, M. Ogasawara. *J. Am. Chem. Soc.* **121**, 11591 (1999).
18. Y. Tokunaga, H. Ueno, Y. Shimomura, T. Seo. *Heterocycles* **57**, 787 (2002).
19. T. Hayashi, T. Senda, M. Ogasawara. *J. Am. Chem. Soc.* **122**, 10716 (2000).
20. T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara. *J. Am. Chem. Soc.* **124**, 5052 (2002).
21. F. Ozawa, A. Kubo, Y. Matsumoto, T. Hayashi, E. Nishioka, K. Yanagi, K. Moriguchi. *Organometallics* **12**, 4188 (1993), and references cited therein.
22. (a) M. Sakai, M. Ueda, N. Miyaura. *Angew. Chem., Int. Ed. Engl*. **37**, 3279 (1998); (b) M. Ueda and N. Miyaura. *J. Org. Chem*. **65**, 4450 (2000).
23. M. Ueda and N. Miyaura. *J. Organomet. Chem*. **595**, 31 (2000).
24. K. Oguma, M. Miura, T. Satoh, M. Nomura. *J. Am. Chem. Soc*. **122**, 10464 (2000).
25. (a) M. Lautens, C. Dockendorff, K. Fagnou, A. Malicki. *Org. Lett*. **4**, 1311 (2002); (b) M. Lautens, K. Fagnou, S. Hiebert. *Acc. Chem. Res*. **36**, 48 (2003).
26. (a) S. Oi, M. Moro, S. Ono, Y. Inoue. *Chem. Lett.* 83 (1998); (b) S. Oi, M. Moro, H. Ito, Y. Honma, S. Miyano, Y. Inoue. *Tetrahedron* **58**, 91 (2002); (c) T.-S. Huang and C.-J. Li. *Org. Lett.* **3**, 2037 (2001); (d) S. Venkatraman, Y. Meng, C.-J. Li. *Tetrahedron Lett*. **42**, 4459 (2001).
27. (a) S. Oi, Y. Honma, Y. Inoue. *Org. Lett.* **4**, 667 (2002); (b) S. Oi, M. Moro, Y. Inoue. *Organometallics* **20**, 1036 (2001); (c) A. Mori, Y. Danda, T. Fujii, K. Hirabayashi, K. Osakada. *J. Am. Chem. Soc*. **123**, 10774 (2001); (d) T. Koike, X. Du, A. Mori, K. Osakada. *Synlett* 301 (2002); (e) A. Mori and T. Kato. *Synlett* 1167 (2002).
28. S. Venkatraman and C.-J. Li. *Tetrahedron Lett*. **42**, 781 (2002).
29. S. Oi, A. Taira, Y. Honma, Y. Inoue. *Org. Lett*. **5**, 97 (2003).
30. (a) T. Hayashi and M. Ishigedani. *J. Am. Chem. Soc*. **122**, 976 (2000); (b) T. Hayashi and M. Ishigedani. *Tetrahedron* **57**, 2589 (2001).
31. T. Hayashi, N. Tokunaga, K. Yoshida, J. W. Han. *J. Am. Chem. Soc*. **124**, 12102 (2002).