Synthesis of Planar Chiral (1,2-Disubstituted arene)chromium Tricarbonyl Compounds and Their Application in Asymmetric Hydroboration

Seung Uk Son, Hye-Young Jang, In Su Lee, and Young Keun Chung*

Department of Chemistry and Center for Molecular Catalysis, College of Natural Sciences, Seoul National University, Seoul 151-742, Korea

Received March 26, 1998

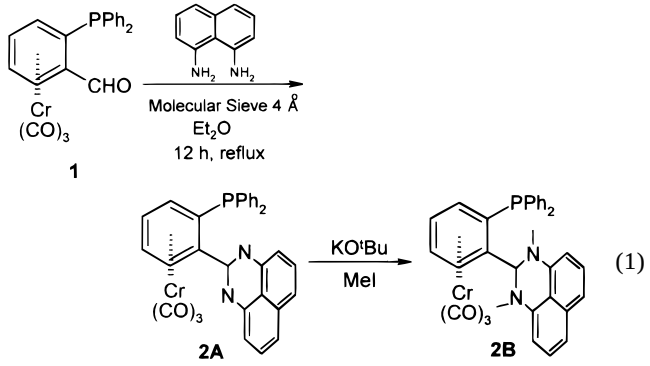
Optically active (1,2-disubstituted arene)chromium tricarbonyl complexes with a diamine and a phosphorus group in the two ortho benzylic positions were stereoselectively synthesized from a commercially available (+)-(4,6-*O*-benzylidene)methyl-α-D-glucopyranoside. These chromium complexes have been used as chiral ligands in the preparation of rhodium catalysts for the hydroboration of styrene derivatives. Moderate enantioselectivities were observed in the hydroboration of vinylarenes.

Introduction

(π-Arene)tricarbonylchromium complexes play a very important role in stereoselective reactions,[1] and some asymmetric syntheses are based on the use of optically pure chiral complexes as chiral ligands.[2] Most of the reactions studied are restricted to asymmetric stoichiometric reactions. A number of groups have established particular utilities of optically active (arene)chromium complexes for a variety of synthetic applications. However, the utilization of optically pure chiral complexes as chiral ligands has been hampered by the limited availability of enantiomerically enriched (arene)tricarbonylchromium complexes.[3] Recently, we reported a new and easy method for the asymmetric synthesis of chiral benzaldehyde complexes modified by a sugar moiety.[4] As part of this process, we designed a new type of chiral ligand, an amine−phosphine hybrid ligand, from glucopyranoside. The P,N ligand represents a class of chiral auxiliaries that are amenable to easy steric and electronic tuning,[5] an aspect that is anticipated to play an important role in the future development of asymmetric catalysis. We investigated the possibility of preparation of planar chiral (disubstituted arene)$Cr(CO)_3$ complexes containing phosphine and amine groups. Herein we report the synthesis of new chiral diamine ligands having chromium carbonyls and phosphorus and their rhodium complexes, which exhibit moderate enantioselectivity in the reduction of styrenes.

Results and Discussion

Synthesis of Planar Chiral (Arene)$Cr(CO)_3$ Compounds. The planar chiral *N*,*N*-acetal compounds **2A** and **2B** were synthesized from **1** (eq 1). Compound **1**



(1)

(1) (a) Solladié-Cavallo, A. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. Ed.; JAI: Greenwich, CT, 1989; Vol. 1, pp 99−133. (b) Uemura, M. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. Ed.; JAI: Greenwich, CT, 1991; Vol. 2, pp 199−245. (c) Kündig, E. P.; Bernardinelli, G.; Liu, R.; Ripa, A. *J. Am. Chem. Soc.* **1991**, *113*, 9676. (d) Mukai, C.; Miyakawa, M.; Mihira, A.; Hanaoka, M. *J. Org. Chem.* **1992**, *57*, 2034. (e) Uemura, M.; Miyake, R.; Nakayama, K.; Shiro, M. Hayashi, Y. *J. Org. Chem.* **1993**, *58*, 1238. (f) Kündig, E. P.; Xu, L. H.; Romanens, P.; Bernardinelli, G. *Tetrahedron Lett.* **1993**, *34*, 7049. (g) Davies, S. G.; Hume, W. E. *J. Chem. Soc., Chem. Commun.* **1995**, 251. (h) Davies, S. G.; Correia, M. A. R. B. *J. Chem. Soc., Chem. Commun.* **1996**, 1803. (i) Kamikawa, K.; Watanabe, T.; Uemura, M. *J. Org. Chem.* **1996**, *61*, 1375. (j) Taniguchi, N.; Kaneta, N.; Uemura, M. *J. Org. Chem.* **1996**, *61*, 6088. (k) Schmalz, H.; Siegel, S.; Schwarz, A. *Tetrahedron Lett.* **1996**, *37*, 2947. (l) Semmelhack, M. F.; Schmalz, H. *Tetrahedron Lett.* **1996**, *37*, 3089. (m) Pearson, A. J.; Gontchartov, A. V.; Woodgate, P. D. *Tetrahedron Lett.* **1996**, *37*, 3087. (n) Quattropani, A.; Anderson, G.; Bernardinelli, G.; Kündig, E. P. *J. Am. Chem. Soc.* **1997**, *119*, 4773.

