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Rhodium-Catalyzed 1,4-Addition of Arylboronic Acids to α,β-Unsaturated Carbonyl Compounds: Large Accelerating Effects of Bases and Ligands

Ryoh Itooka, Yuki Iguchi, and Norio Miyaura*

Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

miyaura@org-mc.eng.hokudai.ac.jp

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The effects of ligands and bases in the rhodium(I)-catalyzed 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds were reinvestigated to carry out the reaction under mild conditions. Rhodium(I) complexes possessing a 1,5-cyclooctadiene (cod) and a hydroxo ligand such as $[RhOH(cod)]_2$ exhibited excellent catalyst activities compared to those of the corresponding rhodium−acac or −chloro complexes and their phosphine derivatives. The reaction was further accelerated in the presence of KOH, thus allowing the 1,4-addition even at 0 °C. A cationic rhodium(I)−(*R*)-binap complex, [Rh(*R*-binap)(nbd)]BF_4, catalyzed the reaction at 25−50 °C in the presence of Et_3N with high enantioselectivities of up to 99% ee for α,β-unsaturated ketones, 92% for aldehydes, 94% for esters, and 92% for amides.

The conjugate addition of nucleophiles to activated alkenes is a widely used process in organic chemistry. Since the reaction often yields a stereogenic center at the β-carbon, considerable efforts have been devoted to the development of its asymmetric versions.[1] Perhaps the most commonly used metal catalyst is copper in combination with organolithium,[2] -magnesium,[3] or -zinc[4] reagents,[1a,d] but rhodium-catalyzed reactions of organoboranes,[5−8] -silicones,[9,10] and -stannanes[11,12] are an attractive alternative because of their insensitivity to functional groups and the availability of various chiral phosphine ligands for rhodium catalysts. It was recently demonstrated that rhodium(I) complexes are excellent

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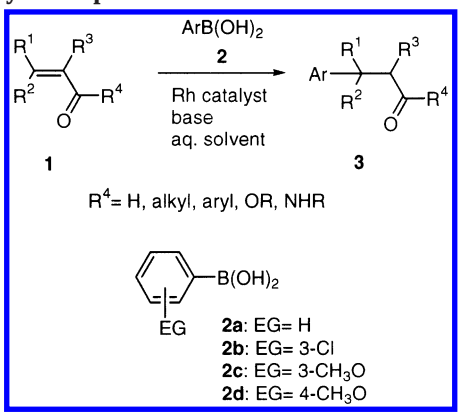
SCHEME 1. 1,4-Addition to α,β-Unsaturated Carbonyl Compounds



catalysts for the conjugate additions of aryl- and alkenylboronic acids to α,β-unsaturated ketones, esters, and amides.[5] The protocol was extended to the addition to unactivated C−C multiple bonds such as norbornene,[8f] oxanorbornene,[8a,b] vinylarenes,[8e] and internal alkynes.[8c,d] Among these reactions, the additions to α,β-unsaturated ketones,[7a,b,d,e,k−m] esters,[7g,j] amides,[7c,f] phosphonates,[7i] nitroalkenes,[7h] and oxanorbornenes[8a] were carried out in the presence of rhodium(I)−chiral phosphine catalysts. These reactions, however, often required the use of large excesses of organoboronic acids because of a competitive hydrolytic B−C bond cleavage of organoboronic acids and perhaps the Rh−C bond cleavage of the rhodium intermediate due to a low catalyst efficiency requiring a temperature of over 100 °C in an aqueous solvent. Very recently, [RhOH-binap]$_2$ was found to be an efficient catalyst that completes the reaction within 3 h at 35 °C.[7a] In connection with our interests in metal-catalyzed reactions of organoboronic acids,[13] we report here the effects of catalysts and bases reinvestigated for the 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds (Scheme 1).[14] The (hydroxo)rhodium(I)−cod complex or the catalyst in situ generated from a (chloro)-rhodium(I)−cod complex and a base was recognized to be the most efficient system that allows the reaction at a temperature lower than room temperature. The results were easily extended to asymmetric addition at room temperature, using a cationic rhodium−binap complex and triethylamine (Scheme 2).

