Bis(oxazolinyl)phenylrhodium(III) Aqua Complexes: Synthesis, Structure, Enantioselective Allylation of Aldehydes, and Mechanistic Studies

Yukihiro Motoyama, Masanori Okano, Hiroki Narusawa, Nobuyuki Makihara, Katsuyuki Aoki, and Hisao Nishiyama*

School of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan

Received January 9, 2001

The reaction of (Phebox)$SnMe_3$ (**4**; Phebox = 2,6-bis(oxazolinyl)phenyl) and $[(cyclooctene)_2RhCl]_2$ in the presence of CCl_4 provided the air-stable and water-tolerant (Phebox)$RhCl_2(H_2O)$ complexes **5**. These neutral (noncationic) aqua complexes **5** acted as asymmetric catalysts for enantioselective allylation of aldehydes with allyltin reagents in the presence of 4 Å molecular sieves (MS 4A). Furthermore, these aqua complexes could be recovered quantitatively from the reaction media. Detailed mechanistic studies of this catalytic system using X-ray and NMR spectroscopy revealed that the (Phebox)$RhCl_2$ fragment, generated by releasing H_2O from aqua complex **5**, is an active catalyst and the reaction proceeds by a Lewis acid catalyzed mechanism. The relative stereochemistry of the major adduct of the reaction of benzaldehyde with crotyltin reagents was *anti* (*threo*). The observed *anti* diastereoselectivity and *si*-face attack of allyltins on the carbonyl carbon of aldehydes were explained by the inverse antiperiplanar transition-state model.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

Introduction

The development of chiral Lewis acid catalysts, particularly for carbon−carbon (C−C) bond forming reactions, is one of the most challenging and formidable endeavors in organic synthesis.[1] Among various C−C bond forming reactions, asymmetric allylation of carbonyl compounds is a valuable means of construction of chiral functionalized structures. Therefore, many chiral allylmetal reagents have been designed and synthesized,[2] and numerous delightful works on reactions using stoichiometric amounts of these reagents have been reported.[3]

The reaction of aldehydes with allyltrialkyltin reagents proceeds in the presence of Lewis acids.[4] Allyltin reagents or produced alkoxystannanes sometimes undergo ligand exchange with Lewis acids easily in the reaction media to form new allylmetal species or to decompose the Lewis acid catalysts.[5] Therefore, many of these reactions need an equivalent (or excess) amount of Lewis acids (Lewis acid promoted reaction). Accordingly, there are only a few methods for catalytic processes[6] using chiral Lewis acid complexes (Lewis acid-catalyzed reaction), including a chiral (acyloxy)borane (CAB) complex (**A**)[7] (Chart 1), binaphthol-

(1) Reviews: (a) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1982; Vol. 8. (b) Morrison, J. D. *Asymmetric Synthesis*; Academic Press: New York, 1984; Vol. 3B. (c) Bosnich, B. *Asymmetric Catalysis*; Martinus Nijhoff: Dordrecht, The Netherlands, 1986. (d) Noyori, R.; Kitamura, M. In *Modern Synthetic Methods 1989*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1989; Vol. 5. (e) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994.

(2) Reviews: (a) Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1. (b) Biellmann, J. F.; Ducep, J. B. *Org. React.* **1982**, *27*, 1. (c) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. (d) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Heathcock, C. H., Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 2, p 1. (e) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (f) Bach, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 417. (g) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262.

(3) Allylboranes: (a) Brown, H. C.; Jadhav, P. K. *J. Am. Chem. Soc.* **1983**, *105*, 2092. (b) Short, R. P.; Masamune, S. *J. Am. Chem. Soc.* **1989**, *111*, 1892. (c) Racherla, U. S.; Brown, H. C. *J. Org. Chem.* **1991**, *56*, 401. Allylboronates: (d) Herold, T.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 768. (e) Hoffmann, R. W.; Herold, T. *Chem. Ber.* **1981**, *114*, 375. (f) Roush, W. R.; Walts, A. E.; Hoong, L. K. *J. Am. Chem. Soc.* **1985**, *107*, 8186. (g) Roush, W. R.; Banfi, L. *J. Am. Chem. Soc.* **1988**, *110*, 3979. (h) Roush, W. R.; Hoong, L. K.; Palmer, M. A. J.; Park, J. C. *J. Org. Chem.* **1990**, *55*, 4109. (i) Reetz, M. T.; Zierke, T. *Chem. Ind.* **1988**, 663. Allylboradiazolidines: (j) Corey, E. J.; Yu, C.-M.; Kim, S. S. *J. Am. Chem. Soc.* **1989**, *111*, 5495. Allyltitanates: (k) Riediker, M.; Duthaler, R. O. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 494. (l) Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 99. (m) Hafner, A.; Duthaler, R. O.; Marti, R.; Rihs, G.; Rothe-Streit, P.; Schwarzenbach, F. *J. Am. Chem. Soc.* **1992**, *114*, 2321. Allylaluminum derivatives: (n) Minowa, N.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3697. Allylstannanes: (o) Otera, J.; Kawasaki, Y.; Mizuno, H.; Shimizu, Y. *Chem. Lett.* **1983**, 1529. (p) Otera, J.; Yoshinaga, Y.; Yamaji, T.; Yoshioka, T.; Kawasaki, Y. *Organometallics* **1985**, *4*, 1213. (q) Boldrini, G. P.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Chem. Soc., Chem. Commun.* **1986**, 685. (r) Boldrini, G. P.; Lodi, L.; Tagliavini, E.; Tarasco, C.; Trombini, C.; Umani-Ronchi, A. *J. Org. Chem.* **1987**, *52*, 5447. (s) Boga, C.; Savoia, D.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Organomet. Chem.* **1988**, *353*, 177. Allylchromium complexes: (t) Sugimoto, K.; Aoyagi, S.; Kibayashi, C. *J. Org. Chem.* **1997**, *62*, 2322.

(4) Reviews: (a) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31. (b) See also ref 2.

(5) (a) Gambaro, A.; Peruzzu, V.; Plazzogna, G.; Tagliavini, G. *J. Organomet. Chem.* **1980**, *197*, 45. (b) Keck, G. E.; Abbott, D. E.; Boden, E. P.; Enholm, E. J. *Tetrahedron Lett.* **1984**, *25*, 3927. (c) Denmark, S. E.; Wilson, T.; Wilson, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 984. (d) Keck, G. E.; Andrus, M. B.; Castellino, S. *J. Am. Chem. Soc.* **1989**, *111*, 8136.

(6) Only two catalytic systems using achiral Lewis acids were reported. $Yb(OTf)_3$: (a) Greeves, N.; Aspinall, H. C.; Browning, A. F.; Ravenscroft, P. *Tetrahedron Lett.* **1994**, *35*, 4639. (b) Aspinall, H. C.; Dwyer, J. L. M.; Greeves, N.; McIver, E. G.; Woolley, J. C. *Organometallics* **1998**, *17*, 1884. (c) Aspinall, H. C.; Greeves, N.; McIver, E. G. *Tetrahedron Lett.* **1998**, *39*, 9283. Bulky aluminum phenoxides: (d) Marx, A.; Yamamoto, H. *Synlett* **1999**, 584.

10.1021/om010018y CCC: $20.00 © 2001 American Chemical Society
Publication on Web 03/22/2001

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

Chart 1

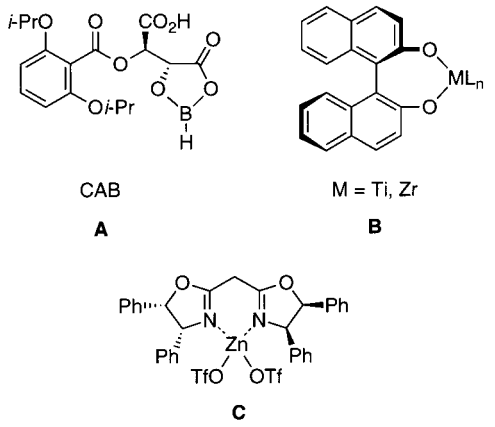
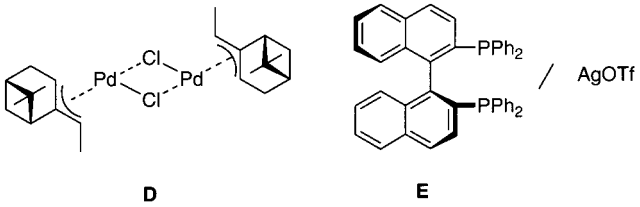


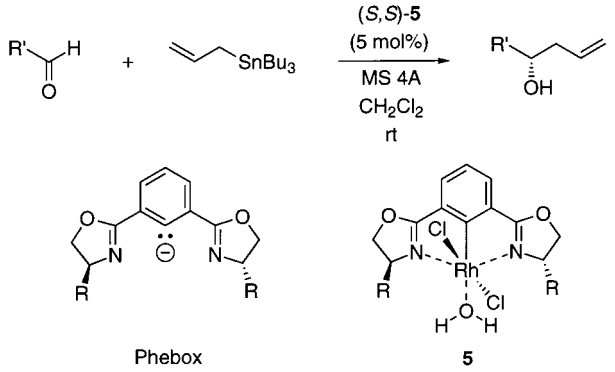
Chart 2



derived titanium[8] and zirconium complexes (**B**),[9] and a bis(oxazoline)-derived zinc complex (**C**).[10] However, the structural identification of chiral catalysts or their active intermediates being Lewis acid−aldehyde complexes has not yet been clarified.

Recently, Nakamura and Yamamoto reported that catalytic amounts of Pd(II) and Pt(II) complexes catalyze the reaction of aldehydes with allylic stannanes.[11] In their catalytic system, a key intermediate is a bis(π-allyl)metal complex which is generated by transmetalation of the corresponding Pd(II) or Pt(II) precursors with allyltin reagents. The bis(π-allyl)metal complexes capture aldehydes to form (π-allyl)(σ-allyl)M(aldehyde) complexes (M = Pd, Pt), and then the allylation proceeds via intramolecular allyl transfer to the bound aldehydes. They also reported asymmetric allylation of aldimines with allyltributyltin using a catalytic amount of a chiral bis(π-allyl)palladium complex (**D**)[12] (Chart 2). Then, Yanagisawa and Yamamoto created a new catalytic process using a BINAP−Ag(I) complex generated in situ from BINAP and AgOTf, resulting in excellent enantioselectivity (**E**).[13] However, it is ambiguous whether the allylation reaction catalyzed with the BINAP−Ag(I) complex proceeds by a Lewis acid mechanism or the transmetalation pathway.

Scheme 1



We have developed a chiral 2,6-bis(oxazolinyl)phenyl derivative (Phebox) as an N−C−N type tridentate ligand with one central covalent bond to a metal and synthesized rhodium(III),[14a] palladium(II),[14a] and platinum(II) and -(IV)[14b] complexes bearing Phebox as chiral ligands. We preliminary reported the first example of a Rh(III)-catalyzed enantioselective addition of allyltributyltin to aldehydes (Scheme 1).[15a] To consider the transition states, it is important to clarify the structure of the catalyst and their active intermediates such as Lewis acid−aldehyde complexes or allylmetal species. Here, we wish to report full details of the synthesis of the chiral Phebox-derived rhodium(III) complexes **5**, and a catalytic asymmetric allylation of aldehydes with allyltin reagents. We also describe X-ray crystallographic and NMR evidence for the basis of the reaction mechanism and transition-state assembly in this catalytic system.

Results and Discussion

1. Synthesis of Phebox Compounds. 1.1. Synthesis of (Phebox)SnMe$_3$ Compounds 4. Synthesis of the (Phebox)SnMe$_3$ compounds **4**, which are the precursor of the Phebox ligands, strated from bromo-*m*-xylene (**1**). The oxidation reaction of **1** with $KMnO_4$ gave 2-bromoisophthalic acid, which then was treated with $SOCl_2$ to obtain 2-bromoisophthaloyl chloride (**2**) in 56% yield. The acid chloride **2** was treated with appropriate amino alcohols and subsequently with thionyl chloride, followed by base-promoted cyclization to give the (Phebox)-Br compounds **3**. The (Phebox)SnMe$_3$ compounds **4** were synthesized by treatment of **3** with *n*-BuLi followed by addition of Me_3SnCl (Scheme 2).[16]

1.2. Synthesis and Structure of (Phebox)RhCl$_2$-(H$_2$O) Complexes 5. At first, the (*i*-Pr-Phebox)$RhCl_2$-(H_2O) complex **5a** was synthesized by the transmeta-

(7) (a) Marshall, J. A.; Tang, Y. *Synlett* **1992**, 653. (b) Marshall, J. A.; Palovich, M. R. *J. Org. Chem*. **1998**, *63*, 4381.

