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Electron-Poor Chiral Diphosphine Ligands: High Performance for Rh-Catalyzed Asymmetric 1,4-Addition of Arylboronic Acids at Room Temperature

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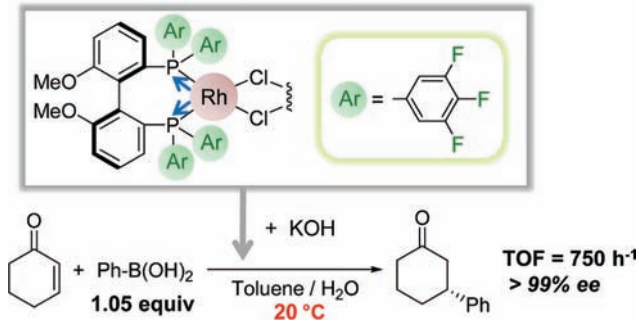
ABSTRACT



Electron-poor chiral diphosphine ligands, MeO-F_{28}-BIPHEP (1a) and MeO-F_{12}-BIPHEP (1b), were synthesized for controlling a transition-metal catalyst electronically. The 1b-ligated Rh catalyst showed excellent catalytic activity with high % ee for asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated carbonyls at 20 °C. The strong π-acceptor ability of 1b induces transmetalation of arylboronic acid to catalyst precursor [RhCl(1b)]$_2$ directly in the first step of the catalytic cycle.

Phosphine ligands have played a significant role in both steric and electronic adjustment of transition-metal-catalyzed reactions. Although a large majority of phosphine ligands are more electron-rich than triphenylphosphine,[1] there are quite a few examples of applications of electron-poor phosphine ligands, in particular, fluorinated aryl phosphines.[2] However, only a few examples of those chiral ligands having prominent catalytic effects have been reported in asymmetric reactions,[3] and most of them concern P,N-ligands bearing both electron-poor phosphorus and donative nitrogen atoms.[3b−e] Electron-poor diphosphine ligands are well-suited to take full advantage of the π-acceptor character for controlling the catalyst electronically. Specifically, a biaryl diphosphine (BINAP-type) ligand,[4] which has a biaryl backbone and two arylphosphorus substituents, has the highest potential due to its flexibility for facile complexation with metals and its

(1) (a) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2008**, *47*, 6338. (b) Valentine, D. H., Jr.; Hillhouse, J. H. *Synthesis* **2003**, 2437.

(2) Pollock, C. L.; Saunders, G. C.; Smyth, E. C. M. S.; Sorokin, V. I. *J. Fluorine Chem.* **2008**, *129*, 142.

(3) (a) Jana, C. K.; Studera, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 6542. (b) Tani, K.; Behenna, D. C.; McFadden, R. M.; Stoltz, B. M. *Org. Lett.* **2007**, *9*, 2529. (c) Moran, W. J.; Morken, J. P. *Org. Lett.* **2006**, *8*, 2413. (d) Legault, C. Y.; Charette, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 8966. (e) Garcia-Yebra, C.; Janssen, J. P.; Rominger, F.; Helmchen, G. *Organometallics* **2004**, *23*, 5459. (f) Hayashi, T.; Hirate, S.; Kitayama, K.; Tsuji, H.; Torii, A.; Uozumi, Y. *J. Org. Chem.* **2001**, *66*, 1441.

(4) (a) Berthod, M; Mignani, G.; Woodward, G.; Lemaire, M. *Chem. Rev.* **2005**, *105*, 1801. (b) Shimizu, H.; Nagasaki, I.; Saito, T. *Tetrahedron* **2005**, *61*, 5405. (c) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345.

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paramount steric influence for high asymmetric induction.[4c] Although many BINAP-type ligands have been reported, it is surprising that few have been reported for the ligand bearing fluorine atoms.[5,6] In addition, those ligands have only one or two fluoro-functional groups on each monoaromatic ring, and accordingly they should be endowed with an insufficient π-acceptor ability. In this Letter, we report the development of novel electron-poor BINAP-type ligands **1**, which are MeO-BIPHEP analogues[7] bearing three or more fluoro-functional groups on each phosphorus phenyl ring. These groups would incorporate not only strong π-acceptor ability but also steric bulkiness into the chiral diphosphine. The performance of ligands **1** was demonstrated by using Rh-catalyzed asymmetric 1,4-addition.[8]