SCHEME 2. Asymmetric 1,4-Addition to α,β-Unsaturated Carbonyl Compounds

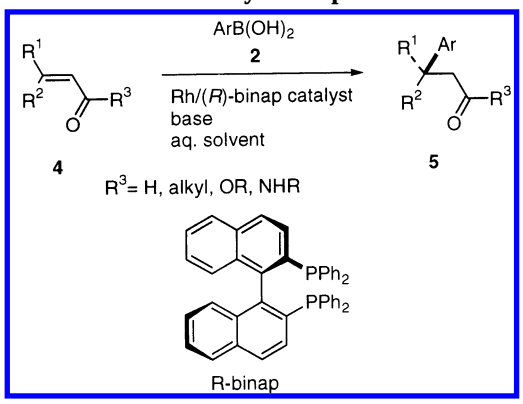


TABLE 1. Effects of Rhodium Complexes and Ligands[a]

entry	Rh(I) precursor	ligand/ equiv[b]	yield/%[c] (50 °C)	yield/%[c] (90 °C)
1	$[Rh(cod)_2]BF_4$	none	25	93
2	$[Rh(cod)(MeCN)_2]BF_4$	none	74	84
3	$[RhCl(cod)]_2$	none	93	99
4	$[RhCl(nbd)]_2$	none	trace	trace
5	$[RhCl(nbd)]_2$	cod (1)		93
6	$[RhCl(coe)_2]_2$	none	trace	trace
7	$[RhCl(coe)_2]_2$	cod (3)		91
8	Rh(acac)(cod)	none	83	86
9	Rh(acac)$(coe)_2$	none	trace	trace
10	Rh(acac)$(coe)_2$	cod (1)	-	90
11	Rh(acac)$(coe)_2$	R_3P[d]	trace	0−22
12	Rh(acac)$(coe)_2$	dppm (1)	trace	88
13	Rh(acac)$(coe)_2$	dppe (1)	trace	7
14	Rh(acac)$(coe)_2$	dppp (1)	3	36
15	Rh(acac)$(coe)_2$	dppb (1)	6	38
16	Rh(acac)$(coe)_2$	binap (1)	17	52
17	Rh(acac)$(coe)_2$	dppf (1)	6	23
18	Rh(acac)$(coe)_2$	DPFphos (1)	trace	5
19	Rh(acac)$(coe)_2$	Xantphos (1)	trace	9
20	Rh(acac)$(coe)_2$	DBEphos (1)	trace	3

[a] All reactions were carried out for 6 h at 50 °C or 90 °C in aqueous dioxane (6/1, 3 mL) in the presence of 2-cyclohexenone (1 mmol), *p*-tolylboronic acid (1.5 mmol), a rhodium complex (3 mol % of Rh), and a ligand (3−9 mol %). [b] Equivalents to rhodium metal. [c] GC yields. [d] The representative monophosphines resulted in the following yields at 90 °C: P(*t*-Bu)$_3$P (trace), Cy_3P (trace), (*i*-Pr)$_3$P (2%), (*p*-MeOPh)$_3$P (13%), Ph_3P (7%), (*p*-CF_3Ph)$_3$P (22%), $(C_6F_5)_3P$ (11%).

Reaction Conditions

The effects of rhodium(I) precursors and ligands in the conjugate addition of *p*-tolylboronic acid to 2-cyclohexenone are summarized in Table 1. There was a large difference between the catalyst activities of the rhodium−cod complexes and those of other alkene complexes. Various cationic and neutral rhodium complexes possessing a cod ligand commonly exhibited an excellent catalyst efficiency (entries 1−3), whereas the rhodium(I)−norbornadiene (nbd) (entry 4), −cyclooctene (coe) (entries 6 and 9), and −ethylene complexes did not catalyze the reaction at all. On the other hand, the addition of 1,5-cyclooctadiene (1−3 equiv) to the rhodium−nbd and −coe complexes resulted in almost quantitative conversions within 6 h at 90 °C (entries 5, 7, and 10). Although rhodium−phosphine complexes have been investigated extensively to extend the reactions to asymmetric synthesis, a small and less-donating cod is the best ligand for achieving high conversions under mild conditions.

