J|A|C|S
ARTICLES
Published on Web 07/09/2002

Hemilabile Amidomonophosphine Ligand−Rhodium(I) Complex-Catalyzed Asymmetric 1,4-Addition of Arylboronic Acids to Cycloalkenones

Masami Kuriyama, Kazushige Nagai, Ken-ichi Yamada, Yoshinao Miwa, Tooru Taga, and Kiyoshi Tomioka*

Contribution from the Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Received March 14, 2002

Abstract: The asymmetric 1,4-addition reaction of arylboronic acids with cycloalkenones was catalyzed by 1 mol % of an amidomonophosphine−rhodium(I) catalyst in a 10:1 mixture of 1,4-dioxane and water at 100 °C, affording 3-arylcycloalkanones in reasonably high enantioselectivity and high yields. It was revealed by NMR, IR, and X-ray spectroscopies that this bidentate amidomonophosphine behaves as a hemilabile ligand that contains a hard donor site in addition to the soft donor in a molecule. Phosphorus atom strongly bonds to rhodium(I), and the amide carbonyl oxygen is coordinatively labile. The reaction efficacy of phenylboronic acid with cyclopent-2-en-1-one was significantly dependent on the possibility of coordination of the amide carbonyl oxygen to rhodium(I).

Introduction

The discovery and development of new and efficient chiral catalysts are of fundamental importance for efficient and clean organic synthesis.[1,2] In particular, asymmetric carbon−carbon bond-forming processes have become a focus for advanced materials and pharmaceuticals. Of interest is that a chiral amidomonophosphine **1**[3]−copper(I) catalyzes conjugate addition of alkylzinc and alkyl Grignard reagents to enones, resulting in production of the corresponding adducts in reasonably high enantioselectivity.[4,5] However, the addition reaction suffers from unsatisfactory poor efficacy with the addition of aryl groups.[6,7] In 1997, Miyaura and co-workers discovered a phosphine−rhodium(I) complex catalyst for 1,4-addition of aryl- and alkenylboronic acids to α,β-unsaturated ketones, giving the corresponding β-substituted ketones in high yield.[8] In 1998, on the basis of this finding, Hayashi and Miyaura developed a rhodium(I)−catalyzed asymmetric 1,4-addition reaction of organoboron reagents with enones, enoates, alkenylphosphonates, nitroalkenes, and alkenamides.[9,10,11] High enantioselectivity and high yields were achieved only when (*S*)-binap[12] was used as a chiral bisphosphine ligand for rhodium(I). The catalysis performance was critically dependent on the structural features of the phosphine ligands. Some other bisphosphines, (*S*,*S*)-diop,[13] (*S*,*S*)-chiraphos,[14] (*S*)-(*R*)-bppfa,[15] and (*S*,*S*)-me-duphos,[16] and monodentate phosphines, (*R*)-meo-mop[17] and (*S*)-ip-phox,[18]

* Corresponding author. E-mail: tomioka@pharm.kyoto-u.ac.jp.

(1) (a) Tomioka, K. *Synthesis* **1990**, 541−549. (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis;* John Wiley and Sons: New York, 1994. (c) Tomioka, K.; Nagaoka, Y. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds; Springer: New York, 1999; Vol. III, Chapter 31. (d) Lagasse, F.; Kagan, H. B. *Chem. Pharm. Bull.* **2000**, *48*, 315−324. (e) Bolm, C.; Hildebrand, J. P.; Muñiz, K.; Hermanns, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 3284−3308. (f) Trost, B. M. *Chem. Pharm. Bull.* **2002**, *50*, 1−14.

(2) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice;* Oxford University Press: Oxford, 1998.

(3) (a) Nakagawa, Y.; Kanai, M.; Nagaoka, Y.; Tomioka, K. *Tetrahedron* **1998**, *54*, 10295−10307. (b) Kanai, M.; Nakagawa, Y.; Tomioka, K. *Tetrahedron* **1999**, *55*, 3843−3854.

(4) (a) Nakagawa, Y.; Matsumoto, K.; Tomioka, K. *Tetrahedron* **2000**, *56*, 2857−2863, and references therein. (b) Mori, T.; Kosaka, K.; Nakagawa, Y.; Nagaoka, Y.; Tomioka, K. *Tetrahedron: Asymmetry* **1998**, *9*, 3175−3178.

(5) The amidophosphine and its derivatives were useful in copper-catalyzed asymmetric ethylation of imines. (a) Fujihara, H.; Nagai, K.; Tomioka, K. *J. Am. Chem. Soc.* **2000**, *122*, 12055−12056. (b) Nagai, K.; Fujihara, H.; Kuriyama, M.; Yamada, K.; Tomioka, K. *Chem. Lett.* **2002**, 8−9.

(6) Tomioka, K. in *Modern Carbonyl Chemistry;* Otera, J., Ed.; Wiley-VCH, Germany, 2000; Chapter 12.

(7) For recent examples of asymmetric arylation, see: (a) Asano, Y.; Iida, A.; Tomioka, K. *Tetrahedron Lett*. **1997**, *38*, 8973−8976. (b) Xu, F.; Tillyer, R. D.; Tschaen, D. M.; Grabowski, E. J. J.; Reider, P. J. *Tetrahedron: Asymmetry* **1998**, *9*, 1651−1654. (c) Chung, K.-G.; Miyake, Y.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 15−18.

(8) Sakai, M.; Hayashi, H.; Miyaura, N. *Organometallics* **1997**, *16*, 4429−4231.

(9) (a) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc*. **1998**, *120*, 5579−5580. (b) Takaya, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron Lett*. **1998**, *39*, 8479−8482. (c) Takaya, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron Lett.* **1999**, *40*, 6957−6961. (d) Takaya, Y.; Senda, T.; Kurushima, H.; Ogasawara, M.; Hayashi, T. *Tetrahedron: Asymmetry* **1999**, *10*, 4047−4056. (e). Hayashi, T.; Senda, T.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc*. **1999**, *121*, 11591−11592. (f) Hayashi, T.; Senda, T.; Ogasawara, M. *J. Am. Chem. Soc*. **2000**, *122*, 10716−10717. (g) Senda, T.; Ogasawara, M.; Hayashi, T. *J. Org. Chem*. **2001**, *66*, 6852−6856. (h) Hayashi, T. *Synlett*. **2001**, 879−887.

(10) (a) Sakuma, S.; Sakai, M.; Itooka, R.; Miyaura, N. *J. Org. Chem*. **2000**, *65*, 5951−5955. (b) Sakuma, S.; Miyaura, N. *J. Org. Chem.* **2001**, 66, 8944−8946.

(11) Reetz and co-workers have recently discovered that BINOL-based diphosphonites were also useful in rhodium-catalyzed asymmetric 1,4-addition of arylboronic acids. Reetz, M. T.; Moulin, D.; Gosberg, A. *Org. Lett.* **2001**, *3*, 4083−4085.

(12) Takaya, H.; Akutagawa, S.; Noyori, R. *Org. Synth*. **1989**, *67*, 20−32.

(13) Kagan, H. B.; Dang, T.-P. *J. Am. Chem. Soc.* **1972**, *94*, 6429−6433.

(14) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc*. **1977**, *99*, 6262−6267.

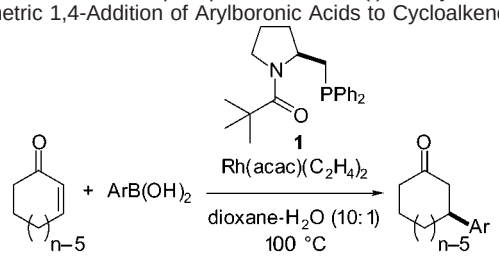
(15) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138−1151.

(16) Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125−10138.

(17) Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem*. **1993**, *58*, 1945−1948.