We designed MeO-F_{28}-BIPHEP (**1a**) and MeO-F_{12}-BIPHEP (**1b**) as shown in Figure 1. These potentials were

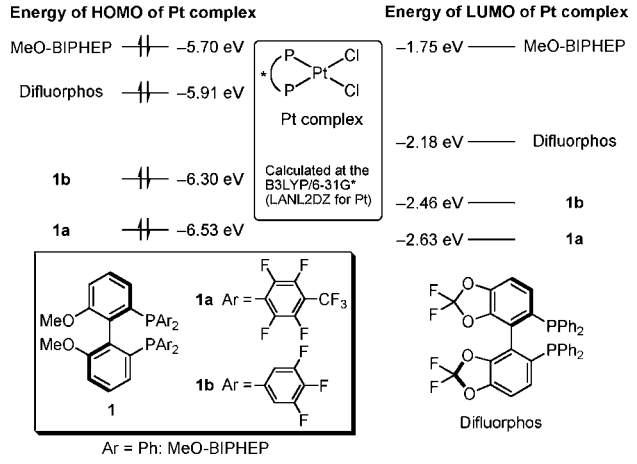
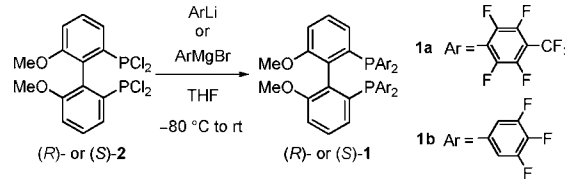


Figure 1. Ability of electron-poor diphosphine ligands **1** on metal complex.

predicted by DFT calculations of Pt complexes at the B3LYP/6-31G* (LANL2DZ for Pt) level (Figure 1).[9] The energies of the HOMO and LUMO of both Pt-**1a** and Pt-**1b** are lower than those of electron-poor Difluorphos.[5b] The results promise the effectiveness of the ligands **1a** and **1b** as strong π-acceptor ligand for transition metal catalysis.

Novel ligands **1a** and **1b** were synthesized according to the preparation methods of MeO-BIPHEP analogues[7] from (*R*)- or (*S*)-**2** (Scheme 1). The compound **2** was treated with

Scheme 1. Synthesis of Electron-Poor Diphosphine Ligands **1**



an excess of C_7F_7Li or $C_6F_3H_2MgBr$ in THF at −80 °C to give the corresponding enantiomer of **1a** or **1b** in a moderate yield, respectively.

The electronic properties of **1** were estimated by comparison with the carbonyl stretching frequencies (υ_{CO}) of the corresponding [RhCl(diphosphine)(CO)] complexes **3**,[5b] which were prepared from $[RhCl(CO)]_2$. The υ_{CO} value of **3b** is higher than those of known diphosphines including electron-poor ones, indicating that **1b** has sufficient π-acidic character as compared with the known diphosphines (Table 1). Unfortunately, **3a** could not be prepared by the reaction

Table 1. Electronic Properties of **1a** and **1b**

diphosphine (L*)	υ_{CO} of [RhCl(L*)(CO)] (cm^{-1})	reduction potential of $[PtCl_2(L^*)]$ (V)[d]
1a	- [**3a**]	−1.49 [**5a**]
1b	2036[a] [**3b**]	−1.77 [**5b**]
MeO-BIPHEP	2014[b]	−1.94
BINAP	2017[b]	
p-F-BINAP	2018[c]	
difluorophos	2023[b]	

[a] In $CHCl_3$. [b] From ref 5b. [c] From ref 5h. [d] See Supporting Information.

of **1a** with $[RhCl(CO)_2]_2$, which gave $[RhCl(\mathbf{1a})]_2$ (**4a**), suggesting that **1a** has strong π-acceptor ability.[10] To