(8) (a) Aoki, S.; Mikami, K.; Terada, M.; Nakai, T. *Tetrahedron* **1993**, *49*, 1783. (b) Costa, A. L.; Piazza, M. G.; Tagliavini, E.; Trombini, C.; Umani-Ronchi, A. *J. Am. Chem. Soc.* **1993**, *115*, 7001. (c) Keck, G. E.; Tarbet, K. H.; Geraci, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 8467. (d) Weigand, S.; Brückner, R. *Chem. Eur. J*. **1996**, *2*, 1077.

(9) (a) Bedeschi, P.; Casolari, S.; Costa, A. L.; Tagliavini, E.; Umani-Ronchi, A. *Tetrahedron Lett*. **1995**, *36*, 7897. (b) Casolari, S.; Cozzi, P. G.; Orioli, P.; Tagliavini, E.; Umani-Ronchi, A. *Chem. Commun*. **1997**, 2123.

(10) Cozzi, P. G.; Orioli, P.; Tagliavini, E.; Umani-Ronchi, A. *Tetrahedron Lett*. **1997**, *38*, 145.

(11) (a) Nakamura, H.; Asao, N.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun*. **1995**, 1273. (b) Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc*. **1996**, *118*, 6641.

(12) Nakamura, H.; Nakamura, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4242.

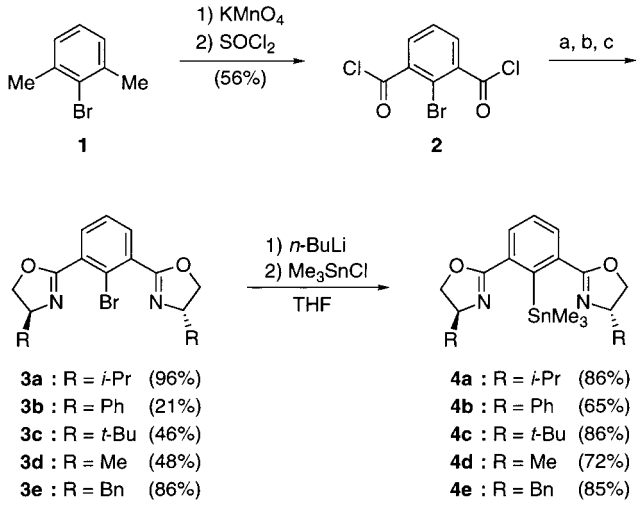
(13) (a) Yanagisawa, A.; Nakashima, H.; Ishiba, A.; Yamamoto, H. *J. Am. Chem. Soc*. **1996**, *118*, 4723. (b) Yanagisawa, A.; Ishiba, A.; Nakashima, H.; Yamamoto, H. *Synlett* **1997**, 88.

(14) (a) Motoyama, Y.; Makihara, N.; Mikami, Y.; Aoki, K.; Nishiyama, H. *Chem. Lett*. **1997**, 951. (b) Motoyama, Y.; Mikami, Y.; Kawakami, H.; Aoki, K.; Nishiyama, H. *Organometallics* **1999**, *18*, 3584.

(15) (a) Motoyama, Y.; Narusawa, H.; Nishiyama, H. *Chem. Commun*. **1999**, 131. Recently, the allylation of aldehydes with allyltributyltin catalyzed with chiral pyrrolidine-derived rhodium(III) complexes was reported, see: (b) Shi, M.; Lei, G.-X.; Masaki, Y. *Tetrahedron: Asymmetry* **1999**, *10*, 2071.

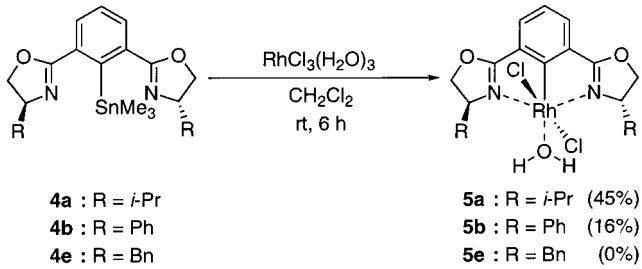
(16) (a) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Spek, A. L.; Schoone, J. C. *J. Organomet. Chem*. **1978**, *148*, 233. (b) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G. *Organometallics* **1989**, *8*, 1373.

Scheme 2[a]



[a] Legend: (a) amino alcohol/Et_3N/CH_2Cl_2; (b) $SOCl_2/CH_2Cl_2/\Delta$; (c) $NaOH/H_2O/\Delta$.

Scheme 3



lation reaction of (*i*-Pr-Phebox)$SnMe_3$ (**4a**) with $RhCl_3(H_2O)_3$ in dichloromethane.[17] This transmetalation reaction was occurred smoothly at room temperature to give the complex **5a** in 45% yield (Scheme 3). On the basis of the elemental analysis and ^1H NMR spectrum, one molecule of H_2O is coordinated to the rhodium atom (H_2O: δ 3.55 ppm). The ^1H and ^{13}C NMR spectra of **5a** indicated a C_2-symmetric structure in which H_2O is coordinated at the equatrial position in the Phebox plane and the two chlorine atoms are located in a *trans* configuration at the apical positions.[18] However, the chemical yields of the other complexes **5b**,**e** (**5b**, R = Ph; **5e**, R = Bn) were very low by this method (16% for **5b** and 0% for **5e**, respectively).

Next, we tried to synthesize these aqua complexes **5** from Rh(I) compounds, because we had already reported the synthesis of the complex (Pybox)$RhCl_3$ (Pybox = 2,6-bis(oxazolinyl)pyridine) by the reaction of Pybox and $[(cyclooctene)_2RhCl]_2$ in the presence of CCl_4.[19a] The

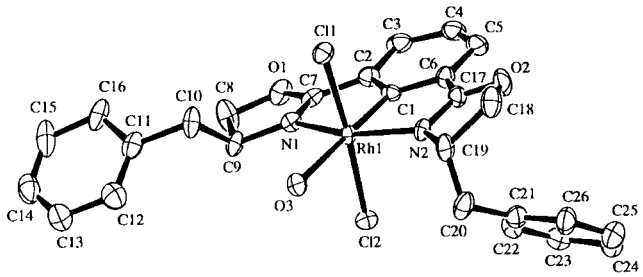
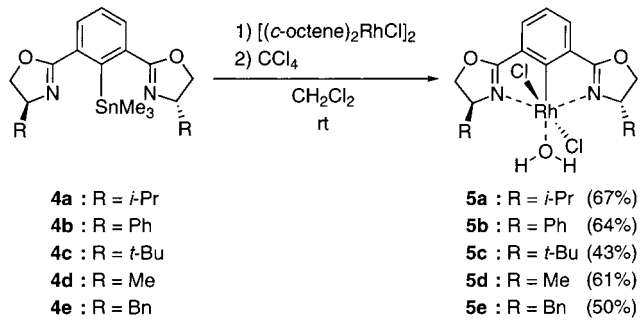


Figure 1. ORTEP drawing of (Bn-Phebox)$RhCl_2(H_2O)$ (**5e**).

Scheme 4



reaction of (*i*-Pr-Phebox)$SnMe_3$ **4a** with $[(cyclooctene)_2RhCl]_2$ in dichloromethane followed by treatment with CCl_4 at ambient temperature gave the desired aqua complex **5a** in 67% yield after silica gel chromatography. Other aqua substituent complexes **5b**−**e** were obtained from the corresponding stannyl compounds **4b**−**e** in a similar manner (Scheme 4). The structure of the Bn-Phebox-derived complex **5e** in the crystalline state was determined by an X-ray diffraction study.[20] Figure 1 shows the distorted-octahedral geometry; the N(1)−Rh(1)−N(2) angle is 158.7°, wherein two chlorine atoms have a *trans* configuration and the H_2O ligand is coordinated in the Phebox plane. These aqua complexes **5** were water-tolerant and air-stable for months at ambient temperature. The (*i*-Pr-Phebox)$RhCl_2(H_2O)$ complex **5a** was also obtained by the reaction of **4a** and $[(cyclooctene)_2RhCl]_2$ followed by treatment with $CuCl_2(H_2O)_2$,[21] instead of CCl_4, as a chlorinating reagent in 75% yield.

2. Asymmetric Allylation Catalyzed with (Phebox)$RhCl_2(H_2O)$ Complexes 5. 2.1. Allylation of Benzaldehyde with Allyltin Reagents. The optimization of the allylation reaction conditions employed benzaldehyde and allyltin reagents in the presence of 5 mol % of the (*S*,*S*)-(Phebox)$RhCl_2(H_2O)$ complex **5** as a chiral catalyst (Table 1). First of all, the rate of this allylation reaction was strongly dependent on the solvent; allylation with allyltributyltin proceeded smoothly in dichloromethane, but using tetrahydrofuran or an aromatic solvent such as benzene or toluene, the

(17) The N−C−N type ligand-coordinated Pd complexes prepared by the transmetalation of stannane or silane derivatives were reported by van Koten; see: Steenwinkel, P.; Jastrzebski, J. T. B. H.; Deelman, B.-D.; Grove, D. M.; Kooijman, H.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 5486.

(18) From the X-ray analysis of the N−C−N ($C_6H_3(CH_2NMe_2)_2$) ligand-derived rhodium complex, H_2O is located at the equatorial position; see: van der Zeijden, A. A. H.; van Koten, G.; Luijk, R.; Vrieze, K.; Slob, C.; Krabbendam, H.; Spek, A. L. *Inorg. Chem*. **1988**, *27*, 1014.

(19) (a) Nishiyama, H.; Horihata, M.; Hirai, T.; Wakamatsu, S.; Itoh, K. *Organometallics* **1991**, *10*, 2706. Vrieze reported the oxidative addition of carbon−chloride bonds to Rh(I) complexes containing terdentate nitrogen ligands [2,6-($C(R^1)$=NR^2)$_2C_5H_3N$]; see: (b) Haarman, H. F.; Ernsting, J. M.; Kranenburg, M.; Kooijman, H.; Veldman, N.; Spek, A. L.; van Leeuwen, P. W. N. M.; Vrieze, K. *Organometallics* **1997**, *16*, 887.

(20) Selected bond distances (Å) and angles (deg) for **5e**: Rh(1)−Cl(1) = 2.325(3), Rh(1)−Cl(2) = 2.331(3), Rh(1)−O(3) = 2.291(5), Rh(1)−N(1) = 2.075(6), Rh(1)−N(2) = 2.082(6), Rh(1)−C(1) = 1.921(7); Cl(1)−Rh(1)−Cl(2) = 175.10(9), Cl(1)−Rh(1)−O(3) = 89.8(3), Cl(1)−Rh(1)−N(1) = 92.3(2), Cl(1)−Rh(1)−N(2) = 86.9(2), Cl(1)−Rh(1)−C(1) = 89.7(4), O(3)−Rh(1)−C(1) = 179.3(5), N(1)−Rh(1)−N(2) = 158.7(2).