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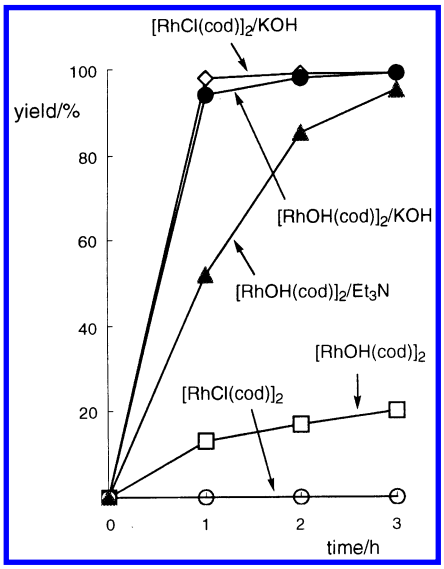

FIGURE 1. Effect of bases. All reactions were carried out at 5 °C in aqueous DME (6/1, 3 mL) in the presence of 2-cyclohexenone (1 mmol), *p*-tolylboronic acid (1.5 mmol), a rhodium complex (3 mol % of Rh), and a base (1 mmol), if used.

The effects of phosphine ligands are shown in entries 11−20. All monophoshines were ineffective (entry 11). On the other hand, dppm was recognized to be the best ligand among the representative diphosphines (entries 12−20). The dppm complex (∠P−Rh−P, 72°) gave an 88% yield of product at 90 °C, which was a much higher yield than that of the dppp, dppb, binap, or dppf complex having a bite angle in a range of 90−99° (entries 12−17).[15] These phosphine complexes catalyzed the reaction efficiently at 90 °C but very slowly at 50 °C.

The addition of an inorganic base, such as $NaHCO_3$, Na_2CO_3, K_3PO_4, or KOH, to a mixture of *p*-tolylboronic acid, 2-cyclohexenone, and $[RhCl(cod)]_2$ (1.5 mol %) in aqueous 1,4-dioxane exerted a remarkable accelerating effect, in contrast to a very sluggish reaction under neutral conditions. The reaction at 0 °C for 6 h in the presence of a base (1 equiv) showed an accelerating effect depending on the basic strengths: e.g., KOH (83%) > K_3PO_4 (49%) > K_2CO_3 (34%) > none (trace). The accelerating effect of a base was also significant for other rhodium complexes possessing a cod ligand, a cod complex in situ prepared from an appropriate rhodium precursor and cod, and a cationic rhodium complex such as $[Rh(cod)(MeCN)_2]BF_4$.

The reaction proceeds through a catalytic cycle[7a,g,n,o] involving (a) transmetalation between $ArB(OH)_2$ and an Rh(OH) complex yielding an Ar−Rh species, (b) insertion of an alkene into the Rh−C bond, and finally (c) hydrolysis of a rhodium enolate intermediate with simultaneous regeneration of an Rh(OH) species. In good agreement with this mechanism, a change in the rhodium catalyst from $[RhCl(cod)]_2$ or Rh(acac)(cod) to $[Rh(OMe)(cod)]_2$ or $[Rh(OH)(cod)]_2$ allowed reaction at room temperature in the absence of bases.[5d] Thus, the results strongly suggested that bases play a role in generating a (hydroxo)-rhodium(I) complex[16] that is effective for transmetalation with arylboronic acids.

TABLE 2. Turnover Number of Catalyst (TON)[a]

entry	mol %[b]	temp (°C)/ time (h)	yield/%[c]	TON
1	0.01	90/16	98	9 800
2	0.005	90/24	67	13 400
3	0.005	90/36	97	18 400
4	0.001	100/36	97	97 000
5	0.0005	100/36	96	192 000
6	0.0002	100/36	75	375 000

[a] A mixture of 2-cyclohexenone (1 mmol), *p*-tolylboronic acid (1.5 mmol), $[RhCl(cod)]_2$ (0.0002−0.01 mol % of Rh), cod (3 mol % for entries 1−3 and 9 mol % for entries 4−6), and $NaHCO_3$ (1 mol %) in aqueous dioxane (6/1, 3 mL) was stirred in a sealed tube for 16−36 h at the temperature and for the period shown in the table. [b] mol % of Rh. [c] Isolated yields.