(5) (a) Kim, D. E.; Choi, C.; Kim, I. S.; Jeulin, S.; Ratovelomanana-Vidal, V.; Genet, J.-P.; Jeong, N. *Synthesis* **2006**, 4053. (b) Jeulin, S.; Duprat de Paule, S.; Ratovelomanana-Vidal, V.; Genet, J.-P.; Champion, N.; Dellis, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 320. (c) Driessen-Hoelscher, B.; Kralik, J.; Agel, F.; Steffens, C.; Hu, C. *Adv. Synth. Catal.* **2004**, *346*, 979. (d) Jeong, N.; Kim, D. H.; Choi, J. H. *Chem. Commun.* **2004**, 1134. (e) Scalone, M.; Waldmeier, P. *Org. Process Res. Dev.* **2003**, *7*, 418. (f) Koh, J. H.; Larsen, A. O.; Gagne, M. R. *Org. Lett.* **2001**, *3*, 1233. (g) Jendralla, H.; Li, C. H.; Paulus, E. *Tetrahedron: Asymmetry* **1994**, *5*, 1297. (h) Mashima, K.; Kusano, K.; Sato, N.; Matsumura, Y.; Nozaki, K.; Kumobayashi, H.; Sayo, N.; Hori, Y.; Ishizaki, T.; Akutagawa, S.; Takaya, H. *J. Org. Chem.* **1994**, *59*, 3064. (i) Murata, M.; Morimoto, T.; Achiwa, K. *Synlett* **1991**, 827.

(6) Among them, Difluorphos (ref 5b) has been used recently. (a) Liao, X.; Weng, Z.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 195. (b) Du, Y.; Xu, L.-W.; Shimizu, Y.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2008**, *130*, 16146. (c) Oisaki, K.; Zhao, D.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2007**, *129*, 7439. (d) Yamamoto, Y.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 7082.

(7) Schmid, R.; Broger, E. A.; Cereghetti, M.; Crameri, Y.; Foricher, J.; Lalonde, M.; Muller, R. K.; Scalone, M.; Schoettel, G.; Zutter, U. *Pure Appl. Chem.* **1996**, *68*, 131.

(8) Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002**, *124*, 5052.

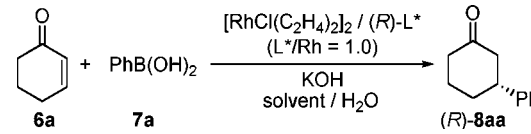
(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Jr. Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision E.01*; Gaussian, Inc.: Pittsburgh, PA, 2004.

evaluate **1a**, cyclic voltammetries were examined for air-stable [$PtCl_2$(**1**)] (**5**), which was prepared from [$PtCl_2$-($PhCN)_2$]. The reduction potential increased with the increasing number of fluorine atoms in **5** (Table 1), indicating that the π-acceptor ability of the fluoroaromatic group on phosphorus has a significant effect on the orbital energy of the central metal.

The performance of the electron-poor ligands **1** was evaluated by the Rh-catalyzed 1,4-addition of $PhB(OH)_2$ to 2-cyclohexenone.[8] It was expected that the electron-poor ligand would accelerate both transmetalation[11] and insertion[12] steps in the catalytic cycle.[8] To start with, we examined the preparation of **4a** (see above) and [RhCl(**1b**)]$_2$ (**4b**), which were used for the catalyst precursor.[8] Complex (*R*,*R*)-**4b** was readily prepared from (*R*)-**1b** using [RhCl($C_2H_4)_2]_2$. The X-ray crystal structure of (*R*,*R*)-**4b** (see Supporting Information) was compared with that of [RhCl{(*R*)-binap}]$_2$ [(*R*,*R*)-**4c**].[13] The Rh−P lengths of the (*R*,*R*)-**4b** [2.195(3) and 2.200(3) Å] and the bite angle (P−Rh−P) of **1b** in (*R*,*R*)-**4b** [91.22(11)°] are similar to those of (*R*,*R*)-**4c**. Although the Rh−Cl length of (*R*,*R*)-**4b** is similar to that of (*R*,*R*)-**4c**, the angle of Rh−Cl−Rh in (*R*,*R*)-**4b** is larger by ca. 10°. As a result, the Rh···Rh distance in (*R*,*R*)-**4b** (3.511 Å) is significantly longer than that of (*R*,*R*)-**4c** (3.287 Å). The elongation results from weakening the interaction between Rh···Rh with less σ-donating ligand, which is unfavorable for the d_{z^2} orbital of Rh.[14]