10.1021/ja0261933 CCC: $22.00

Scheme 1. Amidomonophosphine−Rhodium(I)-Catalyzed Asymmetric 1,4-Addition of Arylboronic Acids to Cycloalkenones



conveyed poor enantioselectivity and poor yields.[10,19] We were very pleased to find that a high level of catalysis performance in enantioselectivity and yield was attainable in the asymmetric 1,4-addition of a variety of arylboronic acids to cycloalkenones using amidomonophosphine **1** as a monophosphine ligand for rhodium(I) (Scheme 1).[20]

Amidomonophosphine **1**, which we designed, contains a carbonyl oxygen atom as the hard donor site in addition to the soft phosphorus atom donor. It is interesting that **1** may behave as a bidentate hemilabile ligand. The concept of hemilability in coordination chemistry was introduced at the end of 1970s,[21] and the chemistry of hemilabile ligands, which contain both subsitutionally inert and labile groups, has received considerable attention in recent years.[22] Late-transition-metal complex catalysts often employ phosphines as stabilizing and selectivity-controlling ligands. In catalytic and stoichometric reactions, the phosphorus atoms in hemilabile ligands keep them anchored to transition-metal centers. The hard donor sites are capable of temporarily holding coordination sites at reactive transition metal centers in the absence of small molecule substrates and can be easily displaced by small molecule substrates to form a metal−small molecule complex.[23] Here, we describe that amidomonophosphine **1** behaves as a hemilabile ligand in which the phosphorus atom strongly bonds to rhodium(I) and the amide carbonyl oxygen is weakly bonding, and the reaction efficacy of phenylboronic acid with cyclopent-2-en-1-one significantly depends on the possibility of coordination of the amide carbonyl oxygen to rhodium(I).

Results and Discussion

NMR of the Rhodium−Amidomonophosphine Complex Prepared from Rh(acac)(C_2H_4)$_2$ and Amidomonophosphine 1. The benzene-d_6 solutions of Rh(I)−**1** complex were prepared in various molar ratios from 1:1 to 1:3 of Rh(acac)(C_2H_4)$_2$[24]/**1**. A representative procedure is given for the preparation of a 1:1 Rh−**1** complex. In an NMR sample tube were placed **1** (0.048 mmol) and Rh(acac)(C_2H_4)$_2$ (0.048 mmol). The tube was filled with argon, and C_6D_6 (0.6 mL) was added to form a yellow solution. The ^{31}P NMR spectrum of a 1:1 Rh−**1** complex showed only one doublet signal of 186 Hz coupling constant due to large heteronuclear Rh−P coupling at 42.7 ppm (Figure 1a). When the molar ratio of Rh(acac)(C_2H_4)$_2$/**1** was raised to 1:1.5, a new doublet signal appeared at 39.9 ppm (J = 194 Hz) (Figure 1b), and the signal of 42.7 ppm disappeared when the molar ratio of Rh(acac)(C_2H_4)$_2$/**1** was 1:2 (Figure 1c). This revealed that only one Rh−**1** complex, in which one molecule of **1** coordinated to one molecule of Rh, was generated when the molar ratio of Rh/**1** was 1:1 (Scheme 2). When the molar ratio of Rh(acac)(C_2H_4)$_2$/**1** was 1:3, the singlet signal of free amidomonophosphine **1** was observed at −21.7 ppm in addition to the doublet signal at 39.9 ppm (Figure 1d). The signal at 39.9 ppm corresponds to the Rh−**1** complex in which two molecules of **1** coordinate to one molecule of Rh. This result meant that the composition of the Rh−**1** complex changed as shown in Scheme 2 when the Rh(I)−**1** complex was prepared in molar ratios from 1:1 to 1:3 of Rh(acac)(C_2H_4)$_2$/**1**.

Then, we analyzed the solution behavior of the amide carbonyl group of the 1:1 molar ratio complex of Rh(acac)-

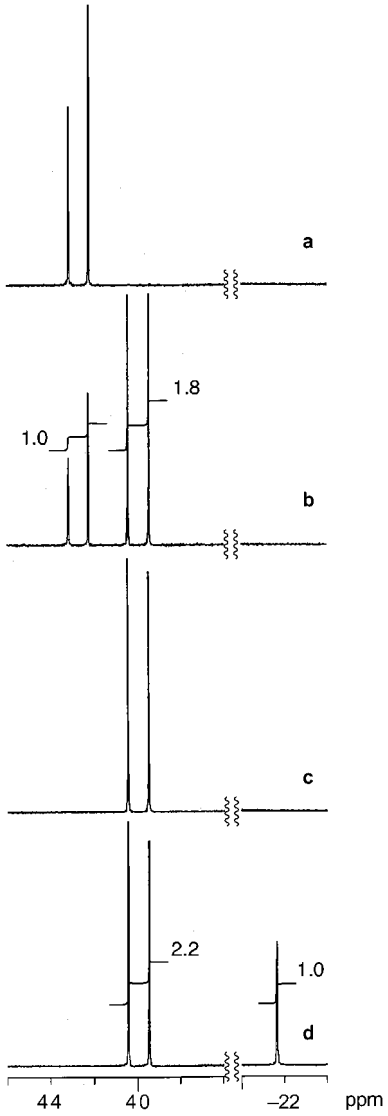


Figure 1. ^{31}P NMR spectrum (202 MHz, C_6D_6) of Rh−**1** complex with the following molar ratio of Rh(acac)(C_2H_4)$_2$/**1**: (a) 1:1; (b) 1:1.5; (c) 1:2; (d) 1:3.

Scheme 2

$$\mathrm{Rh(acac)(C_2H_4)_2} \xrightarrow{\mathbf{1}} \mathrm{Rh\text{-}\mathbf{1}} \xrightarrow{\mathbf{1}} \mathbf{1}\text{-Rh-}\mathbf{1} \xrightarrow{\mathbf{1}} \mathbf{1}\text{-Rh-}\mathbf{1} + \mathbf{1}$$

(18) (a) Dawson, G. J.; Frost, C. G.; Williams, J. M. J.; Coote, S. J. *Tetrahedron Lett.* **1993**, *34*, 3149−3150. (b) Matt, P. von; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566−568.
(19) Takaya, Y.; Ogasawara, M.; Hayashi, T. *Chirality* **2000**, *12*, 469−471.
(20) Kuriyama, M.; Tomioka, K. *Tetrahedron Lett.* **2001**, *42*, 921−923.
(21) Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658−2666.
(22) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233−350, and references therein.
(23) For recent examples of asymmetric C−C bond-forming reactions with use of hemilabile ligands, see: (a) Gladiali, S.; Alberico, E.; Pulacchini, S.; Kollàr, L. *J. Mol. Catal. A* **1999**, *143*, 155−162. (b) Nandi, M.; Jin, J.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1999**, *121*, 9899−9900. (c) Verdaguer, X.; Moyano, A.; Pericàs, M. A.; Riera, A.; Maestro, M. A.; Mahía, J. *J. Am. Chem. Soc.* **2000**, *122*, 10242−10243.
(24) Cramer, R. *Inorg. Synth.* **1974**, *15*, 16−17.

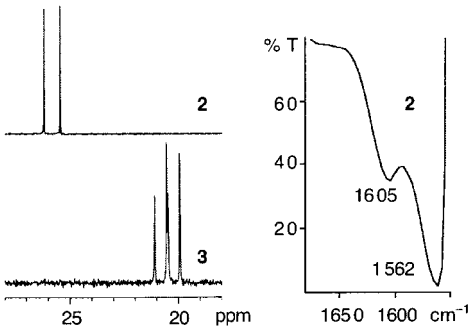
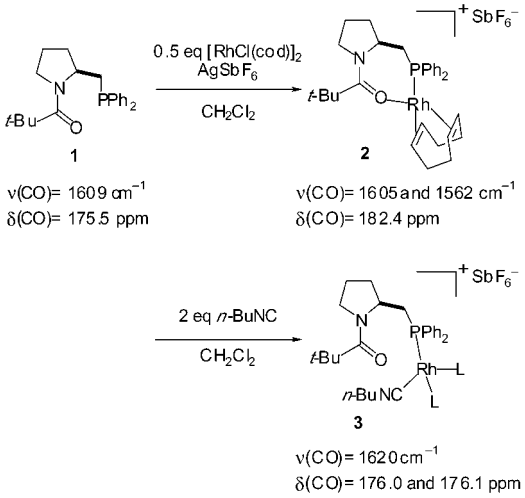


Figure 2. ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) and IR spectrum (CH_2Cl_2) of the complex of the cationic Rh−**1** complex **2** and **3**.

Scheme 3. Hemilability of Amidomonophosphine in the Cationic Rhodium−Amidomonophosphine Complex



$(C_2H_4)_2$/**1**. To our sorrow, we were not able to confirm by IR and NMR spectra that the amide carbonyl oxygen of **1** coordinated to rhodium(I), because the IR bands of the carbonyl groups of **1** and acetylacetonato were observed at almost the same area. The ^{13}C NMR signal of the carbonyl carbon atom was observed at 175.5 ppm and shifted downfield by only 0.1 ppm (the carbonyl carbon atom of free amidemonophosphine **1** was observed at 175.4 ppm in C_6D_6). Attempted isolation of crystals of the 1:1 molar ratio complex of Rh(acac)$(C_2H_4)_2$/**1** for X-ray crystallographical analysis was unsuccessful because of its air sensitivity.