(2) (a) Baldoli, C.; Del Buttero, P. *J. Chem. Soc., Chem. Commun.* **1991**, 982. (b) Heaton, S. B.; Jones, G. B. *Tetrahedron Lett.* **1992**, *33*, 1693. (c) Uemura, M.; Hayashi, Y.; Hayashi, Y. *Tetrahedron: Asymmetry* **1993**, *4*, 2291. (d) Jones, G. B.; Heaton, S. B. *Tetrahedron: Asymmetry* **1993**, *4*, 261. (e) Jones, G. B.; Chapman, B. J.; Huber, R. S.; Beaty, R. *Tetrahedron: Asymmetry* **1994**, *5*, 1199. (f) Jones, G. B.; Chapman, B. J. *Synthesis* **1995**, 475. (g) Jones, G. B.; Huber, R. S.; Chapman, B. J. *Tetrahedron: Asymmetry* **1997**, *8*, 1797. (h) Jones, G. B.; Heaton, S. B.; Chapman, B. J.; Guzel, M. *Tetrahedron: Asymmetry* **1997**, *8*, 3625.

(3) (a) Kondo, Y.; Green, J. R.; Ho, J. *J. Org. Chem.* **1991**, *56*, 7199. (b) Alexakis, A.; Mangeney, P.; Marek, I.; Rose-Munch, F.; Rose, E.; Semra, A.; Robert, F. *J. Am. Chem. Soc.* **1992**, *114*, 8288. (c) Aubé, J.; Heppert, J. A.; Miligan, M. L.; Smith, M. J.; Zenk, P. *J. Org. Chem.* **1992**, *57*, 3563. (d) Price, D. A.; Simpkins, N. S.; MacLeod, A. M.; Watt, A. P. *J. Org. Chem.* **1994**, *59*, 1961. (e) Schmalz, H.; Schellhaas, K. *Tetrahedron Lett.* **1995**, *36*, 5515. (f) Amurrio, D.; Khan, K.; Kündig, E. P. *J. Org. Chem.* **1996**, *61*, 2258. (g) Siwek, M. J.; Green, J. R. *J. Chem. Soc., Chem. Commun.* **1996**, 2359. (h) Ewin, R. A.; MacLeod, A. M.; Price, D. A.; Simpkins, N. S.; Watt, A. P. *J. Chem. Soc., Perkin Trans 1* **1997**, 401.

(4) Han, J. W.; Son, S. U.; Chung, Y. K. *J. Org. Chem.* **1997**, *62*, 8264.

(5) (a) Brown, J. M.; Hulmes, D. I.; Laysell, T. P. *J. Chem. Soc., Chem. Commun.* **1993**, 1673. (b) Schnyder, A.; Hintermann, L.; Togni, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 931. (c) Schnyder, A.; Togni, A.; Wiesli, U. *Organometallics* **1997**, *16*, 255.

S0276-7333(98)00228-3 CCC: $15.00
Publication on Web 06/26/1998

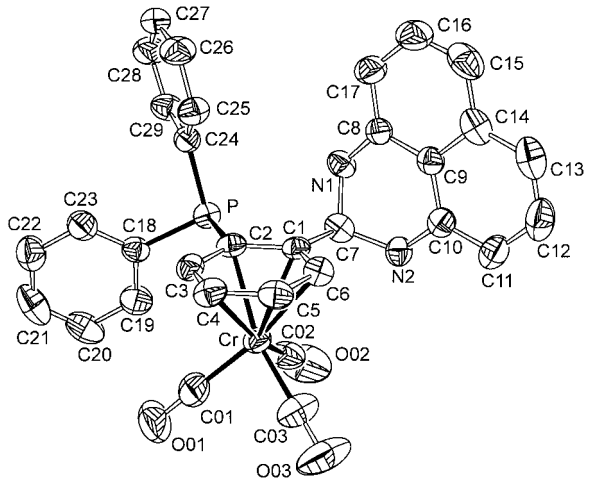


Figure 1. Molecular structure of **2A** giving the labeling scheme.