Asymmetric 1,4-addition reactions were carried out according to the standard conditions [1.5 mol % [RhCl($C_2H_4)_2]_2$ (3 mol % Rh) with diphosphine for in situ formation of **4**, 2.5 equiv of $PhB(OH)_2$ (**7a**) for 2-cyclohexenone (**6a**) with KOH in dioxane/H_2O, at 35 °C for 3 h][8] (Table 2). Although (*R*)-**1a** was found to be less effective,[15] (*R*)-**1b** provided the successful result comparable to that using (*R*)-BINAP[8] in both yield and % ee of (*R*)-**8aa** (entry 1 vs 3 vs 11). Under milder conditions [1.05 equiv of $PhB(OH)_2$ at 20 °C], (*R*)-**1b** still gave 99% enantioselectivity with a yield much higher than that in the case of (*R*)-BINAP (entry 4 vs 12).[16] The result is attributed to the electronic effect of the ligand, because the reaction using (*R*)-MeO-BIPHEP, which bears same backbone as **1**, gave a result similar to that using (*R*)-BINAP (entry 9).

Table 2. Rh-Catalyzed Asymmetric 1,4-Addition



6a **7a** (*R*)-**8aa**

entry	(*R*)-L*	Rh (%)	solvent	temp (°C)	time (h)	yield (%)[f]	ee (%)
1[a]	**1a**	3.0	dioxane	35	3	10	97
2[b]	**1a**	3.0	toluene	20	3	86	96
3[a]	**1b**	3.0	dioxane	35	3	98	>99
4[a]	**1b**	3.0	dioxane	20	5	68	99
5[b]	**1b**	3.0	toluene	20	3	99	>99
6[c]	**1b**	3.0	toluene	20	3	52	>99
7[d]	**1b**	0.2	toluene	20	1	98	>99
8[d]	**1b**	0.1	toluene	20	1	75	>99
9[a]	BIPHEP[e]	3.0	dioxane	20	5	39	99
10[b]	BIPHEP[e]	3.0	toluene	20	3	0	
11[a]	BINAP	3.0	dioxane	35	3	94	99
12[a]	BINAP	3.0	dioxane	20	5	30	97
13[b]	BINAP	3.0	toluene	20	3	0	

[a] 30% KOH. [b] 50% KOH. [c] Without KOH. [d] 20% KOH. [e] MeO-BIPHEP. [f] Isolated yield.

The catalytic activities of **1a** and **1b** were dramatically improved by changing the solvent to toluene (entries 2 and 5). In particular, (*R*)-**1b** increased the rate of reaction, where the amount of Rh could be reduced to 0.2 mol % without loss of yield under the mild conditions for 1 h (entry 7). The turnover frequency (TOF) reaches 750 h^{-1} (entry 8). Although the TOF value did not come close to the best result on the same reaction,[17] it is worthy of attention that our catalytic system achieves both high catalytic activity[18] and almost complete enantioselectivity by using stoichiometric $PhB(OH)_2$ at room temperature.[19] In contrast, the catalysts with (*R*)-BINAP or (*R*)-MeO-BIPHEP showed no catalytic activity in toluene (entries 10 and 13). Although conversion

(10) Atherton, M. J.; Coleman, K. S.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Karacar, A.; Peck, L. A.; Saunders, G. C. *J. Chem. Soc., Dalton Trans.* **1995**, 4029.

(11) Clarke, M. L.; Heydt, M. *Organometallics* **2005**, *24*, 6475.

(12) Chen, Q.; Lin, B.-L.; Fu, Y.; Liu, L.; Guo, Q.-X. *Res. Chem. Intermed.* **2005**, *31*, 759.

(13) Bunten, K. A.; Farrar, D. H.; Poe, A. J.; Lough, A. *Organometallics* **2002**, *21*, 3344.

(14) Aullón, G.; Ujaque, G.; Lledós, A.; Alvarez, S.; Alemany, P. *Inorg. Chem.* **1998**, *37*, 804–813.

(15) The low catalytic activity of the Rh-**1a** catalyst can perhaps be attributed to a steric effect of the 2,6-position of the fluorine atom in the Ar group: Clarke, M. L.; Ellis, D.; Mason, K. L.; Orpen, A. G.; Pringle, P. G.; Wingad, R. L.; Zaher, D. A.; Baker, R. T. *Dalton Trans.* **2005**, *7*, 1294.

(16) The result that the electron-poor ligand is superior to BINAP is consistent with those of Rh-catalyzed 1,4-addition to other α,β-unsaturated substrates by using Difluorophos. (a) Navarre, L.; Martinez, R.; Genet, J.-P.; Darses, S. *J. Am. Chem. Soc.* **2008**, *130*, 6159. (b) Sibi, M. P.; Tatamidani, H.; Patil, K. *Org. Lett.* **2005**, *7*, 2571.