NMR and IR of the Cationic Rhodium−Aamidomonophosphine Complex Prepared from [RhCl(cod)]$_2$, Amidomonophosphine 1, and AgSbF$_6$. We have employed both NMR and IR to analyze the solution behavior of the amide carbonyl group in the cationic rhodium−amidomonophosphine complex **2** (Scheme 3). The complex was obtained by the following procedure. Under argon atmosphere, a test tube was charged with [RhCl(cod)]$_2$ (0.072 mmol), **1** (0.144 mmol), and $AgSbF_6$ (0.144 mmol). To the test tube was added 1.8 mL of CD_2Cl_2 at room temperature, and the whole was ultrasonicated for 5 min. After centrifugal sedimentation, the supernatant was transferred to an NMR tube via cannula. The ^{31}P NMR spectrum of the cationic complex **2** showed only one doublet signal due to large Rh−P coupling (148 Hz) at 25.8 ppm (Figure 2). The coordination of the carbonyl oxygen atom to rhodium(I) caused characteristic changes in the IR and ^{13}C NMR spectra. The IR band of the uncoordinated amide carbonyl group was observed at 1605 cm^{-1} as a weak band and the IR band of the coordinated amide carbonyl group to rhodium(I) was observed at 1562 cm^{-1} as a strong band (Figure 2). The wavenumber of the coordinated carbonyl band in **2** was lowered by ca. 50 cm^{-1} compared to the free amidomonophosphine **1**. The ^{13}C NMR signal of the carbonyl carbon atom was shifted downfield by 6.9 ppm. This result revealed that most of the amide carbonyl oxygen of **1** coordinated to rhodium(I) in the cationic complex in solution. Addition of 2 equiv of *n*-BuNC to the solution of **2** resulted in complete displacement of the carbonyl group of **1** by *n*-BuNC to give the complex **3**; only the IR bands of the uncoordinated amide carbonyl group and coordinated isonitrile were observed at 1620 and 2179 cm^{-1}, respectively (free *n*-BuNC was observed at 2145 cm^{-1}), and the ^{13}C NMR signal of the carbonyl carbon atom was shifted back upfield (Scheme 3). The ^{31}P NMR spectrum of cationic rhodium−amidomonophosphine complex **3** showed two signals at 20.2 ppm (d, J = 123 Hz) and 20.8 ppm (d, J = 125 Hz) (Figure 2). This result meant that the amide carbonyl group, which temporarily held coordination sites of rhodium(I), was easily displaced by *n*-BuNC to form a rhodium(I)−*n*-BuNC complex, and amidomonophosphine **1** behaved as a hemilabile ligand in the cationic rhodium−amidomonophosphine complex in solution.

X-ray Structure of the Cationic Rhodium−Amidomonophosphine Complex Prepared from [RhCl(cod)]$_2$, Amidomonophosphine 1, and AgSbF$_6$. The structure of the 1:1 molar ratio complex of Rh(I)/**1** was unequivocally determined by the X-ray crystallographical analysis of the cationic rhodium−amidomonophosphine complex. The cationic rhodium−amidomonophosphine complex **2** was prepared as yellow cubes in high yield and was subjected to estimation of the coordination behavior of the carbonyl group of **1**. Under argon atmosphere, a reaction tube was charged with [RhCl(cod)]$_2$(0.08 mmol), amidomonophosphine **1** (0.16 mmol), and $AgSbF_6$ (0.16 mmol). To the mixture was added 2 mL of CH_2Cl_2 at room temperature, and the whole was ultrasonicated for 5 min. After centrifugal sedimentation, the supernatant was separated and concentrated to remove CH_2Cl_2 under vacuum. The residue was washed with hexane and filtered to give a yellow solid. This yellow solid was recrystallized from a mixture of hexane and CH_2Cl_2, giving yellow cubes of mp 236−8 °C (dec). FAB-MS *m*/*z*: 564 ([Rh(cod)(**1**)]$^+$). Anal. Calcd for $C_{30}H_{40}F_6NOPRhSb$: C, 45.02; H, 5.04; N, 1.75. Found: C, 44.74; H, 4.95; N, 1.73. The structural information on rhodium species coordinated with **1** was collected from the X-ray crystal structure of **2**. As can be seen in Figure 3a, the conformation of the seven-membered heterometallacyclic ring, which is formed by the chelate coordination of the phosphorus and the amide carbonyl oxygen of **1**, is boat like. This means that the amide carbonyl oxygen of **1** coordinates to rhodium(I) in the crystalline state and **1** is a bidentate ligand. One of the phenyls of diphenylphosphiono group, Ph(A), is oriented axially and Ph(B) is oriented equatorially (Figure 3b). The axial Ph(A) group extrudes toward the same direction as the *tert*-butyl group and the equatorial Ph(B) group extrudes toward the coordination site of the 1,5-cyclooctadiene. The bite angle of **1** is 86.2°, and the Rh−P and the Rh−O distances are 2.277 and 2.106 Å, respectively. The dihedral angle of Rh−O−C−N is 4.0°. It is important to note that at the coordination site B of the cationic complex **2**, as shown in Figure 3c, the upper part is blocked by the two phenyl rings of **1** and the coordination site A is unblocked.

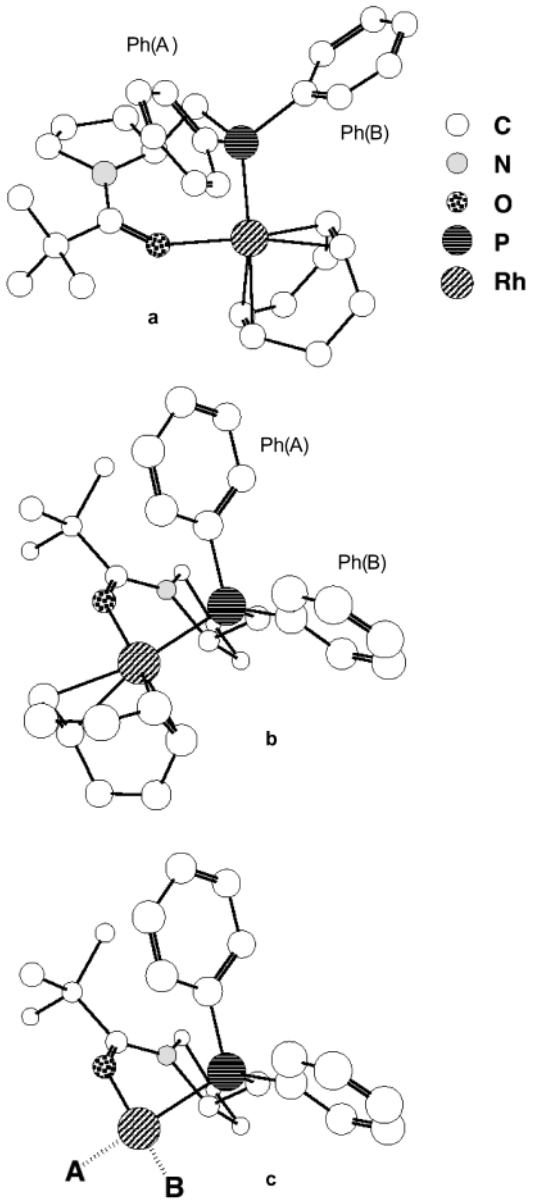


Figure 3. Chem3D presentation of X-ray crystal structure of the cationic rhodium−amidomonophosphine complex **2** (SbF_6^- is omitted for simplicity): (a) the view of the whole **2**, (b) the viewpoint of Ph(B) side, (c) the viewpoint of Ph(B) side (1,5-cyclooctadiene is omitted for simplicity).