Table 1. Crystal Data and Structure Refinement Details for 2A

empirical formula	$C_{32}H_{23}CrN_2O_3P$
fw	566.49
cryst syst	orthorhombic
space group	$P2_12_12_1$
unit cell dimens	
a, Å	13.095(4)
b, Å	13.693(5)
c, Å	14.972(2)
V, Å^3	2684.6(13)
Z	4
d(calcd), g/cm^3	1.402
λ, Å	0.710 73
temp, K	293(2)
F(000)	1168
θ range for data collecn, deg	2.02−24.97
index ranges	$0 \le h \le 15$, $0 \le k \le 16$, $0 \le l \le 17$
no. of rflns collected	2668
no. of indep rflns	2668 (R(int) = 0.0000)
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	2668/0/360
GOF	1.074
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0410, wR2 = 0.0898
R indices (all data)	R1 = 0.0838, wR2 = 0.1045
abs structure param	−0.06(4)
largest diff peak and hole, e Å^{-3}	0.261 and −0.427

was previously prepared by us through the asymmetric lithiation and addition of electrophile.[4] Treatment of **1** with 1,8-naphthalenediamine in the presence of molecular sieves (4 Å) gave **2A** in 85% yield. Compound **2B** was prepared in 95% yield by the reaction of **2A** with KO*t*Bu followed by addition of MeI. At first we expected an imino compound as a product and wanted to prepare a C_2-symmetric diimino compound. However, the ^{1}H NMR spectrum of **2A** did not match with the ^{1}H NMR spectrum of the expected diimino compound, as we could see the peaks of amino protons. Thus, we suspected that the product was not a diimino compound. We grew single crystals of **2A** and solved the X-ray crystal structure of **2A**. Figure 1 shows the three-dimensional molecular structure of **2A** with the atomic numbering. Crystal data and structure refinement details of **2A** are given in Table 1, and selected bond distances and angles are given in Table 2. The stereochemistry of **2A** is the same as that of **1**, as expected.[4] The naphthalene group is upright to the plane of arene coordinated to Cr(CO)$_3$ (the angle between the plane of the arene (C1−C2−C3−C4−C5−C6) and the plane N1−C8−C9−C10−N2 is 93.0°). The phosphorus atom is located 0.024 Å above the plane of the arene, and the nitrogen atom (N1) is located 1.199 Å above the plane of the arene. The distance between P and N1 is 3.351 Å. When we use **2A** as a chiral chelate ligand, the nitrogen atom N2 is not in the direction of a metal and is far away from the metal. Thus, **2A** acts as a chiral P,N ligand, not a P,N,N ligand.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2A

Cr−C1	1.811(8)	Cr−C2	2.214(5)	Cr−C5	2.216(5)	P−C2	1.853(5)
C1−C2	1.439(7)	P−C24	1.832(5)	C1−C7	1.538(7)	C7−N1	1.448(7)
C1−C2−P	118.4(4)	C2−C1−C7	120.7(5)	C2−P−C24	100.7(2)		
C1−C7−N1	112.0(4)	N1−C7−N2	108.3(5)	C7−N1−C8	118.5(5)		

Asymmetric Hydroboration. Although borane and its derivatives react with olefinic substrates in the absence of catalysts, the reaction is markedly accelerated by addition of transition-metal catalysts.[6] The transition-metal catalyst also has a significant effect on the regio- and stereochemistry of the reaction.[7]

Rhodium complexes with **2A** or **2B** have been examined with regard to their catalytic activity and enantioselectivity in the reaction of vinylarenes with catecholborane. The results are summarized in Table 3. To prevent the reaction catalyzed by unmodified rhodium species, 1.2−2.0 equiv of free ligands was added to [Rh(COD)$_2$]BF$_4$ for catalytic reactions.