(21) van Koten reported that $CuCl_2$ oxidizes the N−C−N ligand-coordinated Ni(II) and Pt(II) complexes to Ni(III) and Pt(IV); see: (a) Grove, D. M.; van Koten, G.; Zoet, R.; Murrall, N. W.; Welch, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 1379. (b) Terheijden, J.; van Koten, G.; de Booys, J. L. *Organometallics* **1983**, *2*, 1882.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

Table 1. Asymmetric Catalytic Allylation of Benzaldehyde Catalyzed with (Phebox)$RhCl_2(H_2O)$ Complexes 5[a]

entry	catalyst	solvent	conditions	% yield	% ee[b]
1	**5a**	toluene	room temp, 24 h	23	45
2	**5a**	benzene	room temp, 24 h	64	45
3	**5a**	THF	room temp, 24 h	66	52
4	**5a**	CH_2Cl_2	room temp, 7 h	79	52
5[c]	**5a**	CH_2Cl_2	room temp, 7 h	88	51
6[c]	**5a**	CH_2Cl_2	0 °C, 24 h	46	49
7[c,d]	**5a**	CH_2Cl_2	room temp, 7 h	48	35
8[c,e]	**5a**	CH_2Cl_2	room temp, 7 h	7	27
9[c]	**5b**	CH_2Cl_2	room temp, 7 h	42	6
10[c]	**5c**	CH_2Cl_2	room temp, 7 h	43	46
11[c]	**5d**	CH_2Cl_2	room temp, 7 h	94	56
12[c]	**5e**	CH_2Cl_2	room temp, 7 h	88	61
13[c,f]	**5a**	CH_2Cl_2	room temp, 7 h	88	49

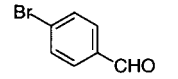
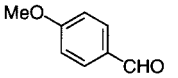
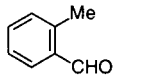
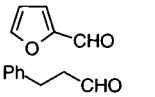
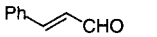
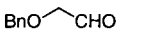
[a] All reactions were carried out using 0.5 mmol of benzaldehyde, 0.75 mmol of allyltin, and 0.025 mmol of chiral catalyst **5** in 2 mL of solvent. [b] Determined by chiral HPLC analysis using Daicel CHIRALCEL OD. [c] In the presence of MS 4A (250 mg). [d] Allyltrimethyltin was used as allylating reagent. [e] Allyltriphenyltin was used as allylating reagent. [f] Recovered catalyst was used.

reaction rates were remarkably slow. However, enantioselectivities were almost the same in all cases (entries 1−4). In the presence of 4 Å molecular sieves (MS 4A), this catalytic reaction was accelerated but the enantiomeric excess of the product **6a** was not changed (entries 4 vs 5). The enantioselectivity did not improve at 0 °C (entries 5 vs 6). Using allyltrimethyltin or allyltriphenyltin as allylating reagents, chemical yields and enantioselectivities of **6a** were both decreased (entries 7 and 8). The substituent on the oxazoline rings had a great effect on the chemical yields and % ee's (entries 5 and 9−12). The catalytic activities of the Ph- and *t*-Bu-Phebox-derived complexes **5b**,**c** were lower than those of the other complexes **5a**,**d**,**e**. The enantioselectivity using the Ph-Phebox-derived complex **5b** was remarkably decreased, but the complex **5d**, having the smallest substituent on the oxazoline rings, CH_3, gave **6a** with 56% ee. Finally, an enantioselectivity of up to 61% ee was achieved using the Bn-Phebox-derived complex **5e**. The absolute configuration of **6a** was determined as *S* by comparison of the optical rotation with the literature value.[3e]

Incidentally, it is worth noting that the complex **5** can be recovered almost quantitatively from the reaction media by silica gel chromatography, and the recovered complex **5** catalyzes the reaction with almost the same catalytic activity and enantioselectivity (entries 5 vs 13).[22]

2.2. Allylation of Other Aldehydes with Allyltributyltin. Table 2 summarizes the results obtained for the allylation reaction of a variety of aldehydes catalyzed with 5 mol % of the complex **5e** in dichloromethane solution in the presence of MS 4A at ambient temperature for 7 h. All reactions resulted in high yields and comparable enantioselectivities with both aromatic and aliphatic aldehydes, except in the case of α-benzyloxyacetaldehyde. The enantioselectivities were remarkably dependent on the substituents on the benzene ring: *p*-H, 61% ee; *p*-Br, 43% ee; *p*-OMe, 80% ee; *o*-Me, 53% ee (entries 1−4). In the reaction with cinnamaldehyde as an enal, the 1,2-addition reaction proceeded exclusively (entry 7). Using α-benzyloxyacetaldehyde as a substrate, which is known as a reactive aldehyde, both chemical yield and enantioselectivity were significantly decreased (entry 8). In all of the cases, allyltributyltin attacks to the *si* face of the aldehyde's C=O plane.

Table 2. Asymmetric Catalytic Allylation of Aldehydes Catalyzed with (Phebox)$RhCl_2(H_2O)$ Complex 5e[a]

entry	aldehyde	product	% yield	% ee[b]	config.[c]
1	PhCHO	**6a**	88	61	*S*
2		**6b**	94	43	*S*[d]
3		**6c**	99	80	*S*
4		**6d**	98	53	*S*[d]
5		**6e**	94	58	*S*[d]
6		**6f**	84	63	*R*
7		**6g**	98	77	*S*
8		**6h**	45	35	*S*[e]

[a] All reactions were carried out using 0.5 mmol of aldehyde, 0.75 mmol of allyltributyltin, and 0.025 mmol of chiral catalyst **5e** in 2 mL of dichloromethane in the presence of MS 4A (250 mg) at room temperature for 7 h. [b] Determined by chiral HPLC analysis. [c] Assignment by comparison of the sign of optically rotation with reported value. [d] By analogy to the other case that is known unambiguously; see Experimental Section. [e] Assignment by analogy.

2.3. Allylation of Benzaldehyde with Crotyltins. The reaction of γ-substituted allyltin derivatives is an important problem with respect to the regioselectivities (α/γ) and diastereoselectivities (*syn*/*anti*). Thus, we examined the Phebox-Rh(III) catalyzed reaction of (*E*)- and (*Z*)-crotyltins with benzaldehyde. Reactivities of the crotyltin reagents were relatively lower than that of allyltributyltin, although use of an increased amount (10 mol %) of the rhodium complexes **5** and crotyltin reagents (2 equiv) resulted in satisfactory yields. The reaction of benzaldehyde with (*E*)-crotyltributyltin (*E*/*Z* = 95:5) in the presence of (*i*-Pr-Phebox)$RhCl_2(H_2O)$ (**5a**) afforded the γ-addition exclusively with an *anti*/*syn* ratio of 71:29 (Table 3, entry 1). The *anti* isomer proved to be 57% ee with 1*S*,2*S* configuration,[23] which is the same π-face selectivity at the carbonyl group as in the case of allyltributyltin. For the obtained *syn*-**7**, however, the enantioselectivity was only 8% ee with a 1*R*,2*S* configuration.[24] Using Bn-Phebox-derived **5e**, a similar enantioface selection, *anti* selectivity, and enantioselectivity were observed (entry 2). Employment of a nearly 1:1 mixture of (*E*)- and (*Z*)-crotyltin (*E*/*Z* = 49:

(22) Other examples of the recoverable chiral complexes are as follows. Ru complex for the cyclopropanation: (a) Nishiyama, H.; Itoh, Y.; Matsumoto, H.; Park, S.-B.; Itoh, K. *J. Am. Chem. Soc.* **1994**, *116*, 2223. Ru complex for the oxidation of sulfides: (b) Schenk, W. A.; Dürr, M. *Chem. Eur. J.* **1997**, *3*, 713. Ru complex for the Diels−Alder reaction: (c) Kündig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1220.

(23) The absolute configuration of *anti*-**7** was determined by the retention time of the chiral HPLC analysis.[13b]

(24) The absolute configuration of *syn*-**7** was determined by the retention time of the chiral HPLC analysis using the authentic sample, which was prepared by Roush's method (57% ee, 1*S*, 2*R*); see: Roush, W. R.; Ando, K.; Powers, D. B.; Palkowits, A. D.; Halterman, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 6339.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

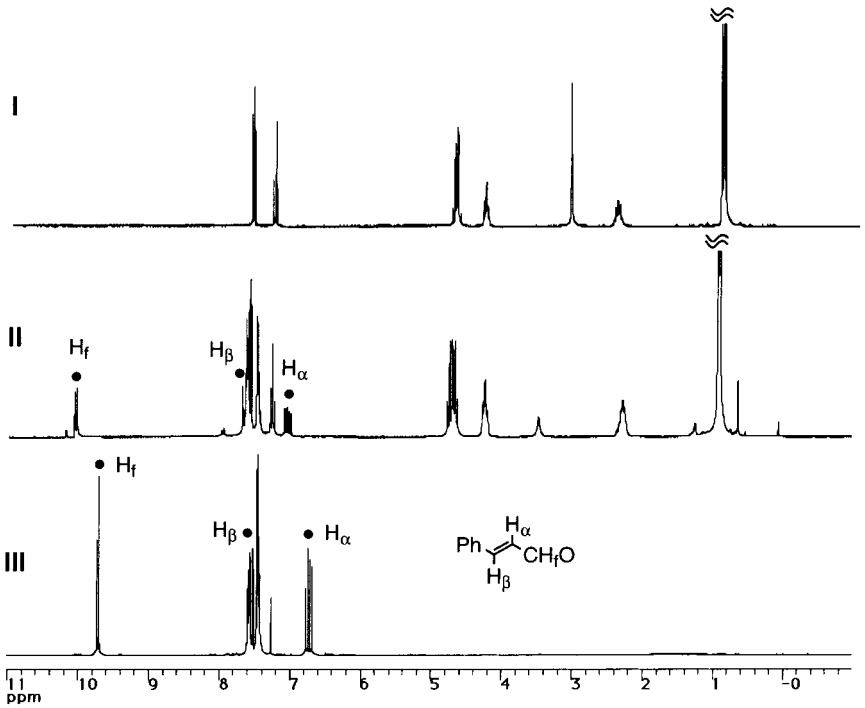
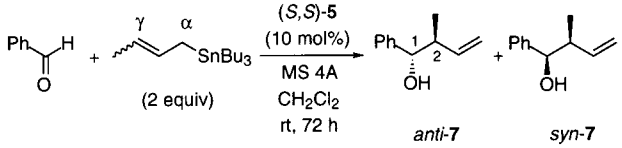


Figure 2. ^{1}H NMR spectra ($CDCl_3$): (**I**) **5a**; (**II**) cinnamaldehyde + **5a**; (**III**) cinnamaldehyde.

Table 3. Asymmetric Allylation of Benzaldehyde with Crotyltins[a]



entry	*E*/*Z* ratio of crotyltin	catalyst	% yield	*anti*/*syn*[b] (% ee)[c]
1	95:5	**5a**	77	71 (57):29 (8)
2	95:5	**5e**	86	64 (59):36 (6)
3	49:51	**5a**	80	66 (58):34 (2)
4	2:98	**5a**	85	63 (60):37 (7)

[a] All reactions were carried out using 0.5 mmol of benzaldehyde, 1.0 mmol of crotyltin and 0.05 mmol of chiral catalyst **5** in 2 mL of CH_2Cl_2 in the presence of MS 4A (250 mg). [b] Determined by ^{1}H NMR analysis. [c] Determined by chiral HPLC analysis using Daicel CHIRALCEL OD-H.

51) or (*Z*)-crotyltin (*E*/*Z* = 2:98) also resulted in a similar *anti* selectivity and enantioselectivity. When the amount of (*Z*)-crotyltin was increased, the chemical yield of **7** was increased but the *anti* selectivity was decreased (entries 1, 3, and 4). In all cases, the recovered crotyltin was not found to be isomerized.

3. Mechanistic Studies. 3.1. Isolation, NMR Studies, and X-ray Analysis of Phebox-Rh(III)-Carbonyl Complexes. First, we checked the complexation between Phebox-Rh(III) complex **5a** and several aldehydes by ^{1}H NMR study. Although rigid complexation was not clearly observed between **5a** and benzaldehyde, the solution of **5a** and (*E*)-cinnamaldehyde showed formation of a new complex. The signals of olefinic protons (H_α and H_β: H_α = α-proton, H_β = β-proton) and the formyl proton (H_f) of coordinated cinnamaldehyde appeared at lower field than the uncomplexed (free) aldehyde (from δ 9.71 to 10.03 ppm for H_f, from δ 7.54 to 7.63 ppm for H_β, and from δ 6.73 to 7.02 ppm for H_α)

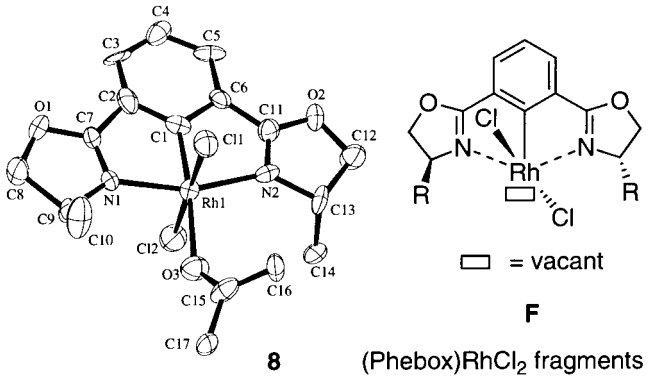
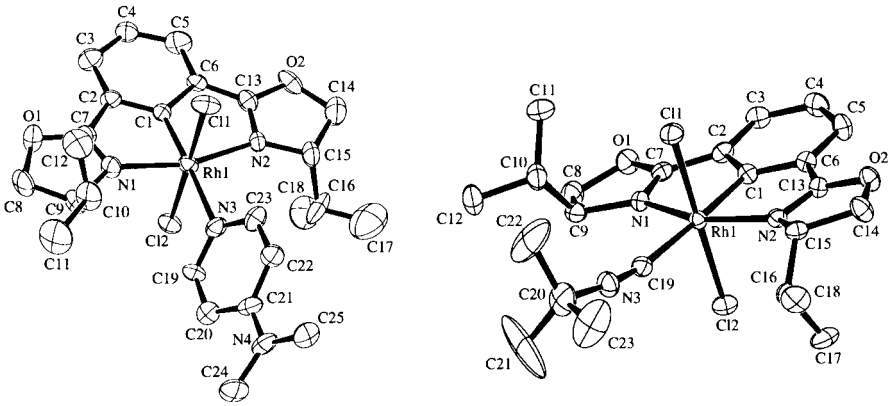


Figure 3. ORTEP drawing of (Me-Phebox)$RhCl_2$(acetone) (**8**) and (Phebox)$RhCl_2$ fragments **F**.