NMR and IR of the Rhodium−Amidomonophosphine Complex Prepared from [RhCl(cod)]$_2$ and Amidomonophosphine 1. The neutral rhodium−amidomonophosphine complex **4** was obtained by the following procedure. Under argon atmosphere, a test tube was charged with [RhCl(cod)]$_2$ (0.024 mmol) and **1** (0.048 mmol). To the test tube was added 0.6 mL of CD_2Cl_2 to form a yellow solution. The ^{31}P NMR spectrum of the neutral complex showed only one doublet signal due to large Rh−P coupling (150 Hz) at 21.5 ppm (Figure 4). The ^{13}C NMR signal of the carbonyl carbon atom was observed at 175.8 ppm downfield shifted by 0.3 ppm from the peak of **1**. The IR band of the uncoordinated amide carbonyl group was observed at 1609 cm^{-1} as a strong band and the IR band of the coordinated amide carbonyl group to rhodium(I) was observed at 1558 cm^{-1} as a weak band (Figure 4). This result revealed that amidomonophosphine **1** behaves as a hemilabile ligand in the neutral

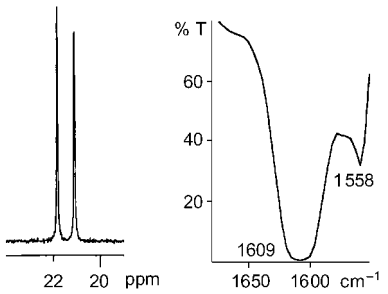
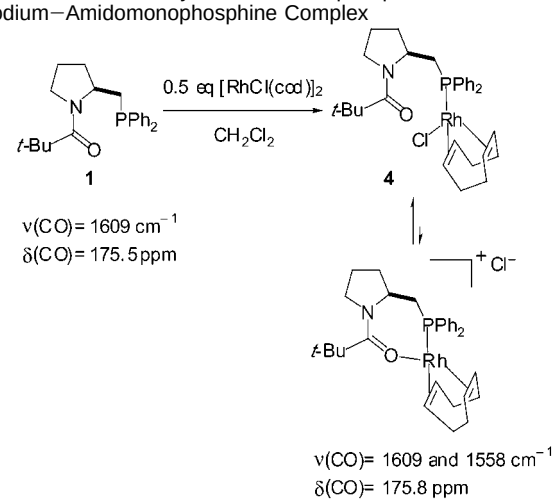
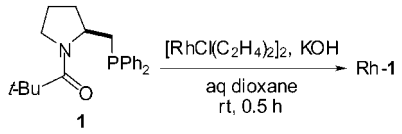


Figure 4. ^{31}P NMR spectrum (202 MHz, CD_2Cl_2) and IR spectrum (CH_2Cl_2) of the neutral complex **4**.

Scheme 4. Hemilability of Amidomonophosphine in the Neutral Rhodium−Amidomonophosphine Complex



Scheme 5



complex whose amide carbonyl group has a fluxional process that involves dissociation and recoordination (Scheme 4).

NMR and IR of the Rhodium−Amidomonophosphine Complex Prepared from [RhCl(C$_2$H$_4$)$_2$]$_2$, Amidomonophosphine 1, and KOH. We examined the hemilability of amidomonophosphine **1** in another neutral complex prepared from [RhCl(C$_2$H$_4$)$_2$]$_2$, **1**, and KOH. This complex was obtained by the following procedure (Scheme 5). Under argon atmosphere, a test tube was charged with [RhCl(C$_2$H$_4$)$_2$]$_2$ (0.04 mmol) and **1** (0.08 mmol). To the test tube were added successively 1,4-dioxane-d_8 (1.0 mL) and 6 M aq KOH (0.67 mL) at 0 °C. The mixture was stirred at room temperature for 0.5 h. The organic layer of this mixture was transferred to an NMR sample tube via cannula. The ^{31}P NMR spectrum of the complex showed two doublet signals at 43.9 ppm (J = 182 Hz) and 44.1 ppm (J = 184 Hz) (Figure 5). The smaller signal at 43.9 ppm corresponded to the phosphorus atom of the complex whose amide carbonyl oxygen coordinates to rhodium(I), and the larger signal at 44.1 ppm was assignable to the phosphorus atom of the complex whose amide carbonyl oxygen uncoordinated to rhodium(I) based on the relative magnitude of IR absorption (vide infra). The IR band of the uncoordinated amide carbonyl group was observed at 1609 cm^{-1} as a strong band, and the IR band of the coordinated amide carbonyl group to rhodium(I) was observed at 1574 cm^{-1} as a weak band (Figure 5). This

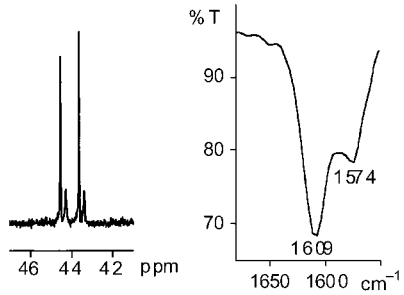
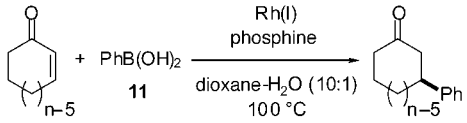


Figure 5. ^{31}P NMR spectrum (202 MHz, 1,4-dioxane-d_8) and IR spectrum (CH_2Cl_2) of the complex generated from **1**, $[RhCl(C_2H_4)_2]_2$, and KOH.

Table 1. Amidomonophosphine−Rhodium-Catalyzed Asymmetric 1,4-Addition of Phenylboronic Acid to Cycloalkenones



entry	*n*	phosphine (mol %)	Rh(I) (mol %)	time, h	yield, %	ee, %
1	6	**1** (1)	$Rh(acac)(C_2H_4)_2$ (1)	1	99	97
2	6	**1** (3)	$Rh(acac)(C_2H_4)_2$ (1)	1	80	94
3	6	**1** (1.3)	$[RhCl(cod)]_2$ (0.5)/$AgSbF_6$	1	99	0
4	6	**1** (1.3)	$[RhCl(cod)]_2$ (0.5)	1	98	0
5	6		$[RhCl(cod)]_2$ (0.5)/$AgSbF_6$	1	65	
6	6		$[RhCl(cod)]_2$ (0.5)	1	61	
7	6	**1** (3.9)	$[RhCl(C_2H_4)_2]_2$ (1.5)/KOH	1	99	94
8	6	**1** (1.3)	$[RhCl(C_2H_4)_2]_2$ (0.5)	1	0	
9	5	**1** (1.3)	$Rh(acac)(C_2H_4)_2$ (1)	6	90	83
10	5	**5** (1.3)	$Rh(acac)(C_2H_4)_2$ (1)	6	21	12
11	5	**6** (1.3)	$Rh(acac)(C_2H_4)_2$ (1)	6	27	4
12	5	**7** (1.3)	$Rh(acac)(C_2H_4)_2$ (1)	6	2	0
13	5	**8** (1.3)	$Rh(acac)(C_2H_4)_2$ (1)	6	16	1

result revealed that amidomonophosphine **1** behaves as a hemilabile ligand in the neutral complex prepared from $[RhCl(C_2H_4)_2]_2$, **1**, and KOH.

Discussion on the Coordination Manner of the Amide Carbonyl Group to Rhodium(I). It is revealed that the amide carbonyl group of amidophosphine **1** coordinates to rhodium(I) and **1** behaves as a hemilabile ligand both in the neutral complex and in the cationic complex in which the seven-membered heterometallacyclic ring is formed. The coordination of the amide carbonyl group to rhodium(I) in the neutral complex is weaker than in the cationic complex because a counteranion directly coordinates to rhodium(I) in the neutral complex. When the coordination of the amide carbonyl group to rhodium(I) is weak, the ^{13}C NMR signal of the amide carbonyl carbon atom is shifted downfield only a little, but the coordination of the amide carbonyl group to rhodium(I) is clearly confirmed as a weak band by the IR spectrum. Consequently, there is the high probability that the amide carbonyl group coordinates to rhodium(I) in the complex prepared from $Rh(acac)(C_2H_4)_2$ and **1**, even if the ^{13}C NMR signal of the amide carbonyl carbon atom is shifted downfield only a little.

