DOI: 10.1002/chem.201001160

Cobalt-Catalyzed Addition Reaction of Organoboronic Acids with Aldehydes: Highly Enantioselective Synthesis of Diarylmethanols

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Transition-metal-catalyzed addition of organometallic reagents to aldehydes is a key method for the synthesis of substituted secondary alcohols.[1] Various organometallic reagents, such as organomagnesium,[2] -zinc,[1,12e–i] -lithium,[3] -silane,[4] -stannane[5] and -boron,[6] have been used in these addition reactions. Among them, organoboron reagents have gained much attention due to the advantages of air and moisture stability, low toxicity, and availability. Rhodium,[1c,7] palladium,[8] platinum,[9a] and nickel[9b,c] complexes efficiently catalyzed the addition reaction of organoboronic acids to aldehydes. Recently, copper- and iron-catalyzed addition reaction of organoboronic acid with aldehydes were also reported.[10] However, the scope of aldehydes in these two addition reactions is rather limited. Only aromatic aldehydes with an electron-withdrawing substituent worked well.[10]

Despite the fact that various metal-catalyzed addition reactions of organoboronic acids with aldehydes are available in the literature,[6–10] only a few reports on asymmetric reactions were discussed.[3a,b,11] In 2006, Zhou et al. reported a rhodium-catalyzed enantioselective addition reaction of aromatic boronic acids with aromatic aldehydes.[11a] In the reaction, enantiomeric excess (*ee*) values of 62–87% for chiral biaryl methanols were observed. Recently, Miyaura and coworkers reported a ruthenium-catalyzed enantioselective addition reaction of aromatic boronic acids with aromatic aldehydes. In the reaction, the expected chiral biarylmethanols were observed in excellent enantiomeric excess.[11b] However, in these reactions specially designed chiral ligands and expensive ruthenium or rhodium catalysts were used. Chiral secondary alcohols are key structural units present in various biologically and pharmaceutically active compounds.[12a–h] The development of new, mild, and convenient methods using a low-cost catalyst for the synthesis of chiral secondary alcohols remains highly attractive.[12]Recently, we have reported a cobalt-catalyzed hydroarylation of alkynes with organoboronic acids[13] and other cobalt-catalyzed reactions.[14] Our continuing interest in developing new reactions using less expensive cobalt complexes as catalysts prompted us to investigate the addition of organoboronic acids with aldehydes and the enantioselective version of this reaction. Herein, we wish to show that cobalt complexes very efficiently catalyze this addition reaction to give diarylmethanols in excellent yields and *ee* values.

Treatment of phenylboronic acid (**1a**) with 4-cyanobenzaldehyde (**2a**) in the presence of $Co(acac)_2$ (5 mol%), 1,2-bis(diphenylphosphino)ethane (dppe; 5 mol%) in THF/CH_3CN (1/1) at 80°C for 12 h gave addition product **3aa** in 96% isolated yield (Table 1, entry 1). In the present reaction, no extra base was required and only 1.2 mmol of boronic acid was used.[13] The use of binary solvent system THF/CH_3CN (1:1) appears to improve the yield of product **3aa**. If the catalytic reaction was carried out in THF, product **3aa** was observed only in 75% yield along with benzene, the protodeboronation product of **1a**, in 18% yield. The catalytic reaction also worked equally well using CoI_2 or $CoCl_2$ (5 mol%), dppe (5 mol%) as the catalyst, and THF as solvent to afford **3aa** in 96–97% yield, but base (K_2CO_3 (1.50 equiv)) was needed to activate the boronic acid.

Under similar reaction conditions, a variety of substituted aromatic aldehydes, heterocyclic aldehydes, and aliphatic aldehydes were examined with phenylboronic acid (**1a**) (Table 1). Thus, benzaldehydes with electron-withdrawing groups, such as 4-NO_2 (**2b**), 4-CHO (**2c**), 4-CO_2Me (**2d**), and 4-CF_3 (**2e**) provided diarylmethanols **3ab**–**3ae** in excellent yields (89–97%; Table 1, entries 2–5). For these substrates, only the CHO group participated in the reaction, the other functional groups remained essentially intact. The reaction of dialdehyde **2c** with **1a** also proceeds selectively at one of the CHO groups. Halo-substituted benzaldehyde derivatives are compatible with the present catalytic reac-

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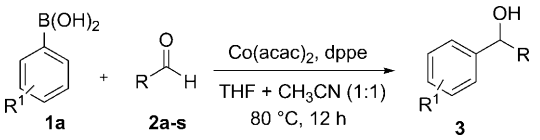
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001160.