(Figure 2). The low-field shift for the carbonyl carbon (from δ 192.9 to 197.3 ppm) was also observed in ^{13}C NMR. It is widely known that chemical shifts of vinylic protons (H_α and H_β) and the formyl proton (H_f) of enals bound to Lewis acids by carbonyl oxygens appear at lower field than those of free enals.[25] Therefore, it can be concluded that cinnamaldehyde is coordinated to the rhodium atom at the carbonyl oxygen (C=O/σ type), not forming the C=C/π or C=O/π complex.

Although single crystals of aldehyde complexes were not obtained, we succeeded in synthesizing and characterizing the acetone-coordinated complex **8**. This acetone complex **8** was obtained by the reaction of (Me-Phebox)$SnMe_3$ (**4d**) and [(cyclooctene)$_2$RhCl]$_2$ in dichloromethane−carbon tetrachloride followed by the addition of acetone. The complex **8** could be purified by silica gel chromatography (2:1 dichloromethane/acetone) in

(25) (a) Furukawa, J.; Kobayashi, E.; Nagata, S.; Moritani, T. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1799. (b) Kuran, W.; Pasynkiewicz, S.; Florjanczyk, K.; Lusztyk, E. *Macromol. Chem.* **1976**, *177*, 2627. (c) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.



9 **10**

Figure 4. Molecular structures of (*i*-Pr-Phebox)$RhCl_2$(DMAP) (**9**) and (*i*-Pr-Phebox)$RhCl_2$(*t*-BuNC) (**10**).

42% yield; however, the bound acetone dissociated easily to form the aqua complex **5d**. An ORTEP drawing of **8** shows that the acetone molecule is bound to the rhodium atom at the carbonyl oxygen (C═O/σ type) and the rhodium atom is located almost in-plane with the acetone plane; Rh(1)−O(3)−C(15)−C(16) is −8°. The bound acetone plane leans toward the Phebox plane from the Cl−Rh−Cl plane; the dihedral angle between the acetone plane and the Cl−Rh−Cl plane (Cl(1)−Rh(1)−O(3)−C(15)) is 44°. This slope of the acetone plane can be considered for the steric repulsion between the CH_3 group of the bound acetone and one chlorine atom at the apical position on the rhodium atom of the octahedral structure **F** (Figure 3).[26] The NMR and X-ray studies thus indicated that the (Phebox)$RhCl_2$ fragments **F**, generated by releasing H_2O from (Phebox)$RhCl_2(H_2O)$, capture cinnamaldehyde at the carbonyl oxygen to make a C═O/σ type complex, not to form a C═O/π or C═C/π complex, just as common Lewis acids.[27]

Such a Lewis acidic character of the (Phebox)$RhCl_2$ fragments **F** was also indicated on the basis of the fact that the corresponding ethylene- and CO-coordinated complexes could not be obtained. However, (dimethylamino)pyridine (DMAP) was bound to the rhodium atom as a Lewis base to give the DMAP-bound complex **9** in dichloromethane at room temperature in 78% yield. The (Phebox)$RhCl_2$ fragments **F** also showed the traditional transition metal character to form the isocyanide (*t*-BuNC) complex **10** in dichloromethane in 90% yield. Structures of both complexes **9**[28] and **10**[29] are shown in Figure 4.

3.2. Reaction Mechanism. To clarify the reaction mechanism of the present allylation reaction using the Phebox-Rh(III) complexes **5**, we first examined the reaction between (*i*-Pr-Phebox)$RhCl_2(H_2O)$ (**5a**) and allyltributyltin in the absence of aldehydes. On the basis of its ^1H NMR spectrum in $CDCl_3$, no transmetalation of the complex **5a** with allyltin proceeded; only the resonances for **5a** and allyltin were detected, and both allyltin and **5a** were recovered quantitatively. Therefore, the possibility that the complex **5a** reacts with allyltributyltin to generate new allylrhodium species could be ruled out. When allyltributyltin was added to the mixture of **5a** and benzaldehyde in CD_2Cl_2 in the presence of MS 4A at room temperature, signals due to [(1-phenyl-3-butenyl)oxy]tributylstannane **11** were spontaneously observed. After quenching by the addition of HCl solution, the product **6a** was formed and the starting aqua complex **5a** was recovered. Therefore, we concluded that the present allylation reaction catalyzed with (Phebox)$RhCl_2(H_2O)$ complexes **5** proceeds via a Lewis acid mechanism and the active catalyst is the (Phebox)$RhCl_2$ fragments **F**. In other words, the (Phebox)$RhCl_2$ fragments **F** can activate the carbonyl group of aldehydes by coordination at the Lewis acidic vacant site. Then the allyltin attacks the activated aldehydes on (Phebox)$RhCl_2$ (Scheme 5).

3.3. Transition State Assembly. The possible structure of the aldehyde-bound intermediate **G**, based on X-ray and NMR studies, is shown in Scheme 6. Aldehydes are coordinated to the rhodium atom at the carbonyl oxygen, and its C═O plane is shifted from the Cl−Rh−Cl plane to the Phebox plane to avoid steric repulsion between the formyl proton and the apical chlorine atom like the acetone and DMAP complexes **8** and **9**. This structure is consistent with the absolute configuration of the allylated products **6**. One of the substituents on the oxazoline rings plays the crucial role of shielding the *re* face of the C═O plane from attack by the allyltin.

Lewis acid catalyzed (or promoted) reactions of aldehydes with allyltin reagents, without transmetalation processes, proceed via "open" transition states;[30] furthermore, crotyltins undergo *syn* (*erythro*)-selective

(26) Selected bond distances (Å) and angles (deg) for **8**: Rh(1)−Cl(1) = 2.341(4), Rh(1)−Cl(2) = 2.338(4), Rh(1)−O(3) = 2.27(1), Rh(1)−N(1) = 2.06(1), Rh(1)−N(2) = 2.12(1), Rh(1)−C(1) = 1.93(2); Cl(1)−Rh(1)−Cl(2) = 177.9(2), Cl(1)−Rh(1)−O(3) = 91.9(3), Cl(1)−Rh(1)−N(1) = 87.9(4), Cl(1)−Rh(1)−N(2) = 91.2(3), Cl(1)−Rh(1)−C(1) = 92.2(5), O(3)−Rh(1)−C(1) = 173.9(6), N(1)−Rh(1)−N(2) = 160.0(5), Rh(1)−O(3)−C(15) = 137(1).

(27) For Lewis acid carbonyl complexation, see: (a) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256. (b) Shambayati, S.; Schreiber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 1, p 283. (c) Delbecq, F.; Sautet, P. *J. Am. Chem. Soc.* **1992**, *114*, 2446.

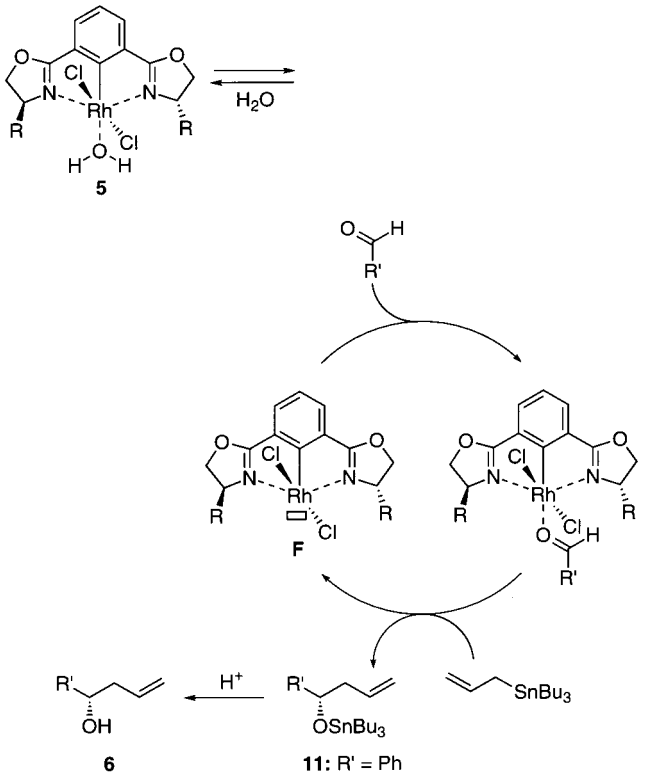
(28) Selected bond distances (Å) and angles (deg) for **9**: Rh(1)−Cl(1) = 2.334(4), Rh(1)−Cl(2) = 2.340(4), Rh(1)−N(1) = 2.08(1), Rh(1)−N(2) = 2.12(1), Rh(1)−N(3) = 2.24(1), Rh(1)−C(1) = 1.87(1); Cl(1)−Rh(1)−Cl(2) = 179.1(1), Cl(1)−Rh(1)−N(1) = 92.1(4), Cl(1)−Rh(1)−N(2) = 87.3(3), Cl(1)−Rh(1)−N(3) = 90.8(4), Cl(1)−Rh(1)−C(1) = 89.1(4), N(3)−Rh(1)−C(1) = 177.5(5), N(1)−Rh(1)−N(2) = 161.0(5).

(29) Selected bond distances (Å) and angles (deg) for **10**: Rh(1)−C(1) = 1.941(7), Rh(1)−C(19) = 2.106(7), Rh(1)−N(1) = 2.053(5), Rh(1)−N(2) = 2.055(5), C(19)−N(3) = 1.145(9); N(1)−Rh(1)−N(2) = 157.3(2), Rh(1)−C(19)−N(3) = 170.2(7).

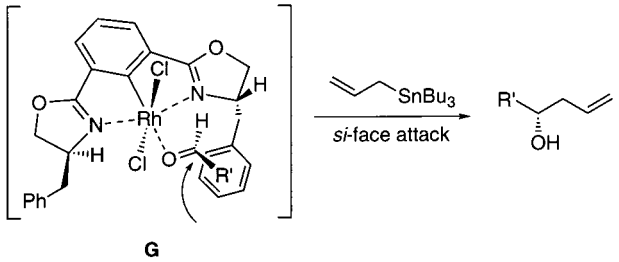
Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

Scheme 5



Scheme 6



reactions with aldehydes which are independent of allyl geometry.[30a,b] The *syn* selectivity of the allylation using crotyltins is explained by the antiperiplanar transition state **I**, proposed by Yamamoto,[30a] or the *syn*-synclinal (stannyl methylene *gauche* to oxygen) alternative **K** suggested by Keck.[30d] In the latter case, there is the possibility for a secondary, stabilizing interaction between the LUMO of the aldehyde and the HOMO of the allyltin reagent. However, the present Phebox-Rh(III) catalyzed reaction should proceed via the inverse antiperiplanar species **H** as follows (Figure 5).[31] Both *syn*- and *anti*-**7** are obtained via the antiperiplanar transition states **H** and **I**, not through *syn*-synclinal transition state **J** or **K**, because for each of the **J**, **K** pairs there is a steric interaction between the bulky stannyl moiety and one chlorine atom on the rhodium, or one substituent on the oxazoline rings. The reason the reaction prefers to proceed through the antiperiplanar **H**, which gives *anti*-**7**, rather than the antiperiplanar **I** is that

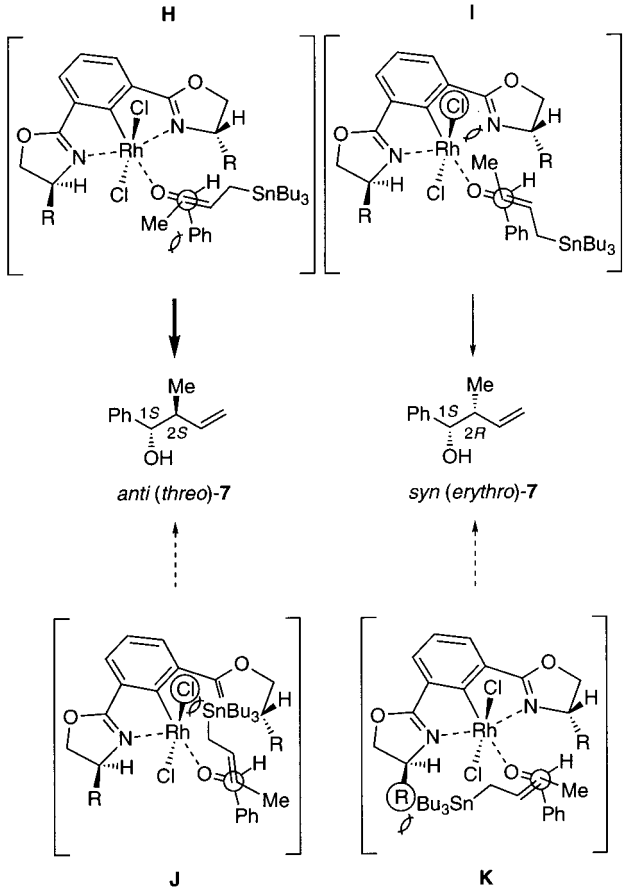


Figure 5. Transition states of antiperiplanar (**H**, **I**) and *syn*-synclinal species (**J**, **K**).

the steric repulsion between methyl group of the crotyltin and the chlorine atom on the rhodium is expected to be more important than that the *gauche* interaction between CH_3 of the stannane and the phenyl group of benzaldehyde.