The accelerating effect of bases is shown in Figure 1. Five reactions of *p*-tolylboronic acid (1.5 equiv) with 2-cyclohexenone were carried out at 5 °C with $[RhOH(cod)]_2$ or $[RhCl(cod)]_2$ (1.5 mol %) in the presence or absence of KOH or Et_3N (1 equiv). Although the RhOH complex (□) was indeed a better catalyst than the RhCl complex (○), the RhOH-catalyzed reaction was found to be further accelerated in the presence of KOH (●) and was almost superimposable to a combination of the RhCl complex and KOH (◇). Both reactions resulted in 93−98% yields after 1 h at 5 °C. The effect of Et_3N is smaller than that of KOH (▲), but it was markedly faster than that carried out in the absence of a base. Thus, there are two roles of bases. The presence of base is critical in generating an active species for transmetalation when the RhCl or Rh(acac) complexes are used as the catalyst precursors. There is no relevant information for the additional effect that accelerated the RhOH(cod)-catalyzed reaction; however, quarternization of arylboronic acids with a base facilitates transmetalation to the RhOH species as is demonstrated in palladium-catalyzed reactions of organoboronic acids.[13] Facilitation of hydrolysis of a rhodium enolate intermediate is another probable effect.[17] Such an effect of bases has been reported for the rhodium-catalyzed addition of organoboronic acids to aldehydes[6a] and the conjugate addition to acetylated enones derived from glycals.[5e]

$[RhCl(cod)]_2$ achieved high turnover numbers of the catalyst (TON) at 90−100 °C (Table 2). The reaction at a temperature over 90 °C suffered from incomplete conversions due to decomposition of the catalyst via dissociation of the cod ligand from the rhodium metal. The addition of 1,5-cyclooctadiene (3−9 mol %) and a small amount of a base ($NaHCO_3$, 1 mol %) was found to be highly effective for maintaining catalyst efficiency. The reaction employing $[RhCl(cod)]_2$ (0.0002 mol % of Rh), cod (9 mol %), and $NaHCO_3$ (1 mol %) at 100 °C gave 75% yield of 3-tolylcyclohexanone after 36 h, corresponding to 375 000 TON (entry 6). At 90−100 °C, there was no

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TABLE 3. Addition of *p*-Tolylboronic Acid to α,β-Unsaturated Carbonyl Compounds[a]

entry	carbonyl compounds	catalyst/base (equiv)/solvent	temp (°C)/ time (h)	product no.	yield/%[b]
1	(*E*)-PhCH=CHCOCH$_3$	[RhCl(cod)]$_2$/NaHCO$_3$ (0.1)/dioxane−H$_2$O	25/16	**3a**	96
2	(*E*)-PhCH=CHCOCH$_3$	[RhOH(cod)]$_2$/KOH (1)/DME−H$_2$O	0/6	**3a**	99
3	(*E*)-PhCH=CHCOPh	[RhOH(cod)]$_2$/KOH (1)/DME−H$_2$O	0/6	**3b**	82
4	β-ionone	[RhCl(cod)]$_2$/NaHCO$_3$ (0.1)/dioxane−H$_2$O	50/16	**3c**	36
5[c]	β-ionone	[RhCl(cod)]$_2$/LiOH (1.5)/dioxane−H$_2$O	50/16	**3c**	92
6	β-ionone	[RhOH(cod)]$_2$/KOH (1)/DME−H$_2$O	0/6	**3c**	35
7	2-cyclohexenone	[RhCl(cod)]$_2$/NaHCO$_3$ (0.1)/dioxane−H$_2$O	25/16	**3d**	94
8	2-cyclohexenone	[RhOH(cod)]$_2$/KOH (1)/DME−H$_2$O	0/6	**3d**	98
9	5-isopropenyl-2-methyl-2-cyclohexenone (carvone)	[RhCl(cod)]$_2$/NaHCO$_3$ (0.1)/dioxane−H$_2$O	90/16	**3e**	trace
10	(*E*)-CH$_3$CH=CHCO$_2$Me	[RhCl(cod)]$_2$/NaHCO$_3$ (0.1)/dioxane−H$_2$O	25/16	**3f**	93
11	(*E*)-CH$_3$CH=CHCO$_2$Me	[RhOH(cod)]$_2$/KOH (1)/DME−H$_2$O	0/6	**3f**	81
12	(*E*)-PhCH=CHCO$_2$Me	[RhOH(cod)]$_2$/KOH (1)/DME−H$_2$O	0/6	**3g**	97
13	CH$_3$CH=C(CO$_2$Et)$_2$	[RhCl(cod)]$_2$/NaHCO$_3$ (0.1)/dioxane−H$_2$O	50/16	**3h**	72
14	CH$_3$CH=C(CO$_2$Et)$_2$	[RhOH(cod)]$_2$/KOH (1)/DME−H$_2$O	0/6	**3h**	85