Table 1. Results of the addition reaction of arylboronic acid with various aldehydes.[a]



Entry	Substrates	Product	Yield[b] [%]
1	**1a**: R^1=H; **2a**: R=4-CN-C_6H_4	**3aa**	96
2	**1a**: R^1=H; **2b**: R=4-NO_2-C_6H_4	**3ab**	97
3	**1a**: R^1=H; **2c**: R=4-CHO-C_6H_4	**3ac**	93
4	**1a**: R^1=H; **2d**: R=4-CO_2Me-C_6H_4	**3ad**	98
5	**1a**: R^1=H; **2e**: R=4-CF_3-C_6H_4	**3ae**	89
6	**1a**: R^1=H; **2f**: R=4-F-C_6H_4	**3af**	92
7	**1a**: R^1=H; **2g**: R=3-F-C_6H_4	**3ag**	82
8	**1a**: R^1=H; **2h**: R=2-F-C_6H_4	**3ah**	80
9	**1a**: R^1=H; **2i**: R=4-Cl-C_6H_4	**3ai**	96
10	**1a**: R^1=H; **2j**: R=4-Br-C_6H_4	**3aj**	84
11	**1a**: R^1=H; **2k**: R=Ph	**3ak**	73
12	**1a**: R^1=H; **2l**: R=1-napthyl	**3al**	75
13	**1a**: R^1=H; **2m**: R=2-napthyl	**3am**	75
14	**1a**: R^1=H; **2n**: R=4-Me-C_6H_4	**3an**	67
15	**1a**: R^1=H; **2o**: R=4-OMe-C_6H_4	**3ao**	57
16	**1a**: R^1=H; **2p**: R=4-pyridinyl	**3ap**	76
17	**1a**: R^1=H; **2q**: R=2-furyl	**3aq**	69
18	**1a**: R^1=H; **2r**: R=2-thienyl	**3ar**	78
19	**1a**: R^1=H; **2s**: R=cyclohexyl	**3as**	79
20	**1b**: R^1=4-Br; **2d**: R=4-CO_2Me-C_6H_4	**3bd**	93
21	**1c**: R^1=4-F; **2d**: R=4-CO_2Me-C_6H_4	**3cd**	93
22	**1d**: R^1=4-CHO; **2d**: R=4-CO_2Me-C_6H_4	**3dd**	84
23	**1e**: R^1=4-Me; **2d**: R=4-CO_2Me-C_6H_4	**3ed**	92
24	**1f**: R^1=4-OMe; **2d**: R=4-CO_2Me-C_6H_4	**3fd**	97
25	**1g**: R^1=2-OMe; **2d**: R=4-CO_2Me-C_6H_4	**3gd**	96
26	**1h**: R^1=4-vinyl; **2d**: R=4-CO_2Me-C_6H_4	**3hd**	75
27	**1i**: (*E*)-styryl; **2d**: R=4-CO_2Me-C_6H_4	**3id**	78

[a] Unless otherwise mentioned, all of the reactions were carried out by using arylboronic acid **1** (1.20 mmol), aldehydes **2** (1.00 mmol), $Co(acac)_2$ (5 mol%), dppe (5 mol%), and THF/CH_3CN (1:1) at 80°C for 12 h. [b] Isolated yields.

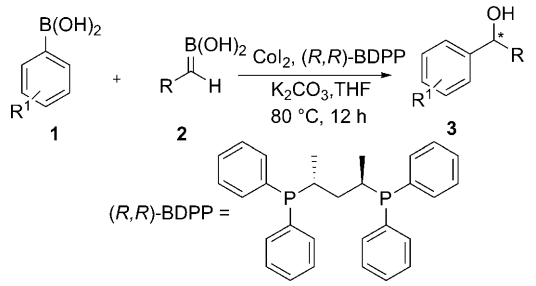
tion.[15] For example, 4-F (**2f**), 3-F (**2g**), 2-F (**2h**), 4-Cl (**2i**), and 4-Br (**2j**) also reacted efficiently with **1a** to give the corresponding diarylmethanols **3af**–**3aj** in good to excellent yields (Table 1, entries 6–10). Similarly, benzaldehyde (**2k**), 1-napthaldehyde (**2l**) and 2-napthaldehyde (**2m**) underwent addition reaction with **1a** to afford products **3ak**–**3am** in good yields (Table 1, entries 11–13). Benzaldehydes containing electron-donating groups, such as 4-Me (**2n**) and 4-OMe (**2o**) also gave addition products **3an** and **3ao** albeit in moderate yields (Table 1, entries 14 and 15). Heterocyclic aldehydes, including 4-formylpyridine (**2p**), 2-formylfuran (**2q**), and 2-formylthiophene (**2r**) also reacted efficiently to give addition products **3ap**–**3ar** in 76, 69, and 78% yields, respectively (Table 1, entries 16–18). Aliphatic aldehyde, cyclohexanecarbaldehyde (**2s**), also effectively participated in the addition reaction affording product **3as** in 79% yield (Table 1, entry 19).