Asymmetric 1,4-Addition of Phenylboronic Acid to Cycloalkenones. We examined the reaction of phenylboronic acid **11** with cyclohex-2-en-1-one **10** using amidomonophosphine **1** as a chiral ligand for Rh(I) (Table 1). It is important to note that the phosphine−rhodium(I) molar ratio influenced enantioselectivity and yield, and the performance of the 1:1 molar ratio Rh(I)/**1** catalyst was better than those of other molar ratio

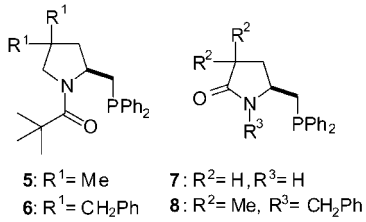


Figure 6.

conditions. For example, while the 1:1 molar ratio Rh(I)/**1** catalyst gave (*S*)-3-phenylcyclohexanone **13**[25,26] in 99% yield and 97% ee (Table 1, entry 1), the 1:3 molar ratio Rh(I)/**1** catalyst gave the adduct in 80% yield and 94% ee (Table 1, entry 2). The enantioselectivity in the asymmetric 1,4-addition of **11** with **10** using the cationic complex **2** was very poor, affording the racemic adduct in 99% yield (Table 1, entry 3), and the catalyst prepared from $[RhCl(cod)]_2$ and **1** gave the racemic adduct in 98% yield (Table 1, entry 4). The reason enantioselectivity was extremely poor was that $[RhCl(cod)]_2$ catalyzed the reaction without **1** (Table 1, entries 5 and 6). The asymmetric 1,4-addition reaction of **11** with **10** was catalyzed by the catalyst prepared from $[RhCl(C_2H_4)_2]_2$, **1**, and KOH, giving the adduct in 99% yield and 94% ee (Table 1, entry 7). On the other hand, the catalyst generated from $[RhCl(C_2H_4)_2]_2$ and amidomonophosphine **1** did not catalyze the reaction (Table 1, entry 8). These results indicated that (hydroxo)rhodium(I) species,[27] which was generated from $[RhCl(C_2H_4)_2]_2$, **1**, and KOH, was an active species for transmetalation, in which the basicity of transition-metal hydroxides and the high oxophilicity of the boron center induced transmetalation.[9h,10,28]

Amidomonophosphine **1** promoted the reaction with cyclopentenone **9**, giving (*S*)-3-phenylcyclopentanone **12**[25,29] in 90% yield and 83% ee (Table 1, entry 9). However, with use of an amidephosphine **5** bearing two methyl groups on the pyrrolidine ring, the reaction was not completed, and afforded the adduct in 21% yield and 12% ee (Table 1, entry 10). The catalytic performance of **6** bearing two bulkier benzyl groups was poorer, giving the product in 27% yield and 4% ee (Table 1, entry 11). Comparison of three amidomonophosphines **1**, **5**, and **6**, bearing no substitution, two methyl, and two benzyl groups on the pyrrolidine ring, indicated that smaller substitution gave better catalytic performance in yield and enantioselectivity (Table 1, entries 9−11). Furthermore, the catalytic performance of **7** and **8**, whose carbonyl groups and phosphorus atoms point toward the opposite directions, was very poor, affording the almost racemic adduct in miserable yield (Table 1, entries 12 and 13). Coordination of both phosphorus and amide carbonyl oxygen atoms to rhodium(I) forms a chelate, which is available only when the carbonyl group and phophorous atom point to the same direction as shown in structure **1** not **7** or **8**. The possibility of coordination of the amide carbonyl oxygen atom to rhodium(I) in forming a chelate is one of the critical factors affecting the reaction efficacy of **11** with **9**.

(25) Larock, R. C.; Yum, E. K.; Yang, H. *Tetrahedron* **1994**, *50*, 305−321.
(26) Schults, A. G.; Harrington, R. E. *J. Am. Chem. Soc.* **1991**, *113*, 4926−4931.
(27) (a) Brune, H.-A.; Unsin, J.; Hemmer, R.; Reichhardt, M. *J. Organomet. Chem.* **1989**, *369*, 335−342. (b) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 126−130. (c) Grushin, V. V.; Kuznetsov, V. F.; Bensimon, C.; Alper, H. *Organometallics* **1995**, *14*, 3927−3932.
(28) Itooka, R.; Iguchi, Y.; Miyaura, N. *Chem. Lett.* **2001**, 722−723.
(29) Barnhart, R. W.; Wang, X.; Noheda, P.; Bergens, S. H.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1994**, *116*, 1821−1830.

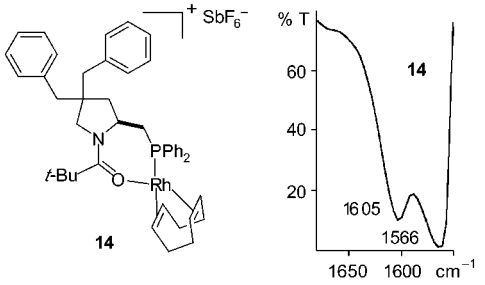
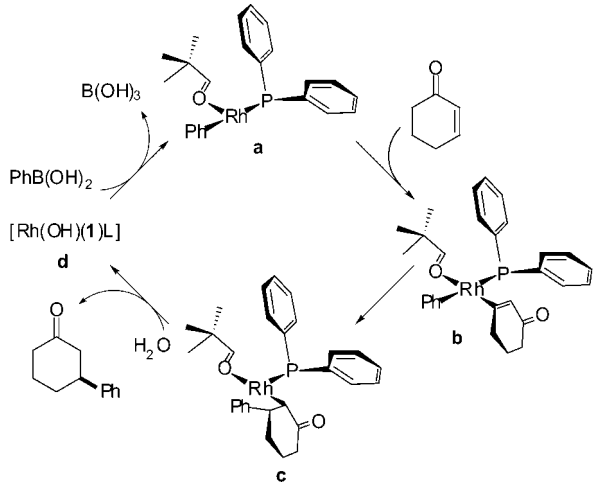


Figure 7. IR spectrum of the cationic rhodium−amidomonophosphine complexes **14** in CH_2Cl_2.

Scheme 6. A Plausible Model of Enantioselection[a]



[a] The pyrrolidine ring in **1** is omitted for simplicity. (a) Ph−Rh(I)−**1** species, (b) Ph−Rh(I)−**1** species coordinated by cyclohex-2-en-1-one, (c) Rh(I)-**1** species after migratory insertion, (d) (hydroxo)rhodium(I) species.

Substituent Influence of the Pyrrolidine Ring on Coordination of the Amide Carbonyl Group to Rhodium(I). The cationic rhodium−amidomonophosphine complex **14** was prepared by following the synthetic procedure of **2** and estimated the influence of substitution of the pyrrolidine ring on coordination behavior of the carbonyl group (Figure 7). In the cationic rhodium−amidomonophosphine complex **2**, the IR band of the uncoordinated amide carbonyl group was observed at 1605 cm^{-1} as a weak band and the IR band of the coordinated amide carbonyl group to rhodium(I) was observed at 1562 cm^{-1} as a strong band (Figure 2). This means that the greater part of the amide carbonyl group coordinates to rhodium(I) in the cationic complex **2**. On the contrary, compared to Figure 2, the cationic rhodium−amidomonophosphine complex **14** showed a band at 1605 cm^{-1} corresponding to the uncoordinated carbonyl group larger than the 1605 cm^{-1} band of **2**. This clearly demonstrated that the influence of the substituent on the pyrrolidine ring prevented coordination of the carbonyl group to rhodium(I). Because the strength of the amide carbonyl oxygen−rhodium-(I) bond, even in the cationic complex **14**, is weak, the amide carbonyl oxygen of **6** hardly coordinates to rhodium(I) in the neutral complex that is generated in the actual asymmetric reaction.

Mechanism and Plausible Stereochemical Pathway. Scheme 6 shows the stereochemical pathway in forming the (*S*)-products in the reaction of cyclohex-2-en-1-one. According to the X-ray structure shown in Figure 3, the Ph−Rh(I) species[10,30] is formed by transmetalation between rhodium(I) and phenylboronic acid at the trans side to phosphorus, which is the most vacant

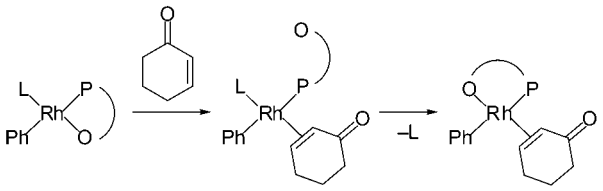


Figure 8.

coordination site and influenced by the trans effect of phosphine (**a** shown in Scheme 6). Amidomonophosphine−rhodium intermediate **a** should have an open space in the bottom part of the vacant coordination site, the upper part being blocked by the two phenyl rings of **1**. The olefinic double bond of cyclohex-2-en-1-one coordinates to rhodium(I) with its 2-*si* face forming **b** rather than its 2-*re* face, which undergoes migratory insertion to form a stereogenic carbon center in **c**, whose absolute configuration is *S*. In this time, cyclohex-2-en-1-one would coordinate to rhodium(I) smoothly, because the amide carbonyl oxygen atom, which is capable of temporarily holding coordination site at rhodium(I), can be readily displaced by cyclohex-2-en-1-one (Figure 8). Then, the amide carbonyl oxygen atom recoordinates to the other coordination site at rhodium(I) (Figure 8), and migratory insertion would be induced.