[a] A mixture of a carbonyl compound (1 mmol), *p*-tolylboronic acid (1.5 mmol), and a base (0.1−1.0 mmol) in an aqueous solvent (6/1. 3 mL) was stirred in the presence a catalyst, unless stated otherwise. [b] Isolated yields by chromatography over silica gel. [c] LiOH (1.5 mmol) and *p*-tolylboronic acid (2 mmol) were used.

great difference between the catalyst efficiency of [RhOH(cod)]$_2$ and that of [RhCl(cod)]$_2$.

Scope and Limitation

The scope for representative α,β-unsaturated carbonyl compounds is summarized in Table 3. Quantitative conversions resulting in over 90% yields were easily realized at room temperature in the presence of [RhCl(cod)]$_2$ (1.5 mol %) and NaHCO$_3$ (0.1 equiv) or in the presence of [RhOH(cod)]$_2$ (1.5 mol %) and KOH (1 equiv) at 0 °C for α,β-unsaturated ketones and esters having no large steric hindrance (entries 1−3, 7, 8, and 10−12). Judging from the observed high yields, aldol condensation of ketones or saponification of esters was not significant, but the use of NaHCO$_3$ at room temperature is recommended for ester derivatives since KOH often resulted in low yields due to competitive saponification (entry 10). The reaction is highly sensitive to steric hindrance and electron density of the double bond. For example, the addition to β-ionone was very slow at room temperature due to steric hindrance of the β-substituent, but the reaction smoothly proceeded at 50 °C in the presence of a strong base (entries 4 and 5). Although all attempts failed for three-substituted ketones and esters such as carvone (entry 9) and ethyl (*E*)-2-methyl-2-butenoate, much electron-deficient diethyl 2-ethylidenemalonate completed the reaction under analogous conditions effective for methyl crotonate (entries 13 and 14).

Asymmetric Addition

Of particular importance is extension of the protocol to asymmetric synthesis.[7] Although inorganic bases exhibited an excellent accelerating effect for the rhodium−binap complexes, the use of inorganic bases suffered from low enantioselectivity. For example, the addition of KOH to [RhCl(*R*-binap)]$_2$ at room temperature resulted in the formation of racemic 3-phenylcyclohexanone in the addition of phenylboronic acid to 2-cyclohexenone in aqueous dioxane. Although [Rh(*R*-binap)(nbd)]BF$_4$[18,19] was found to be a much more selective catalyst than [RhCl(*R*-binap)]$_2$, the use of inorganic bases still suffered from low enantioselectivities that varied depending on the basic strength (entries 2−5 in Table 4). The results may suggest the generation of a free-phosphine rhodium species by coordination of an inorganic base with the rhodium metal center. Finally, triethylamine was recognized to be the best base to achieve 98−99% ee at room temperature (entry 6). Although a catalytic amount of Et$_3$N (10%) allowed room temperature reaction (79% yield), the yield was almost quantitative when 1 equiv of Et$_3$N (98% yield) was used. In contrast, the reaction was very slow in DME and resulted in a significantly low yield and low enatioselectivity in ethanol (entries 7 and 8). Diisopropylethylamine and diisoprpylamine were also effective (entries 9 and 10), but tetramethylethylenediamine strongly retarded the catalyst (entry 11).