To further explore the scope of the addition reaction, various substituted organoboronic acids were examined with methyl 4-formyl benzoate (**2d**). 4-Bromo- (**1b**), 4-fluoro- (**1c**), 4-formyl- (**1d**), 4-methyl- (**1e**), 4-methoxy- (**1f**), 2-methoxy- (**1g**) and 4-vinylphenylboronic (**1h**) acids all reacted effectively with **2d** to furnish substituted diarylmethanols **3bd**–**3hd** in 93, 93, 84, 92, 97, 96, and 75% yield, respectively (Table 1, entries 20–26). These results clearly indicate that the present addition reaction shows excellent tolerance towards Br, F, CHO, Me, and OMe functional groups. The catalytic reaction also worked very well with alkenylboronic acid. Thus, (*E*)-1-phenylvinyl boronic acid (**1i**) reacted with **2d** to afford allylic alcohol **3id** in 78% yield (Table 1, entry 27).

The great importance of chiral secondary alcohols in organic synthesis prompted us to explore the enantioselective addition of organoboronic acids with aldehydes. Phenylboronic acid (**1a**) and **2d** were used as the model substrates in this study. Cobalt catalyst CoI_2 (5 mol%), a bidentate chiral ligand (5 mol%), and K_2CO_3 (1.5 equiv) in THF were used in the reaction. Various bidentate chiral ligands, including (*R*)-Prophos, (*R*)-Tol-BINAP, (*S*)-BINAP, (*S*,*S*)-Chiraphos, (*S*)-BINOL, (*R*,*R*)-Ph-BPE, (*R*)-Quinap, (*R*)-MOP, (*S*,*S*)-DIPAMP, (*R*)-Monophos, (*R*,*R*)-BDPP, and (*S*,*S*)-DIOP, were examined (for the structure of chiral ligands and detailed optimization studies, see the Supporting Information). Among them, (*R*,*R*)-BDPP is most effective, affording (*S*)-diarylmethanol **3ad** in 98% yield with an *ee* value of 94% (Table 2, entry 3).[11] Other ligands provided **3ad** in 44–86% yields with an *ee* value of 10–67%. Under the reaction conditions, (*S*,*S*)-BDPP provided the other enantiomer (*R*)-diarylmethanol **3ad** in 95% yield with an *ee* of 93% (Table 2, entry 4). Another cobalt catalyst, $Co(acac)_2$/(*R*,*R*)-BDPP, in THF without base is also effective, giving chiral (*S*)-**3ad** in 92% yield and 89% *ee*.

In the presence of CoI_2 (5 mol%)/(*R*,*R*)-BDPP (5 mol%) and K_2CO_3 (1.5 equiv) in THF, the reaction of various substituted aldehydes with phenylboronic acid (**1a**) were then examined (Table 2). Electron-withdrawing groups, 4-CN- (**2a**), 4-NO_2- (**2b**), 4-CO_2Me- (**2d**), and 4-CF_3-substituted (**2e**) benzaldehydes afforded chiral (*S*)-diarylmethanols **3aa**, **3ab**, **3ad**, and **3ae** in excellent 97, 95, 98, and 97% yield with 92, 93, 94 and 92% *ee*, respectively (Table 2, entries 1–3, 5). As expected, if CoI_2/(*S*,*S*)-BDPP was employed as the catalyst, the reaction of **1a** with **2d** afforded the corresponding (*R*)-**3ad** in 93% *ee* (Table 2, entry 4). Similarly, by using CoI_2/(*R*,*R*)-BDPP as the catalyst, 4-F- (**2f**), 4-Cl- (**2i**), and 4-Br-substituted (**2j**) benzaldehydes provided (*S*)-diarylmethanols **3af**, **3ai**, and **3aj** in excellent 95–97% yield with 99, 93, and 96% *ee*, respectively (Table 2, entries 6–8). Likewise, 1-naphth- (**2l**) and 2-naphthaldehyde (**2m**), 4-methyl (**2n**), 4-methoxybenzaldehyde (**2o**), and 2-formylthiophene (**2r**) gave (*S*)-diarylmethanols **3al**, **3am**, **3an**, **3ao**, and **3ar**, respectively, in 77–90% yield with 86–93% *ee* (Table 2, entries 9–13). A 2-naphthyl and 2-thienyl group on the aldehyde substrate appears to lower the *ee* value slightly compared with other aryl groups used. In a similar manner, cyclohexanecarbaldehyde (**2s**) yielded (*R*)-**3as** in 84% yield with 97% *ee* (Table 2, entry 14). It is interesting to note that in the present chiral addition reaction with base, even electron-rich-substituted, heteroaromatic and aliphatic aldehydes provided the corresponding addition products in ex-