(17) Hayashi et al. reported that the reaction using 0.05 mol % of the Rh catalyst and 1.2 equiv of **7a** at 30 °C for 1 h gave 95% of product with 96% ee (TOF = 1900 h^{-1}) and the use of $(PhBO)_3$ instead of **7a** gave a TOF value of 14000 h^{-1}. Minnaard and Feringa et al. reported that the reaction using 0.05 mol % of the Rh catalyst and 3 equiv of **7a** at 80 °C for 2 h gave 100% of product with >98% ee (TOF = 1000 h^{-1}). (a) Chen, F.-X.; Kina, A.; Hayashi, T. *Org. Lett.* **2006**, *8*, 341. (b) Boiteau, J.-G.; Minnaard, A. J.; Feringa, B. L. *J. Org. Chem.* **2003**, *68*, 9481.

(18) Except for the prominent results in ref 17, the TOF values of most catalytic systems are less than 100 in Rh-catalyzed asymmetric 1,4-addion of $PhB(OH)_2$ to 1,2-cyclohexenone.

(19) The same reaction as shown in Table 2 at room temperature (20−25 °C). (a) Lukin, K.; Zhang, Q.; Leanna, M. R. *J. Org. Chem.* **2009**, *74*, 929. (b) Mariz, R.; Luan, X.; Gatti, M.; Linden, A.; Dorta, R. *J. Am. Chem. Soc.* **2008**, *130*, 2172. (c) Okamoto, K.; Hayashi, T.; Rawal, V. H. *Org. Lett.* **2008**, *10*, 4387. (d) Gendrineau, T.; Chuzel, O.; Eijsberg, H.; Genet, J.-P.; Darses, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 7669. (e) Feng, C.-G.; Wang, Z.-Q.; Shao, C.; Xu, M.-H.; Lin, G.-Q. *Org. Lett.* **2008**, *10*, 4101. (f) Noël, T.; Vandyck, K.; Eycken, J. V. *Tetrahedron* **2007**, *63*, 12961. (g) Monti, C.; Gennari, C.; Piarulli, U. *Chem. Eur. J.* **2007**, *13*, 1547. (h) Kurihara, K.; Sugishita, N.; Oshita, K.; Piao, D.; Yamamoto, Y.; Miyaura, N. *J. Organomet. Chem.* **2007**, *692*, 428. (i) Berthon-Gelloz, G.; Hayashi, T. *J. Org. Chem.* **2006**, *71*, 8957. (j) Martina, S. L. X.; Minnaard, A. J.; Hessen, B.; Feringa, B. L. *Tetrahedron Lett.* **2005**, *46*, 7159. (k) Defieber, C.; Paquin, J.-F.; Serna, S.; Carreira, E. M. *Org. Lett.* **2004**, *6*, 3873. (l) Hayashi, T.; Ueyama, K.; Tokunaga, N.; Yoshida, K. *J. Am. Chem. Soc.* **2003**, *125*, 11508.

of both (*R*,*R*)-**4b** and (*R*,*R*)-**4c** to the active species of [RhOH(diphosphine)]$_2$ (**9**)[8] by KOH in dioxane for 1 h was observed by ^{31}P NMR (Supporting Information), these complexes **4** were not transformed at all when toluene was used as the solvent (Figure 2a,b for **4b**). Surprisingly,

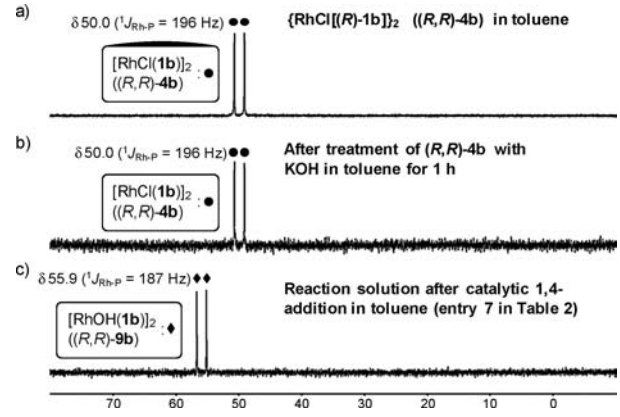


Figure 2. ^{31}P NMR of Rh complexes in toluene.