In previous reports, binap, amidomonophosphine **1**, and diphosphonites progressed the rhodium(I)-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated compounds in high efficacy, but monodentate phosphines and most bisphosphines conveyed poor yields.[10,11,19,20] The electron-donating ability of monodentate phosphines to rhodium(I) would be too poor, such as meo-mop and ip-phox, and the reaction hardly takes place. On the other hand, the high electron-donating ability of electron-rich bisphosphines, such as diop, whose phosphorus is substituted by alkyl groups, would prevent the reaction and give 10−45% yields, with the exception of me-duphos and chiraphos. The steric hindrance of the coordination site surmounts the electron-donating ability of me-duphos and chiraphos to prevent the efficient coordination of phosphorus atom to rhodium(I). Binaps, whose phosphorus is substituted only by aryl groups, diphosphonites, whose phosphorus is substituted by binaphthols, and amidomonophosphine **1** exert the moderate electron-donating abilitiy by the coordination of phosphorus to catalyze the reaction in the high efficiency. The reason the catalytic performance was very poor in case of amidomonophosphine **5** and **6** is that the amide carbonyl group would not be able to donate an electron to rhodium(I) because the P−CH_2 bond rotates away by the steric repulsion of substituents on the pyrrolidine ring and phenyl groups on the phosphorus atom (Figure 9).

Conclusion

We found that a high level of catalysis performance for enantioselectivity and yield is attainable in the asymmetric 1,4-addition of arylboronic acids to cycloalkenones using an amidomonophosphine **1** as a hemilabile phosphine ligand for rhodium(I). The structural features of the Rh(I)−**1** complex were

(30) The arylrhodium(I) complexes are key intermediates for carrying out various coupling reactions with organic halides and additions to alkenes and alkynes. (a) Michman, M.; Balog, M. *J. Organomet. Chem.* **1971**, *31*, 395−402. (b) Semmelhack, M. F.; Ryono, L. *Tetrahedron Lett.* **1973**, *14*, 2967−2970. (c) Hegedus, L. S.; Kendall, P. MLo, S. M.; Sheats, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 5448−5452.

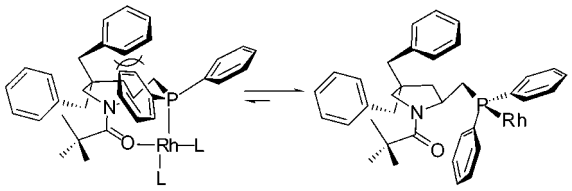


Figure 9.

clarified by NMR, IR, and X-ray analyses. And it was revealed that amidomonophosphine **1** behaves as a hemilabile ligand whose phosphorus atom strongly bonds to rhodium(I), the amide carbonyl oxygen atom has a fluxional process involving dissociation and recoordination, and the reaction efficacy of phenylboronic acid with cyclopent-2-en-1-one was significantly dependent on the capability of coordination of the amide carbonyl oxygen atom to rhodium(I), giving a chelate.

Experimental Section

General. All melting points are uncorrected. IR spectra were expressed in cm^{-1}. ^1H, ^{13}C, and ^{31}P NMR spectra were taken at 500, 125, and 202 MHz, respectively. Chemical shift values are expressed in ppm relative to internal or external TMS or to external 85% H_3PO_4. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Preparation Procedure of $[Rh(cod)(1)]^+SbF_6^-$ (2). Under argon atmosphere, a test tube was charged with $[RhCl(cod)]_2$ (39.4 mg, 0.08 mmol), **1** (56.5 mg, 0.16 mmol), and $AgSbF_6$ (55.0 mg, 0.16 mmol). To the mixture was added 2.0 mL of methylene chloride at room temperature, and the whole was ultrasonicated for 5 min. After centrifugal sedimentation, the supernatant was separated and concentrated to remove methylene chloride under vacuum. The residue was washed with hexane and filtered to give a yellow solid (127 mg, 99% yield). The yellow solid (30 mg) was recrystallized from a mixture of hexane and methylene chloride (Hex/CH_2Cl_2 = 8:5), giving yellow cubes of mp 236−8 °C (dec) (23 mg). $[\alpha]^{24}_D$: −22.1 (*c* 0.96, CH_2Cl_2). ^1H NMR (CD_2Cl_2): 0.79 (9H, s), 1.86−1.90 (1H, m), 2.01−2.27 (7H, m), 2.38−2.45 (2H, m), 2.62−2.73 (2H, m), 2.77−2.81 (2H, m), 3.07 (1H, m), 3.23−3.28 (2H, m), 3.66−3.71 (1H, m), 5.29−5.35 (1H, m), 5.39−5.44 (2H, m), 6.99−7.03 (2H, m), 7.33−7.40 (3H, m), 7.60−7.66 (3H, m), 8.03−8.07 (2H, m). ^{13}C NMR (CD_2Cl_2): 23.3, 26.3, 26.7, 28.3, 31.2, 31.4, 34.3 (d, J = 3.1), 34.8 (d, J = 22.7), 39.9, 47.9, 58.9 (d, J = 5.2), 68.0 (d, J = 15.5), 68.4 (d, J = 15.5), 108.8 (dd, J = 3.0, 10.3), 109.5 (dd, J, 3.0, 10.3), 127.2 (d, J = 45.5), 128.5 (d, J = 9.3), 129.3 (d, J = 13.4), 129.5 (d, J = 45.5) 130.2 (d, J = 2.0), 130.7 (d, J = 9.3), 132.1 (d, J = 2.0), 134.2 (d, J = 13.4), 182.4. ^{31}P NMR (CD_2Cl_2): 25.8 (d, J = 148). IR (CH_2Cl_2): 1605 (shoulder), 1562 cm^{-1}. FAB-MS *m*/*z*: 564 ([Rh(cod)(**1**)]$^+$). Anal. Calcd for $C_{30}H_{40}F_6NOPRhSb$: C, 45.02; H, 5.04; N, 1.75. Found: C, 44.74; H, 4.95; N, 1.73.

NMR of the 1:1 Molar Ratio Complex of $Rh(acac)(C_2H_4)_2$/1 (Figure 1a). In an NMR sample tube were placed **1** (16.9 mg, 0.048 mmol) and $Rh(acac)(C_2H_4)_2$ (12.4 mg, 0.048 mmol). The tube was filled with argon, and C_6D_6 (0.6 mL) was added. ^1H NMR (C_6D_6): 1.19 (9H, s), 1.27−1.34 (1H, m), 1.54−1.59 (1H, m), 1.80 (6H, s), 1.93−2.03 (1H, m), 2.20−2.26 (1H, m), 2.82−3.00 (1H, m), 3.10 (2H, m), 3.41 (1H, m), 4.91 (1H, m), 5.30 (1H, s), 6.98−7.11 (6H, m), 7.77−8.05 (4H, m). ^{13}C NMR (C_6D_6): 25.4, 27.2, 27.8, 27.99, 28.03, 31.1, 31.6 (d, J = 23.7), 39.3, 47.7, 57.7, 99.4, 128.09, 128.14, 128.3, 128.5, 129.7, 133.5 (d, J = 43.3), 133.9, 135.5 (d, J = 43.3), 175.5, 184.0, 187.4. ^{31}P NMR (C_6D_6): 42.7 (d, J = 186).

NMR of the 1:1.5 Molar Ratio Complex of $Rh(acac)(C_2H_4)_2$/1 (Figure 1b). In an NMR sample tube were placed **1** (25.4 mg, 0.072 mmol) and $Rh(acac)(C_2H_4)_2$ (12.4 mg, 0.048 mmol). The tube was filled with argon, and C_6D_6 (0.6 mL) was added. ^{31}P NMR (C_6D_6): 39.9 (1P, d, J = 194), 42.7 (2P, d, J = 186).

NMR of the 1:2 Molar Ratio Complex of $Rh(acac)(C_2H_4)_2$/1 (Figure 1c). In an NMR sample tube were placed **1** (33.9 mg, 0.096 mmol) and $Rh(acac)(C_2H_4)_2$ (12.4 mg, 0.048 mmol). The tube was filled with argon, and C_6D_6 (0.6 mL) was added. ^1H NMR (C_6D_6): 1.19 (18H, s), 1.32−1.35 (2H, m), 1.66 (6H, s), 1.69−1.77 (4H, m), 2.13−2.18 (2H, m), 2.76−2.82 (2H, m), 3.15−3.27 (6H, m), 5.05−5.13 (2H, m), 5.45 (1H, s), 6.91−7.05 (12H, m), 8.00−8.06 (8H, m). ^{13}C NMR (C_6D_6): 25.4, 27.4, 27.9, 29.7−29.9 (m), 30.1, 39.3, 47.7, 58.3, 99.8, 127.35−127.42 (m), 127.6−127.7 (m), 128.3, 128.5, 133.2−133.3 (m), 133.9−134.0 (m), 138.3−138.7 (m), 138.9−139.2 (m), 175.0, 184.0. ^{31}P NMR (C_6D_6): 39.9 (d, J = 194).