Conclusion

Recently, much attention has been focused on chiral transition metal Lewis acids in asymmetric reactions.[32] We have succeeded in synthesizing the air-stable and water-tolerant (Phebox)$RhCl_2(H_2O)$ complexes by the reaction of (Phebox)$SnMe_3$ and $[(cyclooctene)_2RhCl]_2$ followed by treatment with carbon tetrachloride or copper(II) chloride. We have found that these neutral (noncationic) aqua complexes acted as asymmetric catalysts for enantioselective allylation of aldehydes

(30) (a) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107. (b) Yamamoto, Y.; Yatagai, H.; Ishihara, Y.; Maeda, N.; Maruyama, K. *Tetrahedron* **1984**, *40*, 2239. (c) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970. (d) Keck, G. E.; Savin, K. A.; Cressman, E. N. K.; Abbott, D. E. *J. Org. Chem.* **1994**, *59*, 7889. Also see: (e) Yamamoto, Y. *Aldrichim. Acta* **1987**, *20*, 45. (f) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243.

(31) Other examples of *anti*-selective allylation of aldehydes with γ-substituted (*E*)-allyltins without chelation or transmetalation were reported. One of these *anti*-selective allylations was only preceded by the use of aryl-substituted allyltins. The authors explained that these observations were due to a chairlike cyclic transition state; see: (a) Koreeda, M.; Tanaka, Y. *Chem. Lett.* **1982**, 1299. (b) Nishigaichi, Y.; Takuwa, A. *Chem. Lett.* **1994**, 1429. Another case was the use of the γ-substituted (*E*)-allyltins with a bulky substituent such as the *tert*-butyl or trialkylsilyl group at the β-position. This reaction was assumed to proceed via the inverse antiperiplanar acyclic transition state as in our case; see: (c) Nishigaichi, Y.; Ishida, N.; Nishida, M.; Takuwa, A. *Tetrahedron Lett.* **1996**, *37*, 3701.

(32) Reviews: (a) Bosnich, B. *Aldrichim. Acta* **1998**, *31*, 76. (b) Nishiyama, H.; Motoyama, Y. In *Lewis Acid Reagents: A Practical Approach*; Yamamoto, H., Ed.; OUP: Oxford, U.K., 1999; Chapter 13. (c) Kündig, E. P.; Saudan, C. M. In *Lewis Acids in Organic Synthesis*; Yamamoto, H., Ed.; Wiley-VCH: Weinheim, Germany, 2000; Vol. 2, Chapter 14.

with allyltin reagents, and these aqua complexes can be recovered from the reaction media. We have clarified that the chiral (Phebox)$RhCl_2$ fragments, generated by releasing H_2O from (Phebox)$RhCl_2(H_2O)$, is an active catalyst and the reaction proceeded via a Lewis acid mechanism. We also elucidated that both *si* enantioface selectivity and *anti* (*threo*) diastereoselectivity are attributed to the octahedral structure of the (Phebox)-$RhCl_2$ fragments.

To our knowledge, the chiral (Phebox)$RhCl_2(H_2O)$ complexes reported herein are the first examples of neutral transition metal Lewis acid catalysts for asymmetric carbon−carbon bond formation. Investigations are now underway to investigate the scope of the Phebox-Rh(III) aqua complexes as Lewis acid catalysts in organic synthesis.

Experimental Section

General Methods. Anhydrous dichloromethane and tetrahydrofuran were purchased from Kanto Chemical Co. Carbon tetrachloride and copper(II) chloride were purchased from Kishida Chemical Co. Bromo-*m*-xylene, trimethyltin chloride, and 4 Å molecular sieves (activated powder) were purchased from Aldrich Chemical Co. ^{1}H and ^{13}C NMR spectra were measured on JEOL GNM-270 (270 MHz) and VARIAN Inova-400 (400 MHz) spectrometers. Chemical shifts in ^{1}H NMR are described in parts per million downfield from tetramethylsilane as an internal standard (δ 0) in $CDCl_3$, unless otherwise noted. Chemical shifts of ^{13}C NMR are expressed in parts per million in $CDCl_3$ as an internal standard (δ 77.1), unless otherwise noted. IR spectra were measured on a JASCO FT/IR-230 spectrometer. Melting points were measured on a Yamato MP-21 and Yanaco MP-J3. Elemental analyses were measured on Yanaco CHN CORDER MT-3 and MT-6 instruments. High-performance liquid chromatography (HPLC) analyses were performed with a JASCO PU-980 HPLC pump, UV-975 and 980 UV/vis detector, and CO-966 column thermostat (at 25 °C) using Daicel CHIRALCEL OD, OB, OJ, OD-H, and CHIRALPAK AD columns. Optical rotations were measured on a JASCO DIP-140 polarimeter. Column chromatography was performed with silica gel (Merck, Art. No. 7734). Analytical thin-layer chromatography (TLC) was performed on glass plates and aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F_{254}, layer thickness 0.25 and 0.2 mm, respectively). Visualization was accomplished by UV light (254 nm), anisaldehyde, and phosphomolybdic acid. All reactions were carried out under a nitrogen or argon atmosphere. [(cyclooctene)$_2$RhCl]$_2$ was prepared by the literature method.[33] Both (*E*)- and (*Z*)-crotyltributyltin were prepared by the literature method.[34]

Synthesis of (Phebox)$SnMe_3$ Compounds. (*i*-Pr-Phebox)$SnMe_3$ (4a). To a stirred solution of 2-bromo-*m*-xylene (5.0 mL, 37.5 mmol) in H_2O (100 mL) was added $KMnO_4$ (63.7 g, 403 mmol) at room temperature. After it was refluxed for 1 day, the resultant mixture was filtered through a pad of Celite to remove MnO_2 and concentrated under reduced pressure. The residue was dissolved in concentrated HCl and then evaporated under reduced pressure to give crude 2-bromoisophthalic acid containing KCl, which was used in the next step without further purification.

To a suspension of 2-bromoisophthalic acid obtained above in benzene (80 mL) was added $SOCl_2$ (11 mL, 150 mmol) at 0 °C. After the mixture was refluxed for 5 h, excess $SOCl_2$ was removed under reduced pressure. The residue was dissolved in benzene, and then the resultant suspension was filtered through a pad of Celite to remove KCl and concentrated under reduced pressure to give 2-bromoisophthaloyl chloride (**2**) as a pale yellow solid in 56% yield (5.94 g, 21.1 mmol) from 2-bromo-*m*-xylene, which was used in the next step without further purification.

To a solution of (*S*)-valinol (3.08 g, 30.0 mmol) and triethylamine (8 mL, 60.0 mmol) in dichloromethane (60 mL) was slowly added a solution of 2-bromoisophthaloyl chloride **2** (4.21 g, 15.0 mmol) in dichloromethane (40 mL) at 0 °C. After it was stirred for 20 h at 30 °C, the reaction mixture was concentrated under reduced pressure to give crude bromo-2,6-bis[(1′-(*S*)-isopropyl-1′-hydroxymethyl)methylcarbamoyl]-benzene containing Et_3N·HCl, which was used in the next step without further purification.

To a stirred solution of bromo-2,6-bis[(1′-(*S*)-isopropyl-1′-hydroxymethyl)methylcarbamoyl]benzene obtained above in dichloromethane (60 mL) was added $SOCl_2$ (9 mL) at 0 °C. After it was stirred for 1 h at ambient temperature and then refluxed for 5 h, the resultant mixture was poured into saturated $NaHCO_3$ at 0 °C and extracted with tetrahydrofuran. The combined organic layers were washed with brine, dried over $MgSO_4$, and then concentrated under reduced pressure, giving crude bromo-2,6-bis[(1′-(*S*)-isopropyl-1′-chloromethyl)methylcarbamoyl]benzene as a pale brown solid, which was used in the next step without further purification. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.05 (d, J = 6.8 Hz, 6H), 1.07 (d, J = 6.5 Hz, 6H), 1.99 (m, 2H), 3.78 (dd, J = 9.7, 2.0 Hz, 2H), 3.84 (dd, J = 9.7, 2.0 Hz, 2H), 4.17 (m, 2H), 6.04 (d, J = 9.2 Hz, 2H), 7.35−7.52 (m, 3H).

To a stirred solution of bromo-2,6-bis[(1′-(*S*)-isopropyl-1′-chloromethyl)methylcarbamoyl]benzene obtained above in methanol (150 mL) was slowly added a solution of NaOH (3.0 g) in water (30 mL) at 0 °C. After the mixture was stirred for 1 day at 40 °C, methanol was removed under reduced pressure. The residue was extracted five times with dichloromethane (totally 500 mL), and then the extract was dried over Na_2SO_4. After concentration under reduced pressure, a yellow oil was obtained. Purification by silica gel chromatography (2:1 hexane/ether) gave (*i*-Pr-Phebox)Br (**3a**) in 96% yield (5.44 g, 14.3 mmol) from 2-bromoisophthaloyl chloride as a pale yellow oil. IR (CH_2Cl_2): 1662, 1465, 1360, 1115, 870 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.98 (d, J = 6.8 Hz, 6H), 1.04 (d, J = 6.8 Hz, 6H), 1.92 (m, 2H), 4.10−4.23 (m, 4H), 4.43 (m, 2H), 7.37 (t, J = 8.3 Hz, 1H), 7.64 (d, J = 8.3 Hz, 6H). ^{13}C NMR (68.7 MHz, $CDCl_3$): δ 18.2, 18.8, 32.6, 70.6, 72.9, 121.3, 127.0, 132.3, 132.6, 163.1.

To a stirred solution of bromo-2,6-bis(4′-(*S*)-isopropyloxazolin-2′-yl)benzene (**3a**; 759 mg, 2.0 mmol) in tetrahydrofuran (8 mL) was added *n*-BuLi in hexane (1.65 N, 1.24 mL, 2.05 mmol) at −78 °C. After the mixture was stirred for 10 min, trimethyltin chloride (408 mg, 2.05 mmol) was added and the reaction mixture was warmed to −20 °C and stirred for 1 h. After it was diluted with ether (8 mL), the reaction mixture was washed twice with water (10 mL total), dried over Na_2SO_4, and concentrated under reduced pressure. Purification by silica gel chromatography (3:1 hexane/ethyl acetate) gave (*i*-Pr-Phebox)$SnMe_3$ (**4a**) in 86% yield (797 mg, 1.72 mmol): white solid; mp 64.5−65.5 °C. IR (KBr): ν 2960, 2900, 1647, 1465, 1345, 1115, 977 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, satellite J_{Sn-H} = 55.6, 53.2 Hz, 9H), 0.93 (d, J = 6.8 Hz, 6H), 1.05 (d, J = 6.8 Hz, 6H), 1.82 (dsept, J = 7.2, 6.8 Hz, 2H), 4.03 (ddd, J = 9.2, 7.6, 7.2 Hz, 2H), 4.07 (dd, J = 9.2, 8.8 Hz, 2H), 4.45 (dd, J = 8.8, 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, satellite J_{Sn-H} = 5.6 Hz, 1H), 7.90 (d, J = 7.6 Hz, satellite J_{Sn-H} = 12.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.6 (satellite J_{Sn-C} = 384.3, 367.2 Hz), 18.8, 19.3, 33.2, 71.1, 73.5, 127.8 (satellite J_{Sn-C} = 8.0 Hz), 130.9 (satellite J_{Sn-C} = 31.4 Hz), 136.2 (satellite J_{Sn-C} = 18.9 Hz), 147.3 (satellite J_{Sn-C} = 463.8, 443.3), 165.4 (satellite J_{Sn-C} = 14.4 Hz). Anal. Calcd for

(33) van der Ent, A.; Onderdelinden, A. C. *Inorg. Synth.* **1973**, *14*, 93.

(34) Matarasso-Tchiroukhine, E.; Cadiot, P. *J. Organomet. Chem.* **1976**, *121*, 155, 169.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

$C_{21}H_{32}N_2O_2Sn$: C, 54.46; H, 6.96; N, 6.05. Found C, 54.36;H, 7.10; N, 6.02.