Initially we started to study the hydroboration of 4-methoxystyrene (entries 3−6 in Table 3), which reacts otherwise with catecholborane only at elevated temperatures.[8] Hydroboration of 4-methoxystyrene with catecholborane in the presence of 2 mol % of [Rh(COD)$_2$]BF$_4$ and 1.2 equiv of **2A** in THF at −15 °C for 18 h, followed by oxidation with alkaline hydrogen peroxide, gives the corresponding *sec*-alcohol in 87% yield with 62% ee (entry 1 in Table 3). Many studies indicate that phosphine-to-rhodium ratios are critical in hydroborations of styrene derivatives: higher ratios favor formation of the secondary alcohol even with neutral catalysts.[9] High regioselectivity was observed for other cationic rhodium complexes having tertiary phosphine ligands.[10] When we tried the same reaction using 2.0 equiv of **2A**, the corresponding *sec*-alcohol was obtained in 86% yield with 65% ee (entry 2). However, the effect of the concentration of the chiral ligand was not great. The *in situ* cationic rhodium complex generated by the

(6) Rh complexes: (a) Männig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878. Zr complexes: (b) Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14*, 3127. (c) Pereira, S.; Srebnik, M. *J. Am. Chem. Soc.* **1996**, *118*, 909. Ir complexes: (d) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671. Ni complexes: (e) Gridnev, I. D.; Miyaura, N.; Suzuki, A. *Organometallics* **1993**, *12*, 589. Ru complexes: (f) Burgess, K.; Jaspars, M. *Organometallics* **1993**, *12*, 4197. Pd complexes: (g) Matsumoto, Y.; Naito, M.; Hayashi, T. *Organometallics* **1992**, *11*, 2732. (h) Matsumoto, Y.; Naito, M.; Uozumi, Y.; Hayashi, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1468. Ln complexes: (i) Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220.

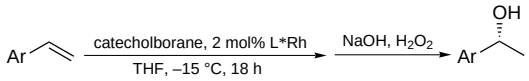
(7) (a) Evans, D. A.; Fu, C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 6917. (b) Evans, D. A.; Fu, C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6679. (c) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350.

(8) (a) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863. (b) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: New York, 1988.

(9) (a) Burgess, K.; van der Donk, W. A.; Kook, A. M. *J. Org. Chem.* **1991**, *56*, 2949. (b) Zhang, J.; Lou, B.; Guo, G.; Dai, L. *J. Org. Chem.* **1991**, *56*, 1670.

(10) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426.

Table 3. Catalytic Asymmetric Hydroboration with Catecholborane[a]

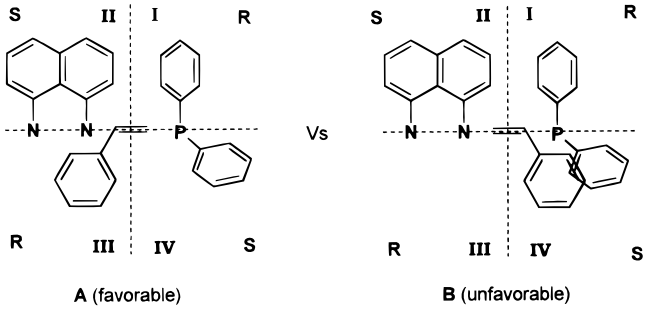


entry no.	substrate	catalyst (amt, mol%)	ligand (equiv of L/Rh)	yield, %[b]	ee, %
1	4-methoxystyrene	$Rh(COD)_2BF_4$ (2)	**2A** (1.2)	87	62
2	4-methoxystyrene	$Rh(COD)_2BF_4$ (2)	**2A** (2.0)	86	65
3	4-methoxystyrene	$[Rh(COD)Cl]_2 + AgBF_4$ (2)[c]	**2A** (1.2)	65	32
4	4-methoxystyrene	$Rh(COD)_2BF_4$ (2)	**2B** (1.2)	80	6
5	4-bromostyrene	$Rh(COD)_2BF_4$ (2)	**2A** (1.2)	80	19
6	styrene	$Rh(COD)_2BF_4$ (2)	**2A** (1.2)	95	53
7	3,4-dimethoxystyrene	$Rh(COD)_2BF_4$ (2)	**2A** (1.2)	65	75
8	2,4-dimethylstyrene	$Rh(COD)_2BF_4$ (2)	**2A** (1.2)	94	81

[a] All reactions were carried out in THF at −15 °C for 18 h. [b] Isolated yields by column chromatography. [c] The cationic rhodium catalyst was prepared *in situ*.