Table 2. Results of the enantioselective addition reaction of various phenylboronic acids with substituted aldehydes.[a]



Entry	Substrates		Yield (*ee*) [%][b]
1	**1a**: R^1 = H; **2a**: R = 4-CN-C_6H_4	(*S*)-**3aa**	97 (92)
2	**1a**: R^1 = H; **2b**: R = 4-NO_2-C_6H_4	(*S*)-**3ab**	95 (93)
3	**1a**: R^1 = H; **2d**: R = 4-CO_2Me-C_6H_4	(*S*)-**3ad**	98 (94)
4	**1a**: R^1 = H; **2d**: R = 4-CO_2Me-C_6H_4	(*R*)-**3ad**	95[c] (93)
5	**1a**: R^1 = H; **2e**: R = 4-CF_3-C_6H_4	(*S*)-**3ae**	97 (92)
6	**1a**: R^1 = H; **2f**: R = 4-F-C_6H_4	(*S*)-**3af**	95 (99)
7	**1a**: R^1 = H; **2i**: R = 4-Cl-C_6H_4	(*S*)-**3ai**	97 (93)
8	**1a**: R^1 = H; **2j**: R = 4-Br-C_6H_4	(*S*)-**3aj**	97 (96)
9	**1a**: R^1 = H; **2l**: R = 1-napthyl	(*S*)-**3al**	77 (89)
10	**1a**: R^1 = H; **2m**: R = 2-napthyl	(*S*)-**3am**	89 (92)
11	**1a**: R^1 = H; **2n**: R = 4-Me-C_6H_4	(*S*)-**3an**	90 (93)
12	**1a**: R^1 = H; **2o**: R = 4-OMe-C_6H_4	(*S*)-**3ao**	85 (92)
13	**1a**: R^1 = H; **2r**: R = 2-thienyl	(*S*)-**3ar**	82 (86)
14	**1a**: R^1 = H; **2s**: R = cyclohexyl	(*R*)-**3as**	84 (97)
15	**1b**: R^1 = 4-Br; **2d**: R = 4-CO_2Me-C_6H_4	(+)-**3bd**	99 (90)
16	**1b**: R^1 = 4-Br; **2k**: R = Ph	(*R*)-**3bk** (*R*)-**3aj**	84 (94)
17	**1e**: R^1 = 4-Me; **2k**: R = Ph	(*R*)-**3ek** (*R*)-**3an**	91 (95)
18	**1f**: R^1 = 4-OMe; **2k**: R = Ph	(*R*)-**3fk** (*R*)-**3ao**	93 (94)
19	**1e**: R^1 = 4-Me; **2d**: R = 4-CO_2Me-C_6H_4	(+)-**3ed**	95 (91)
20	**1f**: R^1 = 4-OMe; **2d**: R = 4-CO_2Me-C_6H_4	(+)-**3fd**	97 (94)
21	**1g**: R^1 = 2-OMe; **2d**: R = 4-CO_2Me-C_6H_4	(+)-**3gd**	92 (90)

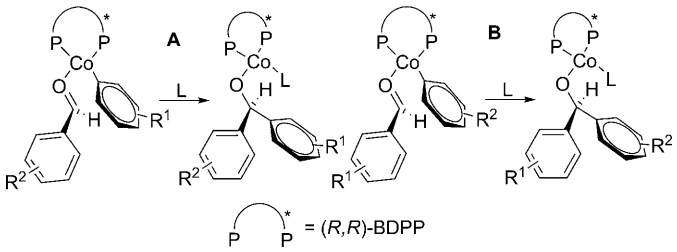
[a] Unless otherwise mentioned, all of the reactions were carried out by using organoboronic acid **1** (1.50 mmol), aldehydes **2** (1.00 mmol), CoI_2 (5 mol%)/(*R*,*R*)-BDPP (5 mol%), K_2CO_3 (1.5 equiv), and THF (2.0 mL) at 80 °C for 12 h. [b] Isolated yields. [c] (*S*,*S*)-BDPP was used.

cellent yields in contrast to the results using $Co(acac)_2$/dppe because the catalyst gave only moderate to good yields.