(Ph-Phebox)SnMe$_3$ (4b): white solid; mp 36 °C. IR (KBr): ν 2980, 2910, 1645, 1495, 1450, 1360, 1130, 980, 760, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, satellite J_{Sn-H} = 55.2, 52.8 Hz, 9H), 4.27 (t, J = 8.8 Hz, 2H), 4.85 (dd, J = 10.4, 8.8 Hz, 2H), 5.44 (dd, J = 10.4, 8.8 Hz, 2H), 7.28−7.32 (m, 10H), 7.46 (t, J = 7.8 Hz, satellite J_{Sn-H} = 5.6 Hz, 1H), 8.09 (d, J = 7.8 Hz, satellite J_{Sn-H} = 11.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.5 (satellite J_{Sn-C} = 385.4, 368.0 Hz), 70.3, 75.1, 126.7, 127.6, 128.0, 128.8, 131.5 (satellite J_{Sn-C} = 30.4 Hz), 135.9 (satellite J_{Sn-C} = 18.2 Hz), 142.1, 148.1 (satellite J_{Sn-C} = 450.7, 430.5 Hz), 166.6 (satellite J_{Sn-C} = 14.4 Hz). Anal. Calcd for $C_{27}H_{31}N_2O_2Sn$: C, 60.70; H, 5.85; N, 5.24. Found: C, 60.99; H, 5.70; N, 5.28.

(*t*-Bu-Phebox)SnMe$_3$ (4c): white solid; mp 83.5−84.5 °C. IR (KBr): ν 2956, 2902, 1656, 1565, 1478, 1354, 1253, 1131, 977, 772, 735 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, satellite J_{Sn-H} = 55.6, 53.2 Hz, 9H), 0.95 (s, 18H), 4.04 (dd, J = 10.0, 8.8 Hz, 2H), 4.18 (t, J = 8,8 Hz, 2H), 4.36 (dd, J = 10.0, 8.8 Hz, 2H), 7.36 (t, J = 7.6 Hz, satellite J_{Sn-H} = 5.6 Hz, 1H), 7.91 (d, J = 7.6 Hz, satellite J_{Sn-H} = 12.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.8 (satellite J_{Sn-C} = 383.9, 366.8 Hz), 26.1, 34.1, 69.2, 76.7, 127.9 (satellite J_{Sn-C} = 7.9 Hz), 131.0 (satellite J_{Sn-C} = 31.1 Hz), 136.2 (satellite J_{Sn-C} = 19.3 Hz), 147.2 (satellite J_{Sn-C} = 461.7, 442.0 Hz), 165.3 (satellite J_{Sn-C} = 14.4 Hz). Anal. Calcd for $C_{23}H_{36}N_2O_2Sn$: C, 56.23; H, 7.39; N, 5.70. Found: C, 56.40; H, 7.47; N, 5.58.

(Me-Phebox)SnMe$_3$ (4d): colorless oil. IR (KBr): ν 2971, 2901, 1651, 1344, 1137, 1065, 974, 770 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, satellite J_{Sn-H} = 55.6, 53.2 Hz, 9H), 1.37 (d, J = 6.8 Hz, 6H), 3.91 (dd, J = 8.4, 8.0 Hz, 2H), 4.37 (ddd, J = 9.6, 8.4, 6.8 Hz, 2H), 4.53 (dd, J = 9.6, 8.0 Hz, 2H), 7.36 (t, J = 8.0 Hz, satellite J_{Sn-H} = 5.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, satellite J_{Sn-H} = 12.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.5 (satellite J_{Sn-C} = 384.3, 367.6 Hz), 21.3, 62.4, 74.6, 127.9 (satellite J_{Sn-C} = 8.4 Hz), 130.9 (satellite J_{Sn-C} = 31.1 Hz), 136.1 (satellite J_{Sn-C} = 18.6 Hz), 147.3 (satellite J_{Sn-C} = 459.1, 438.5 Hz), 165.4 (satellite J_{Sn-C} = 14.8 Hz). Anal. Calcd for $C_{17}H_{24}N_2O_2Sn$: C, 50.16; H, 5.94; N, 6.88. Found: C, 50.30; H, 5.88; N, 6.88.

(Bn-Phebox)SnMe$_3$ (4e): white solid; mp 113 °C. IR (neat): ν 2904, 1646, 1451, 1356, 1134, 978, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, satellite J_{Sn-H} = 55.6, 53.2 Hz, 9H), 2.79 (dd, J = 14.0, 8.4 Hz, 2H), 3.23 (dd, J = 14.0, 5.6 Hz, 2H), 4.09 (t, J = 8.4 Hz, 2H), 4.39 (dd, J = 9.6, 8.4 Hz, 2H), 4.59 (dtd, J = 9.6, 8.4, 5.6 Hz, 2H), 7.20−7.34 (m, 10H), 7.38 (t, J = 7.6 Hz, satellite J_{Sn-H} = 5.6 Hz, 1H), 7.91 (d, J = 7.6 Hz, satellite J_{Sn-H} = 11.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.6 (satellite J_{Sn-C} = 383.9, 366.9 Hz), 41.6, 68.2, 72.4, 126.5, 127.8, 128.5, 129.2, 130.9 (satellite J_{Sn-C} = 30.7 Hz), 136.0 (satellite J_{Sn-C} = 18.2 Hz), 137.9, 147.3 (satellite J_{Sn-C} = 456.4, 435.5 Hz), 165.7 (satellite J_{Sn-C} = 14.8 Hz). Anal. Calcd for $C_{29}H_{32}N_2O_2Sn$: C, 62.28; H, 5.77; N, 5.01. Found: C, 62.31; H, 5.96; N, 5.16.

Synthesis of Phebox-Rh(III) Complexes. (*i*-Pr-Phebox)-RhCl$_2$(H$_2$O) (5a). From RhCl$_3$(H$_2$O)$_3$. To a stirred solution of $RlCl_3(H_2O)_3$ (2.71 g, 10.3 mmol) in methanol (1.5 mL) and dichloromethane (30 mL) was added (*i*-Pr-Phebox)SnMe$_3$ (**4a**; 4.77 g, 10.3 mmol) at room temperature. After it was stirred overnight, the reaction mixture was concentrated under reduced pressure. Purification by silica gel chromatography (100:1 dichloromethane/methanol) gave (*i*-Pr-Pybox)RhCl$_2$-(H$_2$O) (**5a**) in 47% yield (2.40 g, 4.9 mmol): pale yellow solid; mp 158 °C dec. IR (KBr): ν 3375, 2950, 1610, 1592, 1488, 1400, 1385, 1145, 960, 730 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (d, J = 6.8 Hz, 6H), 0.97 (d, J = 6.8 Hz, 6H), 2.42 (dsept, J = 3.2, 6.8 Hz, 2H), 3.55 (bs, 2H, H_2O), 4.29 (ddd, J = 10.0, 6.8, 3.2 Hz, 2H), 4.71 (dd, J = 8.8, 6.8 Hz, 2H), 4.76 (dd, J = 10.0, 8.8 Hz, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.2, 19.5, 29.4, 67.3, 71.3, 123.4, 128.2, 131.5, 170.9 (d, J_{Rh-C} = 3.8 Hz), 179.8 (d, J_{Rh-C} = 23.6 Hz). Anal. Calcd for $C_{18}H_{25}N_2O_3Cl_2Rh$: C, 44.01; H, 5.13; N, 5.70. Found: C, 43.76; H, 5.08; N, 5.73.

From [(cyclooctene)$_2$RhCl]$_2$ and CCl$_4$. To a stirred solution of (*i*-Pr-Phebox)SnMe$_3$ (**4a**; 500 mg, 1.08 mmol) and [(cyclooctene)$_2$RhCl]$_2$ (388 mg, 0.54 mmol) in dichloromethane (15 mL) was added carbon tetrachloride (2 mL) at room temperature under an argon atmosphere. After it was stirred for 2 h, the reaction mixture was concentrated under reduced pressure and the residue was washed with hexane (15 mL). Purification by silica gel chromatography (benzene and then 12:1 dichloromethane/ethyl acetate) gave (*i*-Pr-Phebox)RhCl$_2$-(H$_2$O) (**5a**) in 67% yield (356 mg, 0.72 mmol).

From [(cyclooctene)$_2$RhCl]$_2$ and CuCl$_2$. To a stirred solution of (*i*-Pr-Phebox)SnMe$_3$ (**4a**; 92.6 mg, 0.2 mmol) and [(cyclooctene)$_2$RhCl]$_2$ (71.8 mg, 0.1 mmol) in dichloromethane (5 mL) was added $CuCl_2$ (67.2 mg, 0.5 mmol) at room temperature under an argon atmosphere. After it was stirred for 2 h, the reaction mixture was concentrated under reduced pressure. Purification by silica gel chromatography (100:1 dichloromethane/methanol) gave (*i*-Pr-Pybox)RhCl$_2$(H$_2$O) (**5a**) in 75% yield (73.8 mg, 0.15 mmol).

(Ph-Phebox)RhCl$_2$(H$_2$O) (5b). To a stirred solution of (Ph-Phebox)SnMe$_3$ (**4b**; 266 mg, 0.5 mmol) and [(cyclooctene)$_2$RhCl]$_2$ (180 mg, 0.025 mmol) in dichloromethane (10 mL) was added carbon tetrachloride (2 mL) at room temperature under an argon atmosphere. After it was stirred for 3.5 h, the reaction mixture was concentrated under reduced pressure, and the residue was washed with hexane (10 mL). Purification by silica gel chromatography (benzene and then 12:1 dichloromethane/ethyl acetate) gave (Ph-Pybox)RhCl$_2$(H$_2$O) (**5b**) in 64% yield (179 mg, 0.32 mmol): pale yellow solid; mp 200 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.37 (bs, 2H), 4.54 (dd, J = 10.4, 8.8 Hz, 2H), 5.19 (dd, J = 10.0, 8.8 Hz, 2H), 5.29 (dd, J = 10.4, 10.0 Hz, 2H), 7.28−7.30 (m, 6H), 7.35 (t, J = 8.0 Hz, 1H), 7.40−7.47 (m, 4H), 7.72 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 66.6, 78.5, 123.4, 128.5, 128.78, 128.80, 128.81, 131.4, 137.7, 172.7 (J_{Rh-C} = 3.8 Hz), 182.3 (J_{Rh-C} = 24.3 Hz). Anal. Calcd for $C_{24}H_{21}N_2O_3Cl_2Rh$: C, 51.54; H, 3.78; N, 5.01. Found: C, 51.40; H, 4.05; N, 5.05.

(*t*-Bu-Phebox)RhCl$_2$(H$_2$O) (5c). To a stirred solution of (*t*-Bu-Phebox)SnMe$_3$ (**4c**; 300.0 mg, 0.61 mmol) and [(cyclooctene)$_2$RhCl]$_2$ (218.8 mg, 0.31 mmol) in dichloromethane (15 mL) was added carbon tetrachloride (1 mL) at room temperature under an argon atmosphere. After it was stirred for 12 h, the reaction mixture was concentrated under reduced pressure, and the residue was washed with hexane (10 mL). Purification by silica gel chromatography (benzene and then 20:1 dichloromethane/ethyl acetate) gave (*t*-Bu-Phebox)RhCl$_2$-(H$_2$O) (**5c**) in 43% yield (132.0 mg, 0.254 mmol): pale yellow solid; mp >300 °C. IR (KBr): ν 3452, 2945, 2876, 1612, 1485, 1396, 1218, 962, 810, 733 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.22 (s, 18H), 2.13 (bs, 2H), 4.18 (t, J = 10.3 Hz, 2H), 4.67 (dd, J = 10.3, 8.6 Hz, 2H), 4.86 (dd, J = 10.3, 8.6 Hz, 2H), 7.29 (t, J = 7.8 Hz, 1H), 7.56 (d, J = 7.8 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 26.5, 33.8, 72.0, 72.8, 123.6, 128.6, 131.7, 170.6 (d, J_{Rh-C} = 3.9 Hz), 170.7 (d, J_{Rh-C} = 18.1 Hz). Anal. Calcd for $C_{20}H_{29}N_2O_3Cl_2Rh$: C, 46.26; H, 5.63; N, 5.39. Found: C, 46.24; H, 5.35; N, 5.10.