TABLE 4. Asymmetric Addition of Phenylboronic Acid to 2-Cyclohexenone Catalyzed by [Rh(*R*-binap)(nbd)]BF$_4$[a]

entry	base (equiv)	solvent	yield/%[b]	% ee[c]
1	none	dioxane/H$_2$O	trace	
2	KOH (1.0)	dioxane/H$_2$O	64	78
3	K$_3$PO$_4$ (1.0)	dioxane/H$_2$O	88	99
4	K$_2$CO$_3$ (1.0)	dioxane/H$_2$O	47	99
5	KHCO$_3$ (1.0)	dioxane/H$_2$O	46	98
6	Et$_3$N (0.1−1.5)	dioxane/H$_2$O	79−98	98−99
7	Et$_3$N (1)	DME/H$_2$O	34	97
8	Et$_3$N (1)	EtOH/H$_2$O	16	43
9	*i*-Pr$_2$NEt (1.0)	dioxane/H$_2$O	89	99
10	*i*-Pr$_2$NH (1.0)	dioxane/H$_2$O	88	98
11	TMEDA (1.0)	dioxane/H$_2$O	9	98

[a] A mixture of 2-cyclohexenone (1 mmol), PhB(OH)$_2$ (1.5 mmol), base (0.1−1.5 mmol), and [Rh(R-binap)(nbd)]BF$_4$ (3 mol %) was stirred for 6 h at 25 °C. [b] Isolated yields by chromatography. [c] Enantiomer excess determined by a chiral stationary column (Dicel Chiralcel AD).

The asymmetric additions of arylboronic acids to representative α,β-unsaturated ketones, aldehydes, es-

(18) Cationic rhodium catalysts were used for 1,4-addition of Si and Sn compounds, see: refs 9d,e and 11.

(19) (a) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208. (b) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. Reviews for binap catalysts: (c) Ohkuma, T.; Noyori, R. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, Germany, 1999; Chapter 6.1. (d) Kumobayashi, H.; Miura, T.; Sayo, N.; Saito, T.; Zhang, X. *Synlett* **2001**, 1055. (e) Noyori, R. In *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994; Chapter 1. (f) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345.

TABLE 5. Asymmetric Addition to α,β-Unsaturated Carbonyl Compounds[a]

entry	carbonyl compound	$ArB(OH)_2$ (**2**)	product no.	yield/%[b]	% ee[c]
1	2-cyclohexenone	**2a**	**5a**	99	99
2	2-cyclohexenone	**2c**	**5b**	98	99
3	2-cyclohexenone	**2b**	**5c**	97	99
4	2-cyclohexenone	**2d**	**5d**	87	nd
5	2-cyclopentenone	**2b**	**5e**	99	97
6	(*E*)-$C_5H_{11}CH$=$CHCOCH_3$	**2a**	**5f**	98	83 (86)[d]
7	(*E*)-$C_5H_{11}CH$=$CHCOCH_3$	**2c**	**5g**	91	88 (90)[e]
8[f]	(*E*)-*i*-C_3H_7CH=$CHCOCH_3$	**2a**	**5h**	75	97
9[f]	(*E*)-*i*-C_3H_7CH=$CHCOCH_3$	**2c**	**5i**	82	98
10[f]	(*E*)-CH_3CH=CHCHO	**2c**	**5j**	59	86
11[f]	(E)-C_3H_7CH=CHCHO	**2a**	**5k**	56	92
12	(*E*)-CH_3CH=$CHCO_2$*i*-Pr	**2d**	**5l**	93	94
13[f]	(*E*)-CH_3CH=CHCONHBn	**2a**	**5m**	97	92

[a] A mixture of a carbonyl compound (1 mmol), $ArB(OH)_2$ (1.5 mmol), Et_3N (1 mmol), and [Rh(R-binap)(nbd)]BF_4 (3 mol %) in dioxane/H_2O (6/1, 3 mL) was stirred for 6 h at 25 °C, unless otherwise noted. [b] Isolated yields by chromatography. [c] Enantiomer excess determined by a chiral stationary column (Dicel Chiralcel OD-H, OB-H, or AD). The aldehydes in entries 10 and 11 were reduced to alcohols before HPLC analyses. [d] Additional (*R*)-binap (6 mol %) was added. [e] K_3PO_4 (1 mmol) was used in place of Et_3N. [f] The reactions were conducted at 50 °C for 6 h.