reaction of $[Rh(COD)Cl]_2$ with $AgBF_4$ was not effective (entry 3). Introduction of a methyl group on the amine nitrogen (entry 4) did not increase the ee value, presumably because of a steric constraint: rhodium metal suffered a great steric congestion to coordinate to the nitrogen atom. Thus, there would be no enantiodifferentiation, and a low ee value was eventually obtained. All of the substituted styrenes were transformed into optically active 1-arylethanols. The regioselective formation of (1-arylethyl)boranes was perfect for all the styrenes examined, irrespective of the electron-releasing or electron-withdrawing nature of the substituent group on the phenyl. The enantioselectivity was dependent on the substrate. The enantioselectivity for substituted styrenes ranged from 19% to 81% ee. The order of ee is as follows: 2,4-dimethylstyrene > 3,4-dimethoxystyrene > 4-vinylanisole > styrene > 4-bromostyrene. The ee values (entries 1, 2, 3, and 7) seem to be sensitive to the electronic effect of the substituent on the phenyl. As the electron-donating ability (Br < H < OMe) of the substituent increases, the vinyl group binds more strongly and closely to the rhodium metal and is more easily affected by the chiral ligand. Thus, as the electron-donating ability of the substituent on the phenyl increases, the ee value increases. The origin of the high ee value for entry 8 may be attributable primarily to the steric repulsion between the Me and Ph groups.

Our catalytic system with **2A** and **2B** gives the *R* absolute configuration for all secondary alcohol products. The stereochemical outcome can be explained by assuming the two hypothetical transition states **A** and **B** for the formation of a styrene−rhodium complex. The



A (favorable) B (unfavorable)

transition state **A** is free from the repulsive steric interaction, with styrene fitting better to the chiral environment. The coordination depicted in **A** is consistent with the observed absolute stereochemistry of the product. However, the transition state **B** is less favored because of the repulsive steric interaction between the phenyl group on the phosphorus and the phenyl group on the styrene.

Conclusion

We have demonstrated that the planar chiral *N*,*N*-acetal compounds **2A** and **2B** can be synthesized from the planar chiral chromium benzaldehyde complex **1** and can be used as chiral P,N ligands in the preparation of rhodium catalysts for the hydroboration of styrene derivatives. Moderate enantioselectivities were observed, and the ee values depended on the electronic effect of the substituent on the styrene ring and the steric effect of the ortho substituent on the styrene ring.

Experimental Section

General Considerations. All solvents were purified by standard methods, and all synthetic procedures were done under a nitrogen atmosphere. Reagent grade chemicals were used without further purification.

Elemental analyses were performed at the Chemical Analytic Center, College of Engineering, Seoul National University or the Chemical Analytic Center. ^1H NMR spectra were obtained with a Bruker 300 or a Bruker AMX-500 instrument. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer. Compound **1** was prepared by the published method.[4]

Synthesis of 2A. To compound **1** (0.20 g, 0.46 mmol) in 20 mL of Et_2O was added molecular sieves (4 Å) and 1,8-naphthalenediamine (0.11 g, 0.70 mmol). The resulting solution was heated to reflux for 12 h. After the solution was cooled, any precipitates were filtered off and the filtrate was concentrated and chromatographed on a silica gel column with hexane/Et_2O (v/v, 10:1) as eluent. After removal of the solvent, 0.23 g of product was isolated (yield 85%). Single crystals were grown by slow evaporation of a solution of **2A** in hexane and CH_2Cl_2. IR: ν_{CO} 1974, 1881 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.62 (t, 5.9 Hz, 1 H), 7.53 (m, 4 H), 7.39 (m, 5 H), 7.27 (t, 7.8 Hz, 1 H), 7.18 (d, 8.3 Hz, 1 H), 7.13 (d, 8.1 Hz, 1 H), 7.06 (t, 7.4 Hz, 1 H), 6.67 (d, 7.2 Hz, 1 H), 6.17 (d, 9.1 Hz, 1 H), 5.77 (d, 4.5 Hz, 1 H), 5.50 (d, 7.3 Hz, 1 H), 5.44 (t, 6.3 Hz, 1 H), 5.24 (t, 6.1 Hz, 1 H), 4.75 (d, 6.4 Hz, 1 H), 4.54 (s, 1 H), 3.61 (s, 1 H) ppm. Anal. Calcd for $C_{32}H_{23}CrN_2O_3P$: C, 67.84; H, 4.09; N, 4.94. Found: C, 67.62; H, 3.78; N, 5.22. $[\alpha]^{18}_D = +158$ (*c* 0.1, CH_2Cl_2).