NMR of the 1:3 Molar Ratio Complex of $Rh(acac)(C_2H_4)_2$/1 (Figure 1d). In an NMR sample tube were placed **1** (50.8 mg, 0.144 mmol) and $Rh(acac)(C_2H_4)_2$ (12.4 mg, 0.048 mmol). The tube was filled with argon, and C_6D_6 (0.6 mL) was added. ^{31}P NMR (C_6D_6): −21.7 (1P, s), 39.9 (2P, d, J = 194).

NMR and IR of $[Rh(cod)(1)]^+SbF6^-$ (2). Under argon atmosphere, a test tube was charged with $[RhCl(cod)]_2$ (35.5 mg, 0.072 mmol), **1** (50.8 mg, 0.144 mmol), and $AgSbF_6$ (49.5 mg, 0.144 mmol). To the test tube was added 1.8 mL of methylene chloride-d_2 at room temperature, and the whole was ultrasonicated for 5 min. After centrifugal sedimentation, the supernatant was transferred to an NMR tube via cannula. ^1H NMR (CD_2Cl_2): 0.79 (9H, s), 1.86−1.90 (1H, m), 2.01−2.27 (7H, m), 2.38−2.45 (2H, m), 2.62−2.73 (2H, m), 2.77−2.81 (2H, m), 3.07 (1H, m), 3.23−3.28 (2H, m), 3.66−3.71 (1H, m), 5.29−5.35 (1H, m), 5.39−5.44 (2H, m), 6.99−7.03 (2H, m), 7.33−7.40 (3H, m), 7.60−7.66 (3H, m), 8.03−8.07 (2H, m). ^{13}C NMR (CD_2Cl_2): 23.3, 26.3, 26.7, 28.3, 31.2, 31.4, 34.3 (d, J = 3.1), 34.8 (d, J = 22.7), 39.9, 47.9, 58.9 (d, J = 5.2), 68.0 (d, J = 15.5), 68.4 (d, J = 15.5), 108.8 (dd, J = 3.0, 10.3), 109.5 (dd, J = 3.0, 10.3), 127.2 (d, J = 45.5), 128.5 (d, J = 9.3), 129.3 (d, J = 13.4), 129.5 (d, J = 45.5) 130.2 (d, J = 2.0), 130.7 (d, J = 9.3), 132.1 (d, J = 2.0), 134.2 (d, J = 13.4), 182.4. ^{31}P NMR (CD_2Cl_2): 25.8 (d, J = 148).

Under argon atmosphere, a test tube was charged with $[RhCl(cod)]_2$ (11.8 mg, 0.024 mmol), **1** (16.9 mg, 0.048 mmol), and $AgSbF_6$ (16.5 mg, 0.048 mmol). To the test tube was added 2.4 mL of methylene chloride at room temperature, and the whole was ultrasonicated for 5 min. After the centrifugal sedimentation, the supernatant was transferred to an IR cell via cannula. IR (CH_2Cl_2): 1605 (shoulder), 1562 cm^{-1}.

NMR and IR of the Complex Prepared from $[Rh(cod)(1)]^+SbF_6^-$ and *n*-BuNC (3). Under argon atmosphere, a test tube was charged with $[RhCl(cod)]_2$ (23.7 mg, 0.048 mmol), **1** (33.9 mg, 0.096 mmol), and $AgSbF_6$ (33.0 mg, 0.096 mmol). To the test tube was added 1.2 mL of methylene chloride-d_2 at room temperature, and the whole was ultrasonicated for 5 min. After centrifugal sedimentation, the supernatant was transferred to a flask via cannula. *n*-BuNC (15.9 mg, 0.192 mmol) was added at room temperature, and the whole was stirred for 10 min. The reaction mixture was transferred to an NMR tube via cannula. ^{31}P NMR (CD_2Cl_2): 20.2 (d, J = 123), 20.8 (d, J = 125).

Under argon atmosphere, a test tube was charged with $[RhCl(cod)]_2$ (11.8 mg, 0.024 mmol), **1** (16.9 mg, 0.048 mmol), and $AgSbF_6$ (16.5 mg, 0.048 mmol). To the test tube was added 2.4 mL of methylene chloride at room temperature, and the whole was ultrasonicated for 5 min. After centrifugal sedimentation, the supernatant was transferred to a flask via cannula. *n*-BuNC (8.0 mg, 0.096 mmol) was added at room temperature, and the whole was stirred for 10 min. The reaction mixture was transferred to an IR cell via cannula. IR (CH_2Cl_2): 2179, 1620 cm^{-1}.

NMR and IR of [RhCl(cod)(1)] (4). In an NMR sample tube were placed **1** (16.9 mg, 0.048 mmol) and $[RhCl(cod)]_2$ (11.8 mg, 0.024 mmol). The tube was filled with argon, and methylene chloride-d_2 (0.6 mL) was added. ^1H NMR (CD_2Cl_2): 1.26 (9H, s), 1.88−2.14 (7H, m), 2.33−2.57 (5H, m), 3.04−3.18 (4H, m), 3.65−3.68 (2H, m), 4.75 (1H, m), 5.42 (2H, m), 7.32−7.44 (6H, m), 7.60−7.68 (2H, m), 7.90−7.94 (2H, m). ^{13}C NMR (CD_2Cl_2): 24.7, 27.1, 28.2, 28.6, 29.9, 30.0 (d, J = 20.6), 32.2, 32.9, 38.8, 47.3, 56.7, 69.5 (d, J = 14.4), 70.4 (d, J =

14.4), 103.4, 104.0, 127.56 (d, J = 9.3), 127.62 (d, J = 9.3), 129.3 (d, J = 2.0), 129.8, 131.9 (d, J = 44.4), 132.7 (d, J = 11.3), 133.2 (d, J = 44.4), 134.4 (d, J = 11.3), 175.8. ^{31}P NMR (CD_2Cl_2): 21.5 (d, J = 150).

Under argon atmosphere, a test tube was charged with $[RhCl(cod)]_2$ (11.8 mg, 0.024 mmol), **1** (16.9 mg, 0.048 mmol), and $AgSbF_6$ (16.5 mg, 0.048 mmol). To the test tube was added 2.4 mL of methylene chloride. The reaction mixture was transferred to an IR cell via cannula. IR (CH_2Cl_2): 1609, 1558 (shoulder) cm^{-1}.

NMR and IR of the Complex Prepared from $[RhCl(C_2H_4)_2]_2$, 1, and KOH (Scheme 5). Under argon atmosphere, a test tube was charged with $[RhCl(C_2H_4)_2]_2$ (15.6 mg, 0.04 mmol) and **1** (28.2 mg, 0.08 mmol). To the test tube were added successively 1,4-dioxane-d_8 (1.0 mL) and 6 M aq KOH (0.67 mL) at 0 °C. The mixture was stirred at room temperature for 0.5 h. The organic layer of this mixture was transferred to an NMR sample tube via cannula. ^{31}P NMR (dioxane-d_8): 43.9 (d, J = 182), 44.1 (d, J = 184).

Under argon atmosphere, a test tube was charged with $[RhCl(C_2H_4)_2]_2$ (18.7 mg, 0.048 mmol) and **1** (33.9 mg, 0.096 mmol). To the test tube were added successively 1,4-dioxane (4.8 mL) and 6 M aq KOH (1.5 mL) at 0 °C. The mixture was stirred at room temperature for 0.5 h. The organic layer of this mixture was transferred to the flask via cannula, and the whole was concentrated under vacuum. The residue was dissolved with 12 mL of methylene chloride, and this sample was transferred to an IR cell via cannula. IR (CH_2Cl_2): 1609, 1574 (shoulder) cm^{-1}.

