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Cobalt(II)-Catalyzed 1,4-Addition of Organoboronic Acids to Activated Alkenes: An Application to Highly *cis*-Stereoselective Synthesis of Aminoindane Carboxylic Acid Derivatives

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Transition-metal-catalyzed 1,4-addition of organometallic reagents to activated alkenes is a useful method for the efficient construction of carbon–carbon bonds in organic synthesis.[1] A wide range of organometallic reagents has been commonly employed for this reaction.[2–6] Among these, organoboron reagents exhibit a multifarious advantage, comprising safe handling, availability, and stability to air and moisture.[7] In this context, the rhodium-[8] and palladium-catalyzed[9] 1,4-addition of organoboron reagents to alkenes has received much attention due to its broad scope and high functional-group tolerance. Particularly, extensive studies have been devoted to rhodium-catalyzed asymmetric reactions.[10] Ruthenium,[11] platinum,[12] and nickel[13] complexes are also known to catalyze the 1,4-addition of organoborons to α,β-unsaturated ketones. Recently, the copper-catalyzed 1,4-addition of organoboronates to alkylidene cyanoacetates and α,β-unsaturated carbonyl compounds was also developed.[14] Despite these important developments, the use of less expensive and more easily handled transition metals with a wide substrate scope for the 1,4-addition reaction remains in demand.

Recently, we reported the efficient nickel-catalyzed additions of organoboronic acids to activated alkenes[15a] and nitriles.[15b] We also described cobalt-catalyzed addition reactions of organoboronic acids to alkynes[15c] and aldehydes.[15d,e] Our ongoing interest in the search for new reactions that involve less expensive nickel and cobalt complexes as the catalysts prompted us to use cobalt complexes in 1,4-addition reactions.[15] Herein, we report that cobalt can catalyze the 1,4-addition of organoboronic acids to activated alkenes, such as vinyl ketones, acrylates, acrylamides, and acrylonitrile.[16] In addition, we have also demonstrated a cobalt(II)-catalyzed [3+2] annulation of electron-deficient alkenes with *ortho*-iminophenylboronic acids to synthesize *cis*-1-aminoindane-2-carboxylic acid derivatives with high diastereoselectivity in good to excellent yields.

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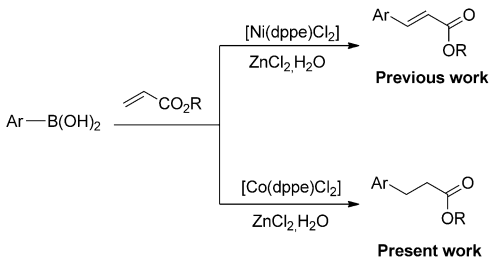
When phenylboronic acid (**1a**; 0.8 mmol) was treated with *n*-butylacrylate (**2a**; 0.4 mmol) and H_2O (0.8 mmol) in a mixture of CH_3CN/THF (3:1) in the presence of [Co(dppe)Cl_2] (5 mol%; dppe = 1,2-bis(diphenylphosphino)ethane) and $ZnCl_2$ (20 mol%) at 80 °C for 12 h, the 1,4-addition product *n*-butyl-3-phenylpropanoate (**3aa**) was obtained in 91% yield. Additionally, benzene, which is a protodeboronation product of **1a**, was also observed. Control experiments revealed that in the absence of either the cobalt complex or $ZnCl_2$ no **3aa** was observed. It is important to mention that in our previously reported nickel-catalyzed addition of boronic acids to alkenes, a Mizoroki–Heck-type product was obtained under similar reaction conditions (Scheme 1).

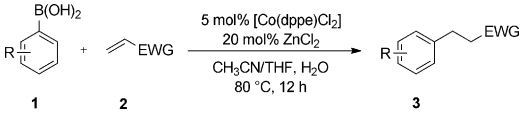


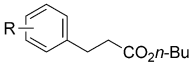
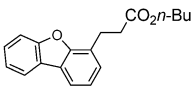
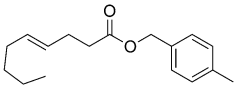
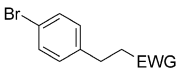
Scheme 1. Nickel- and cobalt-catalyzed 1,4-addition reactions.