precursor **4b** itself showed the catalytic activity without KOH to give (*R*)-**8aa** in a moderate yield (entry 6).[20] Therefore, (*R*,*R*)-**4b** undergoes transmetalation with **7a** directly in consequence of the strong π-acceptor ability of **1b** (Figure 3), while BINAP does not have such activity. At the end of

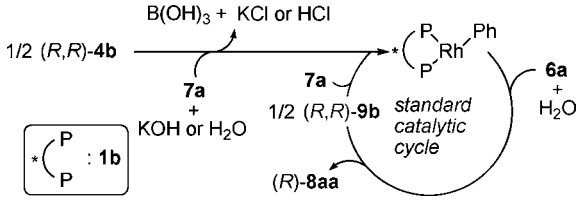
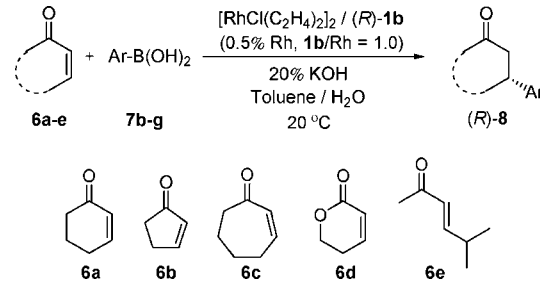


Figure 3. Plausible mechanism using (*R*,*R*)-**4b** in toluene.

the reaction of entry 6 or 7, the resulting Rh complex was {RhOH[(*R*)-**1b**]}$_2$ [(*R*,*R*)-**9b**], and **4b** could not be observed by ^{31}P NMR (Figure 2c). The result suggested that **9b** acts as the active species after the second catalytic cycle just as in the standard Rh-catalyzed 1,4-addition.[8] In toluene, KOH serves to accelerate the transmetalation of **7a**.[20]

The Rh catalyst with **1b** is effective for other substrates. The reactions using 0.5% Rh were successfully applied to a variety of arylboronic acids **7**, and cyclic and acyclic enones **6** to give good yields and enantioselectivities (Table. 3).

Table 3. Rh-Catalyzed Asymmetric 1,4-Addition



entry	**6**	Ar of boronic acid (**7**)	time (h)	yield (%)	*ee* (%)
1	**6a**	3-MeC_6H_4 (**7b**) (1.05 equiv)	0.5	92	>99
2	**6a**	4-MeC_6H_4 (**7c**) (1.05 equiv)	0.5	92	99
3	**6a**	3-MeOC_6H_4 (**7d**) (1.05 equiv)	1.0	94	99
4[a]	**6a**	3-FC_6H_4 (**7e**) (1.05 equiv)	0.5	85	>99
5[a]	**6a**	3-FC_6H_4 (**7e**) (1.20 equiv)	0.5	97	>99
6	**6a**	4-FC_6H_4 (**7f**) (1.20 equiv)	0.5	89	>99
7	**6a**	4-$CF_3C_6H_4$ (**7g**) (1.05 equiv)	0.5	86	>99
8	**6b**	Ph (**7a**) (1.05 equiv)	0.5	96	90
9	**6c**	Ph (**7a**) (1.50 equiv)	3.0	31	98
10[b]	**6c**	Ph (**7a**) (1.50 equiv)	3.0	96	98
11	**6d**	4-$CF_3C_6H_4$ (**7g**) (1.05 equiv)	1.0	90	>99
12	**6e**	Ph (**7a**) (1.30 equiv)	0.5	99	99

[a] 40% of KOH. [b] At 30 °C.

In conclusion, we have succeeded to develop novel and highly electron-poor chiral diphosphine ligands **1**. The strong π-acceptor ability of **1b** was found to greatly improve the catalytic activity for Rh-catalyzed 1,4-addition at room temperature. The utility of **1b** is especially promising for other asymmetric catalytic reactions that can be accelerated by π-acceptor ligands.

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Supporting Information Available: Experimental details, NMR data, figure of CV, Ortep drawing of (*R*,*R*)-**4b**, and CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) The [RhCl(cod)]$_2$ complex without KOH showed no catalytic activity at low temperature. Itooka, R.; Iguchi, Y.; Miyaura, N. *J. Org. Chem.* **2003**, *68*, 6000.