(Me-Phebox)RhCl$_2$(H$_2$O) (5d). To a stirred solution of (Me-Phebox)SnMe$_3$ (**4d**; 360.1 mg, 0.885 mmol) and [(cyclooctene)$_2$RhCl]$_2$ (317.4 mg, 0.443 mmol) in dichloromethane (10 mL) was added carbon tetrachloride (2.0 mL) at room temperature under an argon atmosphere. After it was stirred for 1.5 h, the reaction mixture was concentrated under reduced pressure. Purification by silica gel chromatography at 0 °C (3:1 chloroform/acetone) gave (Me-Phebox)RhCl$_2$(H$_2$O) (**5d**) in 61% yield (234.5 mg, 0.539 mmol): pale yellow solid; mp >300 °C. IR (KBr): ν 3397, 2978, 1618, 1485, 1400, 1209, 1150, 959, 737 cm^{-1}. ^{1}H NMR (270 MHz, CD_3OD): δ 1.48 (d, J = 6.3 Hz, 6H), 4.34 (ddq, J = 9.3, 7.8, 6.3 Hz, 2H), 4.47 (dd, J = 8.3, 7.8

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

Hz, 2H), 5.03 (dd, J = 9.3, 8.3 Hz, 2H), 7.30 (t, J = 7.8 Hz, 1H), 7.61 (d, J = 7.8 Hz, 2H). ^{13}C NMR (67.8 MHz, CD_3OD): δ 20.0, 59.5, 78.9, 123.9, 128.2, 133.6, 172.3 (d, J_{Rh-C} = 3.9 Hz), 184.3 (d, J_{Rh-C} = 22.5 Hz). Anal. Calcd for $C_{14}H_{17}N_2O_3Cl_2Rh$: C, 38.65; H, 3.94; N, 6.44. Found: C, 38.49; H, 3.97; N, 6.52.

(Bn-Phebox)RhCl$_2$(H$_2$O) (5e). To a stirred solution of (Bn-Phebox)SnMe$_3$ (**4e**; 1.00 g, 1.80 mmol) and [(cyclooctene)$_2$RhCl]$_2$ (1.30 g, 0.90 mmol) in dichloromethane (10 mL) was added carbon tetrachloride (2 mL) at room temperature under argon atmosphere. After it was stirred for 3.5 h, the reaction mixture was concentrated under reduced pressure, and the residue was washed with hexane (10 mL). Purification by silica gel chromatography (benzene and then 12:1 dichloromethane/ethyl acetate) gave (Bn-Phebox)RhCl$_2$(H$_2$O) (**5e**) in 50% yield (520 mg, 0.90 mmol). Single crystals for the X-ray diffraction study were obtained from toluene/ether/cyclohexane at room temperature: pale yellow solid; mp >300 °C. IR (KBr): ν 3448, 2924, 1621, 1487, 1340, 1149, 970, 737, 703 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (dd, J = 14.2, 10.0 Hz, 2H), 2.98 (bs, 2H), 3.63 (dd, J = 14.2, 4.0 Hz, 2H), 4.52 (dd, J = 7.6, 6.0 Hz, 2H), 4.63 (dddd, J = 10.0, 8.8, 6.0, 4.0 Hz, 2H), 4.68 (dd, J = 8.8, 7.6 Hz, 2H), 7.20−7.40 (m, 11H), 7.61 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.4, 63.5, 75.5, 123.5, 127.0, 128.4, 129.0, 129.2, 131.5, 136.9, 171.5 (d, J_{Rh-C} = 3.8 Hz), 180.9 (d, J_{Rh-C} = 24.3 Hz). Anal. Calcd for $C_{26}H_{25}N_2O_3Cl_2Rh$: C, 53.17; H, 4.29; N, 4.77. Found C, 53.17; H, 4.35; N, 4.66.

(Me-Phebox)RhCl$_2$(acetone) (8). To a stirred solution of (Me-Phebox)SnMe$_3$ (**4d**; 199 mg, 0.49 mmol) and [(cyclooctene)$_2$RhCl]$_2$ (210.4 mg, 0.29 mmol) in dichloromethane (5 mL) was added carbon tetrachloride (473 μL) at room temperature under an argon atmosphere. After it was stirred for 1.5 h, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in acetone (2 mL) and the resultant solution was stirred for 10 min; then the reaction mixture was concentrated under reduced pressure. Purification by silica gel chromatography at 0 °C (2:1 dichloromethane/acetone) gave (Me-Phebox)RhCl$_2$(acetone) (**8**) in 42% yield (97 mg, 0.20 mmol): pale yellow solid. Single crystals for the X-ray diffraction study were obtained from dichloromethane/acetone/ether at room temperature. Complex **8** is highly moisture sensitive, and bound acetone dissociates in solution easily to form (Me-Phebox)RhCl$_2$(H$_2$O) (**5d**).

(*i*-Pr-Phebox)RhCl$_2$(DMAP) (9). To a stirred solution of (*i*-Pr-Phebox)RhCl$_2$(H$_2$O) (**5a**; 34.8 mg, 0.071 mmol) in dichloromethane (4 mL) was added 4-(dimethylamino)pyridine (DMAP; 9.0 mg, 0.074 mmol) at room temperature under an argon atmosphere. After it was stirred for 3 h, the reaction mixture was concentrated under reduced pressure. Purification by silica gel chromatography (5:1 dichloromethane/acetone) gave (*i*-Pr-Phebox)RhCl$_2$(DMAP) (**9**) in 78% yield (33.0 mg, 0.055 mmol). Single crystals for the X-ray diffraction study were obtained from benzene/ether at room temperature: pale orange solid; mp 105 °C dec. IR (KBr): ν 3474, 2955, 1616, 1532, 1481, 1392, 1332, 1294, 1226, 1145, 1062, 960, 737 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.70 (d, J = 7.2 Hz, 6H), 0.75 (d, J = 6.4 Hz, 6H), 1.60 (qqd, J = 7.2, 6.4, 3.2 Hz, 2H), 3.13 (s, 6H), 4.07 (ddd, J = 10.4, 6.8, 3.2 Hz, 2H), 4.60 (dd, J = 8.8, 6.8 Hz, 2H), 4.72 (dd, J = 10.4, 8.8 Hz, 2H), 6.69 (d, J = 7.2 Hz, 2H), 7.25 (t, J = 7.6 Hz, 1 H), 7.61 (d, J = 7.6 Hz, 2H), 9.20 (d, J = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 19.4, 29.0, 39.3, 66.9, 70.9, 106.9, 122.7, 127.6, 131.9, 151.4, 154.6, 172.4 (d, J_{Rh-C} = 3.5 Hz), 189.0 (d, J_{Rh-C} = 18.6 Hz). Anal. Calcd for $C_{25}H_{33}N_4O_2Cl_2Rh$: C, 50.43; H, 5.59; N, 9.41. Found: C, 50.45; H, 5.62; N, 9.30.

(*i*-Pr-Phebox)RhCl$_2$(*t*-BuNC) (10). To a stirred solution of (*i*-Pr-Phebox)RhCl$_2$(H$_2$O) (**5a**; 246 mg, 0.5 mmol) in dichloromethane (10 mL) was added *tert*-butyl isocyanide (68 mL, 0.6 mmol) at room temperature under an argon atmosphere. After it was stirred for 1 h, the reaction mixture was concentrated under reduced pressure. Purification by silica gel chromatography (100:1 dichloromethane/methanol) gave (*i*-Pr-Phebox)RhCl$_2$(*t*-BuNC) (**10**) in 82% yield (230 mg, 0.4 mmol). Single crystals for the X-ray diffraction study were obtained from dichloromethane/ether at room temperature: pale orange solid; mp 307 °C dec. IR (KBr): ν 2959, 2183, 1619, 1592, 1482, 1206, 957, 740 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (d, J = 6.8 Hz, 6H), 1.00 (d, J = 7.2 Hz, 6H), 1.68 (s, 9H), 2.47 (qqd, J = 7.2, 6.8, 3.2 Hz, 2H), 4.17 (ddd, J = 10.4, 7.2, 3.2 Hz, 2H), 4.65 (dd, J = 8.8, 7.2 Hz, 2H), 4.74 (dd, J = 10.4, 8.8 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.4, 19.4, 29.5, 30.5, 57.0 (t, J^{14}_{N-13C} = 5.1 Hz), 68.0, 71.1, 123.5, 127.9, 130.8, 143.4 (dt, J_{Rh-C} = 36.1 Hz, J^{14}_{N-13C} = 13.3 Hz), 173.4 (d, J_{Rh-C} = 3.0 Hz), 194.3 (d, J_{Rh-C} = 16.0 Hz). Anal. Calcd for $C_{23}H_{32}N_3O_2Cl_2Rh$: C, 49.66; H, 5.80; N, 7.55. Found: C, 49.75; H, 5.76; N, 7.53.

General Procedure for the Asymmetric Allylation of Aldehydes with Allyltributyltin Catalyzed with (Phebox)-RhCl$_2$(H$_2$O) Complexes. To a suspension of MS 4A (250 mg) in solvent (2 mL) was added the (Phebox)RhCl$_2$(H$_2$O) complex **5** (0.025 mmol), aldehyde (0.5 mmol), and allyltributyltin (230 μL, 0.75 mmol) at room temperature. After it was stirred for 7 h at that temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in 5 mL of ether, and this solution was treated with a mixture of 1 N HCl (10 mL) and solid KF (ca. 1 g) at ambient temperature for 30 min. The resultant precipitate was filtered off, and then the filtrate was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by silica gel chromatography (2:1 hexane/ether) gave the homoallylic alcohol: the enantioselectivity was determined by chiral HPLC analysis.

1-Phenyl-3-buten-1-ol (6a). $[\alpha]^{26}_D$ = −33.2° (*c* 0.89, benzene) (45% ee, *S*); lit.[3e] $[\alpha]^{20}_D$ = −17.48° (*c* 7.38, benzene) for 30% ee (*S*). IR (neat): ν 3384, 2908, 1640, 1445, 1044, 917, 757 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.06 (d, J = 3.0 Hz, 1H), 2.42−2.60 (m, 2H), 4.74 (m, 1H), 5.15 (d, J = 9.7 Hz, 1H), 5.16 (d, J = 17.0 Hz, 1H), 5.82 (ddt, J = 17.0, 9.7, 5.0 Hz, 1H), 7.21−7.40 (m, 5H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 43.8, 73.4, 118.3, 125.9, 127.6, 128.5, 134.5, 144.0. Daicel CHIRALCEL OD, UV detector 254 nm, 20:1 hexane/*i*-PrOH, flow rate 0.5 mL/min: t_R = 17.7 min (*R*), 20.3 min (*S*).

1-(*p*-Bromophenyl)-3-buten-1-ol (6b). $[\alpha]^{19}_D$ = −47.9° (*c* 2.29, benzene) (39% ee, *S*); lit.[13a] $[\alpha]^{23}_D$ = −26.1° (*c* 1.1, benzene) for 96% ee (*S*). IR (neat): ν 3386, 2930, 1682, 1588, 1488, 1069, 1007, 919, 825 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.36 (d, J = 3.0 Hz, 1H), 2.37−2.55 (m, 2H), 4.65 (m, 2H), 5.08−5.19 (m, 2H9, 5.76 (m, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 43.8, 72.7, 118.8, 121.3, 127.6, 131.5, 134.0, 142.9. Daicel CHIRALCEL OJ, UV detector 254 nm, 20:1 hexane/*i*-PrOH, flow rate 0.5 mL/min: t_R = 19.6 min (*S*), 21.3 min (*R*).

1-(*p*-Methoxyphenyl)-3-buten-1-ol (6c). $[\alpha]^{22}_D$ = −43.8° (*c* 1.20, benzene) (80% ee, *S*); lit.[3n] $[\alpha]^{23}_D$ = −65.8° (*c* 3.56, benzene) for 80% ee (*S*). IR (neat): ν 3402, 2933, 1640, 1611, 1513, 1300, 1247, 1036, 832 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.03 (bs, 1H), 2.50 (dd, J = 7.2, 6.6 Hz, 2H), 3.80 (s, 3H), 4.69 (t, J = 6.6 Hz, 2H), 5.13 (d, J = 10.3 Hz, 1H), 5.16 (d, J = 17.0 Hz, 1H), 5.80 (ddt, J = 17.0, 10.3, 7.2 Hz, 1H), 6.89 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 43.8, 55.3, 73.1, 113.9, 118.2, 127.1, 134.7, 136.2, 159.1. Daicel CHIRALCEL OD-H, UV detector 254 nm, 30:1 hexane/*i*-PrOH, flow rate 0.5 mL/min: t_R = 23.6 min (*R*), 27.0 min (*S*).