To understand the present catalytic conditions, we examined the 1,4-addition reaction of **1a** and **2a** in the presence of various cobalt complexes by using CH_3CN as the solvent. The dppe complex showed higher reactivity than other bidentate phosphine complexes, such as 1,1-bis(diphenylphosphino)methane (dppm), 1,3-bis(diphenylphosphino)propane (dppp), and 1,4-bis(diphenylphosphino)butane (dppb). Particularly, [Co(dppe)Cl_2] and [Co(dppe)I_2] were active and gave **3aa** in 73 and 41% yield, respectively. The monodentate phosphine complex [Co(PPh_3)$_2Cl_2$]/3PPh_3 and the bidentate nitrogen–cobalt complex [Co(phen)Cl_2] (phen = 1,10-phenanthroline) were inactive for this 1,4-addition reaction. Next, we examined the effects of additives such as NEt_3, K_2CO_3, and water. Of these, water exhibited the highest activity to give **3aa** in high yield, whereas the other additives were ineffective. It is fascinating to note that in this catalytic reaction, organoboronic acids were activated by water instead of the base. Solvents play a vital role in the

success of the reaction. In particular, a binary solvent system of CH_3CN/THF in a ratio of 3:1 was crucial to obtain **3aa** in 91% yield. Based on these optimization studies, we chose $[Co(dppe)Cl_2]$ (5 mol%), $ZnCl_2$ (20 mol%), and water (0.8 mmol) in CH_3CN/THF (3:1) at 80°C for 12 h as the standard reaction conditions (Table 1).

Table 1. Results of the cobalt-catalyzed 1,4-addition reaction of arylboronic acids **1** with activated alkenes **2**.[a]



	1	2	Product 3		Yield [%][b]
1	**1a**	**2a**		**3aa**: R = H	91 (99)
2	**1b**	**2a**		**3ba**: R = 2-MeO	75[c]
3	**1c**	**2a**		**3ca**: R = 3-MeO	91
4	**1d**	**2a**		**3da**: R = 4-Me	88
5	**1e**	**2a**		**3ea**: R = 3-CHO	82
6	**1f**	**2a**		**3fa**: R = 4-CHO	88
7	**1g**	**2a**		**3ga**: R = 2-CHO	65
8	**1h**	**2a**		**3ha**: R = 3-NO_2	79
9	**1i**	**2a**		**3ia**	86
10	**1j**	**2g**		**3jg**	84
11	**1k**	**2a**		**3ka**: EWG = CO_2nBu	92
12	**1k**	**2b**		**3kb**: EWG = CO_2Me	93
13	**1k**	**2c**		**3kc**: EWG = CO_2Et	92
14	**1k**	**2d**		**3kd**: EWG = CO-NEt_2	76
15	**1k**	**2e**		**3ke**: EWG = CN	81
16	**1k**	**2f**		**3kf**: EWG = COMe	75[d]

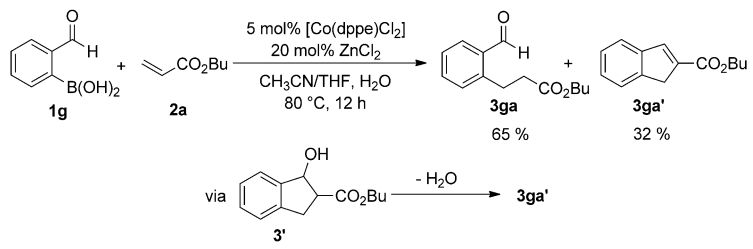
[a] Reactions were carried out by using an arylboronic acid **1** (0.80 mmol), an activated alkene **2** (0.40 mmol), $[Co(dppe)Cl_2]$ (0.020 mmol, 5.0 mol%), $ZnCl_2$ (0.080 mmol, 20.0 mol%), and H_2O (0.80 mmol) in MeCN/THF (3:1; 1.0 mL) at 80°C for 12 h under N_2. [b] Isolated yields; the number in parentheses is the yield determined by ^1H NMR spectroscopy with mesitylene as an internal standard. [c] The reaction was carried out at 90°C. [d] The reaction time was 24 h.