Synthesis of 2B. To **2A** (0.10 g, 0.18 mmol) in 10 mL of THF was added KO*t*Bu (0.42 mL in 1.0 M in THF). After the solution was stirred for 15 min, MeI (0.1 mL) was added. Excess Et_2O (30 mL) and aqueous saturated NH_4Cl (20 mL) were added to quench the reaction and extract the chromium

compound. The ether extract was concentrated and chromatographed on a silica gel column with hexane/Et_2O (v/v, 10:1) as eluent. After evaporation of solvent, 0.10 g of **2B** was isolated (95%). IR: ν_{CO} 1954, 1879 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.52 (t, 5.9 Hz, 1 H), 7.44 (m, 4 H), 7.35 (m, 5 H), 7.35 (t, 7.9 Hz, 1 H), 7.27 (d, 8.4 Hz, 1 H), 7.11 (d, 8.4 Hz, 1 H), 6.99 (t, 7.9 Hz, 1 H), 6.49 (d, 7.5 Hz, 1 H), 5.83 (d, 4.3 Hz, 1 H), 5.17 (d, 7.2 Hz, 1 H), 5.11 (t, 5.6 Hz, 1 H), 4.97 (t, 6.1 Hz, 1 H), 4.82 (d, 6.1 Hz, 1 H), 4.78 (dd, 2.7, 6.2 Hz, 1 H), 3.33 (s, 3 H), 2.87 (s, 3 H) ppm. Anal. Calcd for $C_{34}H_{27}CrN_2O_3P$: C, 68.68; H, 4.58; N, 4.71. Found: C, 68.47; H, 4.74; N, 4.94. $[\alpha]^{20}_D = +52$ (*c* 0.1, CH_2Cl_2).

Catalytic Asymmetric Hydroboration. A typical procedure is given for 4-vinylanisole. A mixture of $[Rh(COD)_2]$-BF_4 (7 mg, 0.017 mmol) and **2A** (11.7 mg, 0.021 mmol) in 3 mL of THF was stirred under nitrogen at room temperature for 1.5 h, and 4-vinylanisole (116 mg, 0.86 mmol) was added at −15 °C. Catecholborane (1.7 mL in 1 M in THF, 1.72 mmol) was added at −15 °C, and the mixture was stirred at −15 °C for 18 h and then quenched with 5 mL of ethanol. To the mixture was added 5 mL of 3 M NaOH and 0.5 mL of 35% H_2O_2, and it was stirred at room temperature for 3 h. Extraction with Et_2O followed by chromatography on a silica gel column with hexane/diethyl ether (v/v, 10:1) as eluent gave 113 mg (86%) of (*R*)-1-(4-methoxyphenyl)ethanol. The regioisomer was not detected by ^{1}H NMR analysis of the crude reaction mixture. To determine the enantiomeric excess (ee) values, we used (*S*)-(+)-mandelic acid as a chiral derivatizing reagent to convert an enantiomeric mixture to a pair of diastereomers and calculated the ee by the inspection of ^{1}H NMR spectra of diastereomers.

X-ray Crystal Structure Determination of 2A. Crystals of **2A** were grown by slow evaporation of a solution of **2A** in hexane. Diffraction was measured on an Enraf-Nonius CAD4 diffractometer by the $\omega-2\theta$ scan method. Unit cells were determined by centering 25 reflections in the approximate 2θ range. Other relevant experimental details are in the Supporting Information. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least squares with SHELXL-93. All non-hydrogen atoms and H1′ and H2′ were refined with anisotropic temperature factors; hydrogen atoms except for H1′ and H2′ were refined isotropically using the riding model, with equivalent isotropic temperature factors of 1.2 times the factors for the atoms to which they are attached. Crystal data and experimental details are given in Table 1.

Acknowledgment. This work was supported by the Ministry of Education (Grant No. BSRI 97-3415) and the KOSEF through the Center for Molecular Catalysis and Grant No. 96-0501-03-0-3.

Supporting Information Available: Tables giving atomic coordinates, thermal parameters, and bond distances and angles for **2A** (8 pages). Ordering information is given on any current masthead page.

OM980228J