1-(*o*-Tolyl)-3-buten-1-ol (6d). $[\alpha]^{20}_D$ = −51.2° (*c* 1.02, benzene) (53% ee, *S*); lit.[13a] $[\alpha]^{26}_D$ = −83.8° (*c* 1.0, benzene) for 97% ee (*S*). IR (neat): ν 3373, 2928, 1640, 1288, 1048, 999, 916, 757 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.94 (d, J = 3.0 Hz, 1H), 2.35 (s, 3H), 2.36−2.60 (m, 2H), 4.98 (ddd, J = 7.8, 4.3, 3.0 Hz, 1H), 5.12 (d, J = 10.3 Hz, 1H), 5.19 (d, J = 17.6 Hz, 1H), 5.87 (dddd, J = 17.6, 10.3, 7.8, 6.2 Hz, 1H), 7.12−7.29 (m, 3H), 7.49 (d, J = 7.3 Hz, 1H). ^{13}C NMR (67.8 MHz,

Table 4. Crystallographic Data for 5e, 8, 9, and 10

	5e	8	9	10
formula	$C_{26}H_{25}N_2O_3Cl_2Rh$	$C_{17}H_{21}N_2O_3Cl_2Rh$	$C_{25}H_{33}N_4O_2Cl_2Rh$	$C_{23}H_{32}N_3O_2Cl_2Rh$
fw	587.31	475.18	595.37	556.34
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
cell constants				
a, Å	12.198(1)	11.976(3)	12.221(2)	9.614(1)
b, Å	8.229(2)	14.844(4)	19.515(4)	11.734(1)
c, Å	13.411(1)	10.696(3)	11.917(3)	11.958(1)
β, deg	113.040(2)			109.098(8)
V, Å^3	1238.8(3)	1901.3(8)	2842.1(10)	1274.8(2)
Z	2	4	4	2
D_{calcd}, g cm^{-3}	1.574	1.660	1.391	1.449
F(000)	596	960	1224	572
μ(Mo Kα), cm^{-1}	9.34	11.95	8.14	9.01
radiation; λ, Å	Mo Kα; 0.710 69	Mo Kα; 0.710 69	Mo Kα; 0.710 69	Mo Kα; 0.710 69
temp, °C	23.0	23.0	23.0	23.0
$2\theta_{max}$, deg	55.0	50.0	53.6	55.0
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan width, deg	$0.94 + 0.30 \tan\theta$	$1.31 + 0.30 \tan\theta$	$1.05 + 0.30 \tan\theta$	$1.10 + 0.30 \tan\theta$
no. of total data collected	3186	1912	2863	3255
no. of unique data	3050 ($R_{int} = 0.021$)	1911 ($R_{int} = 0.189$)		3080 ($R_{int} = 0.021$)
no. of obsd rflns	2540 ($I > 3\sigma$)	1335 ($I > 3\sigma$)	2022 ($I > 3\sigma$)	2601 ($I > 3\sigma$)
no. of variables	306	226	307	279
residuals: R; R_w	0.037; 0.043	0.051; 0.043	0.052; 0.056	0.032; 0.038

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y

$CDCl_3$): δ 19.0, 42.8, 69.7, 118.2, 125.1, 126.2, 127.2, 130.3, 134.3, 134.7, 141.9. Daicel CHIRALPAK AD, UV detector 254 nm, 20:1 hexane/*i*-PrOH, flow rate 0.5 mL/min: $t_R = 14.0$ min (*R*), 15.9 min (*S*).

1-(2-Furyl)-3-buten-1-ol (6e). $[\alpha]^{24}_D = -12.8°$ (*c* 1.14, Et_2O) (58% ee, *S*); lit.[13a] $[\alpha]^{23}_D = -27.2°$ (*c* 1.1, Et_2O) for 93% ee (*S*). IR (neat): ν 3372, 2913, 1641, 1504, 1434, 1228, 1149, 1010, 921, 732 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.03 (d, $J = 4.9$ Hz, 1H), 2.60−2.66 (m, 2H), 4.75 (dt, $J = 4.9$, 5.5 Hz, 1H), 5.15 (d, $J = 10.3$ Hz, 1H), 5.18 (d, $J = 17.0$ Hz, 1H), 5.81 (ddt, $J = 17.0$, 10.3, 6.8 Hz, 1H), 6.25 (d, $J = 3.5$ Hz, 1H), 6.33 (dd, $J = 3.5$, 1.8 Hz, 1H), 7.38 (d, $J = 1.8$ Hz, 1H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 40.0, 66.9, 106.0, 110.1, 118.5, 133.7, 141.9, 156.0. Daicel CHIRALCEL OJ, UV detector 230 nm, 30:1 hexane/*i*-PrOH, flow rate 0.5 mL/min: $t_R = 24.9$ min (*S*), 27.0 min (*R*).

1-Phenyl-5-hexen-3-ol (6f). $[\alpha]^{21}_D = +22.1°$ (*c* 1.10, $CHCl_3$) (63% ee, *R*); lit.[3n] $[\alpha]^{23}_D = +11.1°$ (*c* 3.14, $CHCl_3$) for 53% ee (*R*). IR (neat): ν 3372, 2929, 1641, 1495, 1452, 1049, 917, 700 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.59 (d, $J = 4.3$ Hz, 1H), 1.73−1.85 (m, 2H), 2.19 (m, 1H), 2.33 (m, 1H), 2.62−2.90 (m, 2H), 3.68 (m, 1H), 5.10−5.20 (m, 2H), 5.81 (m, 1H), 7.15−7.37 (m, 5H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 32.1, 38.5, 42.1, 70.0, 118.3, 125.9, 128.5 (2C), 134.7, 142.1. Daicel CHIRALCEL OD-H, UV detector 254 nm, 9:1 hexane/*i*-PrOH, flow rate 0.5 mL/min: $t_R = 12.3$ min (*S*), 16.4 min (*R*).

***trans*-1-Phenyl-1,5-hexadien-3-ol (6g).** $[\alpha]^{23}_D = +12.2°$ (*c* 4.0, Et_2O) (77% ee, *S*); lit.[3e] $[\alpha]^{20}_D = +3.6°$ (*c* 10.08, Et_2O) for 24% ee (*S*). IR (neat): ν 3373, 2912, 1644, 1493, 1440, 1309, 1030, 971, 750 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.78 (d, $J = 3.8$ Hz, 1H), 2.42 (m, 2H), 4.36 (m, 1H), 5.18 (d, $J = 10.3$ Hz, 1H), 5.19 (d, $J = 17.3$ Hz, 1H), 5.87 (ddt, $J = 17.3$, 10.3, 7.2 Hz, 1H), 6.25 (dd, $J = 15.9$, 6.2 Hz, 1H), 6.62 (d, $J = 15.9$ Hz, 1H), 7.20−7.45 (m, 5H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 42.1, 71.8, 118.5, 126.6, 127.7, 128.6, 130.5, 131.7, 134.1, 136.8. Daicel CHIRALCEL OD-H, UV detector 254 nm, 9:1 hexane/*i*-PrOH, flow rate 0.5 mL/min: $t_R = 15.1$ min (*R*), 23.2 min (*S*).

1-Benzyloxy-4-penten-2-ol (6f). IR (neat): ν 3434, 2910, 1641, 1495, 1364, 1102, 915, 699 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.27 (dd, $J = 7.1$, 6.8 Hz, 2H), 2.38 (bs, 1H), 3.38 (dd, $J = 9.8$, 7.3 Hz, 1H), 3.52 (dd, $J = 9.8$, 3.4 Hz, 1H), 3.89 (ddt, $J = 7.3$, 3.4, 6.8 Hz, 1H), 4.56 (s, 2H), 5.10 (d, $J = 9.8$ Hz, 1H), 5.12 (d, $J = 17.1$ Hz, 1H), 5.83 (ddt, $J = 17.1$, 9.8, 7.1 Hz, 1H), 7.20−7.45 (m, 5H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 38.0, 69.8, 73.5, 74.0, 117.7, 127.8, 127.9, 128.5, 134.3, 138.1. Daicel CHIRALCEL OB, UV detector 254 nm, 9:1 hexane/*i*-PrOH, flow rate 0.5 mL/min: $t_R = 20.1$ min (*S*), 23.2 min (*R*).

General Procedure for the Asymmetric Allylation of Benzaldehyde with Crotyltributyltin Catalyzed with (Phebox)RhCl$_2$(H$_2$O) Complexes 5. To a suspension of MS 4A (250 mg) in dichloromethane (2 mL) was added the (Phebox)$RhCl_2(H_2O)$ complex **5** (0.05 mmol), benzaldehyde (65 mg, 0.5 mmol), and crotyltributyltin (345 mg, 1.0 mmol) at room temperature. After it was stirred for 72 h at that temperature, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in 5 mL of ether, and then this solution was treated with a mixture of 1 N HCl (5 mL) and solid KF (ca. 1 g) at ambient temperature for 30 min. The resultant precipitate was filtered off, and then the filtrate was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by silica gel chromatography (3:1 hexane/ether) gave homoallylic alcohols **7**: the *syn*/*anti* ratio was determined by ^{1}H NMR analysis, and the enantioselectivity was determined by chiral HPLC analysis.

***anti*-1-Phenyl-2-methyl-3-buten-1-ol (*anti*-7).** ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (d, $J = 7.0$ Hz, 3H), 2.02 (bs, 1H), 2.50 (m, 1H), 4.36 (d, $J = 7.6$ Hz, 1H), 5.14−5.25 (m, 2H), 5.82 (ddd, $J = 17.3$, 10.3, 8.4 Hz, 1H), 7.20−7.40 (m, 5H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 16.6, 46.3, 78.0, 116.8, 126.9, 127.7, 128.3, 140.7, 142.6. Daicel CHIRALCEL OD-H, UV detector 254 nm, 39:1 hexane/*i*-PrOH, flow rate 0.5 mL/min: $t_R = 17.9$ min (1*S*, 2*S*), 19.9 min (1*R*, 2*R*).

***syn*-1-Phenyl-2-methyl-3-buten-1-ol (*syn*-7).** ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.02 (d, $J = 6.8$ Hz, 3H), 2.02 (bs, 1H), 2.58 (m, 1H), 4.61 (d, $J = 5.1$ Hz, 1H), 5.00−5.12 (m, 2H), 5.76 (ddd, $J = 17.3$, 10.0, 7.0 Hz, 1H), 7.20−7.40 (m, 5H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 14.1, 44.7, 77.4, 115.6, 126.6, 127.4, 128.1, 140.4, 142.7. Daicel CHIRALCEL OD-H, UV detector 254 nm, 39:1 hexane/*i*-PrOH, flow rate 0.5 mL/min: $t_R = 18.7$ min (1*S*, 2*R*), 19.5 min (1*R*, 2*S*).

X-ray Structure Determination and Details of Refinement. X-ray-quality crystals of **5e** and **8**−**10** were obtained directly from the preparations described above and mounted in glass capillaries. Diffraction experiments were performed on a Rigaku AFC-7R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation; $\lambda = 0.710\ 69$ Å. The lattice parameters and orientation matrices were obtained and refined from 25 machine-centered reflections with $29.48 < 2\theta < 29.91°$ for **5e**, from 24 machine-centered reflections with $28.83 < 2\theta < 30.02°$ for **8**, from 24 machine-centered reflections with $29.42 < 2\theta < 29.92°$ for **9**, and from 25 machine-centered

reflections with $29.59 < 2\theta < 29.99°$ for **10**. Intensity data were collected using a $\omega-2\theta$ scan technique, and three standard reflections were recorded every 150 reflections. The data were corrected for Lorentz and polarization effects. Relevant crystal data are given in Table 4. The structure was solved by heavy-atom Patterson methods[35] and expanded using Fourier techniques.[36] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2540 observed reflections ($I > 3\sigma(I)$) and 306 variable parameters for **5e**, on 1335 observed reflections ($I > 3\sigma(I)$) and 226 variable parameters for **8**, on 2022 observed reflections ($I > 3\sigma(I)$) and 307 variable parameters for **9**, and on 2601 observed reflections ($I > 3\sigma(I)$) and 279 variable parameters for **10**. Neutral atom scattering factors were taken from Cromer and Waber.[37] All calculations were performed using the teXsan[38] crystallographic software package. Final refinement details are collected in Table 4, and the numbering schemes employed are shown in Figures 1, 3, and 4, which were drawn with ORTEP as 30% probability ellipsoids.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan. We are grateful to Associate Professor Dr. Akira Yanagisawa of Nagoya University for his helpful discussion.

Supporting Information Available: Tables of crystal structure parameters and details of data collection, bond angles and distances, and atomic positional and thermal parameters of **5b** and **8**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010018Y

(35) Fan, H.-F. SAPI91: Structure Analysis Programs with Intelligent Control; Rigaku Corp., Tokyo, Japan, 1991.

(36) DIRDIF92: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1992.

(37) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.

(38) teXane: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.

Downloaded by CARLI CONSORTIUM on June 29, 2009
Published on March 22, 2001 on http://pubs.acs.org | doi: 10.1021/om010018y