ters, and amides catalyzed by [Rh(R-binap)(nbd)]BF_4/Et_3N are summarized in Table 5. A variety of arylboronic acids can be used for 2-cyclohexenone with excellent isolated yields and perfect enantioselectivities (entries 1−4). All reactions were completed within 6 h at room temperature. Analogously, the additions to 2-cyclopetenone (entry 5), 3-nonen-2-on (entries 6 and 7), and isopropyl crotonate (entry 12) easily proceeded at room temperature, whereas the reaction mixtures were heated to 50 °C for more sterically hindered ketones (entries 8 and 9), α,β-unsaturated aldehydes (entries 10 and 11), and *N*-benzyl crotonamide (entry 13). There were no large differences in selectivity for para and meta substituents of arylboronic acids, but they were highly dependent on substrates and functionalities therein. Aliphatic enones including alicyclic compounds are desirable substrates to achieve high enantioselectivities up to 99% ee (entries 1−9). Among them, the additions to 3-nonene-2-one exceptionally resulted in significantly low enantioselectivities for an unknown reason, though the addition of an excess binap ligand or change of the base to K_3PO_4 slightly improved the selectivity (entries 6 and 7). The effect of the β-substituent (R^1) was significant for enals such as crotonaldehyde and 2-hexenal (entries 10 and 11).[20] These reactions at room temperature resulted in higher isolated yields and higher enantioselectivities than that of an Rh(acac)(binap) catalyst previously employed at 100 °C.[7]

Experimental Section

All reactions were carried out under nitrogen. HPLC analyses were carried out with a chiral stationary phase column, Chiralpak AD, Chiralcel OD-H or OB-H, purchased from Dicel Co., Ltd.

(20) No addition to the CHO group was observed, see ref 6.

Synthesis of [Rh((*R*)-binap)(nbd)]BF_4.[19a] In a 25-mL flask containing a magnetic stirring bar were placed [$Rh(nbd)_2$]-BF_4 (169 mg, 0.452 mmol) and (*R*)-BINAP (310 mg, 0.498 mmol) under argon. CH_2Cl_2 (10 mL) was added and the mixture was then stirred at room temperature for 3 h. THF (10 mL) was slowly added to the resulting orange-red solution. The mixture was allowed to stand in a freezer for 1 day and the solvent was then evaporated. The orange crystal was collected by filtration, washed with THF and ether, and dried. Yield 348 mg (85%); ^{31}P NMR ($CDCl_3$) δ 26.31 (d, J_{Rh-P} = 154.1 Hz). Anal. Calcd for $C_{51}H_{40}BF_4P_2Rh$: C, 67.72; H, 4.46. Found: C, 66.79; H, 4.66.

General Procedure for Table 1. Rhodium complex (0.03 mmol for Rh), a ligand (0−0.09 mmol), and (4-methylphenyl)-boronic acid (1.5 mmol) were added to a 25-mL flask containing a magnetic stirring bar and a septum inlet. The flask was flashed with argon and charged with aqueous 1,4-dioxane (6/1, 3 mL). After being stirred for 30 min, 2-cyclohexenone (1.0 mmol) was added. The mixture was then stirred for 6 h at the temperature shown in Table 1. Yields of products were analyzed by GC, using pentadecane as an internal standard.

General Procedure for Table 5. [Rh((*R*)-binap)(nbd)]BF_4 (0.03 mmol) and arylboronic acid (1.5 mmol) were added to a 25-mL flask equipped with a magnetic stirring bar and a septum inlet. The flask was flashed with argon and charged with aqueous 1,4-dioxane (6/1, 3 mL). Triethylamine (1.0 mmol) and α,β-unsaturated carbonyl compound (1.0 mmol) were then added. The mixture was stirred for 6 h at 25 °C. The product was extracted with benzene, washed with brine, and finally dried over $MgSO_4$. Chromatography over silica gel gave the desired product.

Supporting Information Available: Text describing experimental details and spectral and/or analytical data of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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