The present asymmetric catalytic reaction can be extended successfully to other arylboronic acids. Under similar reaction conditions, using CoI_2/(*R*,*R*)-BDPP as the catalyst, the reaction of 4-bromophenylboronic acid (**1b**) and benzaldehyde (**2k**) gave (*R*)-**3bk** in 84% yield with 94% *ee* (Table 2, entry 16). It is noteworthy that (*R*)-**3bk** is the enantiomer of (*S*)-**3aj** (Table 2, entry 8) prepared from phenylboronic acid (**1a**) and 4-bromobenzaldehyde (**2j**) using the same chiral CoI_2/(*R*,*R*)-BDPP catalyst. In a similar manner, product (*R*)-**3ek** (Table 2, entry 17) is enantiomer of (*S*)-**3an** (Table 2, entry 11) and (*R*)-**3fk** (Table 2, entry 18) is the enantiomer of (*S*)-**3ao** (Table 2, entry 12). Thus, the present catalytic asymmetric addition reaction provides a versatile method to prepare the two enantiomers by using the same chiral catalyst. Moreover, in the present asymmetric reaction, products (*S*)-**3ai** and (*R*)-**3ek** are known to be the key intermediates for biologically active compounds (*S*)-cetirizine and (*R*)-neobenodine, respectively.[12e,f]

In addition, other substituted phenylboronic acids, including 4-bromo- (**1b**), 4-methyl- (**1e**), 4-methoxy- (**1f**), and 2-methoxyphenylboronic **1g** acids, also reacted smoothly with 4-CO_2Me-substituted benzaldehyde **2d** to give diarylmethanols **3bd**, **3ed**, **3fd**, and **3gd** in excellent yields (92–99%) and *ee* values (90–94%), respectively (Table 2, entries 15, 19–21).

It is interesting to note that for the present CoI_2/(*R*,*R*)-BDPP-catalyzed asymmetric addition of phenylboronic acid to various substituted benzaldehydes, only the *S* products were obtained (Table 2, entries 1–13). These results may be explained by the proposed reaction model, **A**, in Scheme 1,



Scheme 1. Proposed addition of an aryl boronic acid to aldehyde catalyzed by CoI_2/(*R*,*R*)-BDPP. Note that enantiomers were obtained from **A** and **B**.

although the exact structure of the cobalt intermediate is not known. The chiral (*R*,*R*)-BDPP ligand appears to control efficiently the relative three-dimensional position of the coordinated phenyl and substituted benzaldehyde. As a result, the coordinated aryl group adds to the aldehyde group from its *si* face leading to the formation of *S* product. If the phenyl group on the boronic acid and aryl group of the aldehyde exchange positions (model **B**), *R* products will be obtained (Table 2, entries 16–18). It is interesting to note that this method provides an alternative to prepare an *R* and *S* enantiomeric pair by using the same chiral ligand. Based on these reaction models, we expect that (+)-**3bd**, (+)-**3fd**, and (+)-**3gd** should have *R* configuration, whereas (+)**3ed** should be an *S* product.

In conclusion, we have demonstrated, for the first time, a cobalt-catalyzed racemic and enantioselective addition of organoboronic acids with aldehydes to give biologically useful, substituted secondary alcohols in excellent yields and enantiomeric excess. In the chiral reaction, highly stable, less expensive CoI_2 catalyst, and commercially available chiral ligand (*R*,*R*)-BDPP were used. A wide scope of organoboronic acids and aldehydes are compatible with this catalytic reaction. Further detailed investigation on the mechanism and the application of this methodology in natural product synthesis are in progress.

Experimental Section

General procedure for the asymmetric arylation of aldehyde: A 10 mL sealed tube containing CoI_2 (0.050 mmol, 5.0 mol%), (*R*,*R*)-BDPP (0.050 mmol, 5.0 mol%), K_2CO_3 (1.5 equiv), **2d** (1.00 mmol) and phenylboronic acid (**1a**) (1.50 mmol) was evacuated and purged with nitrogen gas three times. Then freshly distilled THF (2.0 mL) was added to the system and the reaction mixture was stirred at 80 °C for 12 h. The reaction mixture was filtered through a short Celite and silica gel pad and washed with 3:1 mixture of hexane and ethyl acetate several times. The combined filtrate was concentrated and the residue was purified on a silica gel column using hexane/ethyl acetate as eluent to afford the addition product **3ad**.

Acknowledgements

We thank the National Science Council of Republic of China (NSC 96-2113M-007-020-MY3) for support of this research and we thank Prof. Biing-Jiun Uang for support with chiral HPLC.

Keywords: alcohols · aldehydes · asymmetric synthesis · cobalt · organoboronic acid

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Received: April 30, 2010
Published online: July 2, 2010