NMR and IR of $[Rh(cod)(6)]^+SbF_6^-$ (14). Under argon atmosphere, a test tube was charged with $[RhCl(cod)]_2$ (15.8 mg, 0.032 mmol), **6** (34.2 mg, 0.064 mmol), and $AgSbF_6$ (22.0 mg, 0.064 mmol). To the test tube was added 0.8 mL of methylene chloride-d_2 at room temperature, and the whole was ultrasonicated for 5 min. After centrifugal sedimentation, the supernatant was transferred to an NMR sample tube via cannula. ^{1}H NMR (CD_2Cl_2): 0.84 (9H, s), 1.63−1.68 (1H, m), 1.88−1.93 (1H, m), 1.98−2.05 (1H, m), 2.22−2.33 (3H, m), 2.38−2.44 (2H, m), 2.53−2.58 (1H, m), 2.54 (1H, d, J = 13.4), 2.64−2.73 (3H, m), 2.77 (1H, d, J = 13.4), 2.82 (1H, d, J = 13.8), 2.88 (1H, d, J = 13.8), 3.14−3.16 (1H, m), 3.21−3.23 (1H, m), 3.36 (1H, d, J = 11.3), 3.70 (1H, d, J = 11.3), 5.18−5.21 (1H, m), 5.37−5.40 (1H, m), 5.44−5.50 (1H, m), 6.97−7.01 (2H, m), 7.14−7.15 (2H, m), 7.25−7.45 (11H, m), 7.55−7.63 (3H, m), 7.87−7.91 (2H, m). ^{13}C NMR (CD_2Cl_2): 26.7, 28.7, 31.2, 34.32, 34.34, 37.7 (d, J = 22.6), 38.7 (d, J = 13.4), 39.9, 41.1, 42.8, 46.2, 57.3, 57.8 (d, J = 6.2), 68.4 (d, J = 16.5), 68.9 (d, J = 16.5), 108.0 (dd, J = 6.2, 10.3), 109.4 (dd, J = 6.2, 10.3), 126.6, 126.8, 127.6 (d, J = 44.4), 128.2, 128.3, 128.6 (d, J = 9.3), 129.1 (d, J = 12.4), 129.3 (d, J = 44.4), 130.2, 130.3 (d, J = 2.0), 130.4, 130.6 (d, J = 9.3), 132.0 (d, J = 2.0), 134.4 (d, J = 12.4), 136.4, 136.5, 182.5. ^{31}P NMR (CD_2Cl_2): 27.5 (d, J = 150).

Under argon atmosphere, a test tube was charged with $[RhCl(cod)]_2$ (7.4 mg, 0.015 mmol), **6** (16.0 mg, 0.03 mmol), and $AgSbF_6$ (10.3 mg, 0.03 mmol). To the test tube was added 1.5 mL of methylene chloride at room temperature, and the whole was ultrasonicated for 5 min. After centrifugal sedimentation, the supernatant was transferred to an IR cell via cannula. IR (CH_2Cl_2): 1605, 1566 cm^{-1}.

General Procedure for the Amidomonophosphine−Rhodium(I)-Catalyzed Asymmetric 1,4-Addition of Phenylboronic Acid to Cycloalkenones Using the Complex Prepared from $Rh(acac)(C_2H_4)_2$ and 1 (Table 1, entries 1, 2, and 9−13). Under argon atmosphere, a reaction flask was charged with $Rh(acac)(C_2H_4)_2$ (2.6 mg, 0.01 mmol), amiodomonophosphine (0.01−0.03 mmol), and $PhB(OH)_2$ (610 mg, 5.0 mmol). To the flask were added successively 1,4-dioxane (2.5 mL), water (0.25 mL), and cycloalkenone (1.0 mmol). The mixture was heated to 100 °C and then stirred at 100 °C for 1 or 6 h. After dilution with AcOEt, the mixture was washed with 10% NaOH and brine and then dried over Na_2SO_4. Concentration and purification through silica gel column chromatography gave the desired product.

(*S*)-3-Phenylcyclohexanone[25] (Table 1, entry 1). $[\alpha]^{20}_D$ −21.4 (*c* 1.22, $CHCl_3$). 97% ee (HPLC, Daicel Chiralpak AD, hexane/*i*-PrOH = 50/1, 0.5 mL/min, 254 nm, major 20.0 min and minor 23.6 min). ^{1}H NMR ($CDCl_3$): 1.75−1.90 (2H, m), 2.07−2.11 (1H, m), 2.13−2.18 (1H, m), 2.35−2.42 (1H, m), 2.44−2.49 (1H, m), 2.50−2.56 (1H, m), 2.58−2.63 (1H, m), 3.01 (1H, tt, J = 4.0, 11.9) 7.22−7.35 (5H, m). ^{13}C NMR ($CDCl_3$): 25.5, 32.7, 41.1, 44.7, 48.9, 126.5, 126.6, 128.6, 144.3, 211.0. IR (neat): 1710 cm^{-1}. EIMS *m*/*z*: 174 (M^+). The absolute configuration was determined to be *S* by comparison of the specific rotation with reported $[\alpha]^{20}_D$ +20.5 (*c* 0.58, $CHCl_3$) for (*R*)-3-phenylcyclohexanone (98.7% ee).[26]

(*S*)-3-Phenylcyclopentanone[25] (Table 1, entry 9). $[\alpha]^{20}_D$ −80.7 (*c* 1.23, $CHCl_3$). 83% ee (HPLC, Shiseido RU-1, MeOH only, 0.5 mL/min, 250 nm, major 12.5 min and minor 15.9 min). ^{1}H NMR ($CDCl_3$): 1.95−2.04 (1H, m), 2.27−2.38 (2H, m), 2.42−2.58 (2H, m), 2.67 (1H, dd, J = 7.3, 18.0), 3.39−3.46 (1H, m), 7.23−7.37 (5H, m). ^{13}C NMR ($CDCl_3$): 31.2, 38.8, 42.2, 45.8, 126.7, 128.6, 143.0, 218.4. IR (neat): 1735 cm^{-1}. EIMS *m*/*z*: 160 (M^+). The absolute configuration was determined to be *S* by comparison of the specific rotation with reported $[\alpha]^{RT}_D$ −67.7 (*c* 1.0, $CHCl_3$) for (*S*)-3-phenylcyclopentanone (70% ee).[29]

Procedure for the Amidomonophosphine−Rhodium(I)-Catalyzed Asymmetric 1,4-Addition of Phenylboronic Acid to Cyclohex-2-en-1-one Using the Complex Prepared from $[RhCl(C_2H_4)_2]_2$, 1, and KOH (Table 1, entry 7). Under argon atmosphere, a test tube was charged with $[RhCl(C_2H_4)_2]_2$ (5.8 mg, 0.015 mmol) and **1** (13.8 mg, 0.039 mmol). To the test tube were added successively 1,4-dioxane (0.5 mL) and 6 M aq KOH (0.25 mL) at 0 °C. The mixture was stirred at room temperature for 0.5 h. This mixture was transferred to the reaction flask (washed with 2 mL of 1,4-dioxane), which was charged with $PhB(OH)_2$ (610 mg, 5.0 mmol) under argon atmosphere. After addition of cyclohex-2-en-1-one (96 mg, 1.0 mmol), the mixture was heated to 100 °C and then stirred at 100 °C for 1 h. After dilution with AcOEt, the mixture was washed with 10% NaOH and brine and then dried over Na_2SO_4. Concentration and purification through silica gel column chromatography gave (*S*)-3-phenylcyclohexane.

Procedure for the Amidomonophosphine−Rhodium(I)-Catalyzed Asymmetric 1,4-Addition of Phenylboronic Acid to Cyclohex-2-en-1-one Using the Complex Prepared from $[RhCl(cod)]_2$, 1, and $AgSbF_6$ (Table 1, entry 3). Under argon atmosphere, a test tube was charged with $[RhCl(cod)]_2$ (2.5 mg, 0.005 mmol), **1** (4.6 mg, 0.013 mmol), and $AgSbF_6$ (3.4 mg, 0.01 mmol). To the test tube was added 0.5 mL of 1,4-dioxane at room temperature, and the whole was ultrasonicated for 5 min. After centrifugal sedimentation, the supernatant was was transferred to the flask. This mixture was transferred to the reaction flask (washed with 2 mL of 1,4-dioxane), which was charged with $PhB(OH)_2$ (610 mg, 5.0 mmol) under argon atmosphere. After addition of cyclohex-2-en-1-one (96 mg, 1.0 mmol) and water (0.25 mL), the mixture was heated to 100 °C and then stirred at 100 °C for 1 h. After dilution with AcOEt, the mixture was washed with 10% NaOH and brine and then dried over Na_2SO_4. Concentration and purification through silica gel column chromatography gave 3-phenylcyclohexane.

Acknowledgment. We gratefully acknowledge financial support from a Grant-in-Aid for Scientific Research on Priority Areas (A) "Exploitation of Multi-Element Cyclic Molecules" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Chart listing ^{1}H and ^{13}C NMR data of the some complexes and the crystal data of **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0261933