Under the optimized reaction conditions, various substituted arylboronic acids (**1a–k**) were examined (Table 1, Entries 1–11). The treatment of the electron-donating 2-methoxy- and 3-methoxy phenylboronic acids (**1b** and **1c**, respectively) with *n*-butyl acrylate (**2a**) gave the corresponding 1,4-addition products **3ba** and **3ca** in 75 and 91% yield (Table 1, Entries 2 and 3). Similarly, the reaction of *para*-tolyl boronic acid gave **3da** in 88% yield (Table 1, Entry 4). Electron-withdrawing arylboronic acids with a formyl group at the *meta*- or *para*-position tolerated the 1,4-addition reaction, providing the corresponding products **3ea** and **3fa** in impressive yields (Table 1, Entries 5 and 6). On the other hand, *ortho*-formyl phenylboronic acids provided **3ga** in a slightly lower yield of 65%, due to the formation of the indene product **3ga′** by dehydration of the indanol intermediate **3′** (Table 1, Entry 7; see also Scheme 2). Notably, 3-nitro phenylboronic acid underwent the addition reaction to give **3ha** in 79% yield (Table 1, Entry 8). The heteroaromatic boronic acid **1i** also participated in the reaction to furnish **3ia** in 86% yield (Table 1, Entry 9). Alkenyl boronic acids were also compatible in the reaction; (*E*)-1-hexenylboronic acid (**1j**) reacted with **2g** to give **3jg** in 84% yield (Table 1, Entry 10). The *para*-bromo boronic acid **1k** gave **3ka** in excellent yield (Table 1, Entry 11).

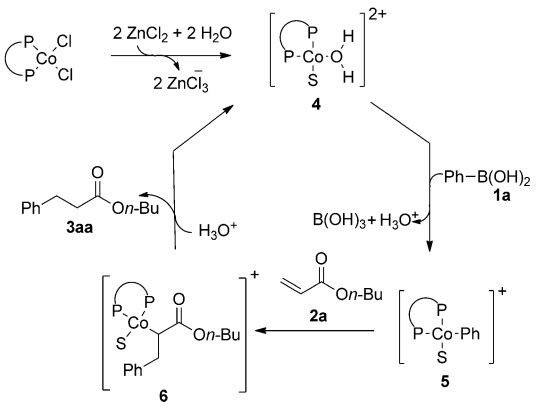
This catalytic reaction was also successfully extended to various activated alkenes (Table 1, Entries 12–16). In addition to *n*-butyl acrylate (**2a**), other acrylates such as methyl acrylate (**2b**) and ethyl acrylate (**2c**) reacted well with **1k** to give **3kb** and **3kc** in excellent yields (Table 1, Entries 12 and 13). In a similar manner, other activated alkenes such as *N,N*-diethyl acrylamide (**2d**), acrylonitrile (**2e**), and methyl vinyl ketone (**2f**) also gave **3kd**, **3ke**, and **3kf** in 76, 81, and 75% yield, respectively (Table 1, Entries 14–16).

The proposed mechanism for the 1,4-addition reaction is shown in Scheme 3. The catalytic reaction is probably initiated by the formation of the Co^{II}·H_2O species **4** through substitution of the coordinated chloride in $[Co(dppe)Cl_2]$ by water and solvent, with the assistance of the Lewis acid $ZnCl_2$. Intermediate **4** then undergoes transmetallation with phenylboronic acid (**1a**) to give the aryl cobalt(II) intermediate **5**. Coordination of *n*-butyl acrylate (**2a**) to the cobalt center and insertion into the cobalt–aryl bond gives the intermediate **6**. Subsequent protonolysis provides the 1,4-addition product **3aa** and the intermediate **4**, which can be used for further catalytic cycles.

The proposed mechanism clearly explains the requirement for a catalytic amount of the Lewis acid $ZnCl_2$ and the role of water in the reaction. Water not only provides the hydroxyl group for the arylboronic acid, but also acts as a proton source for the formation of either the 1,4-addition adduct **3aa** or the protodeboronation product. Furthermore, the observation of deboronation product and the absence of biaryl compounds (ArAr) indicate that the Co^{II} species is not reduced.



Scheme 2. Formation of the indene byproduct **3ga′**.



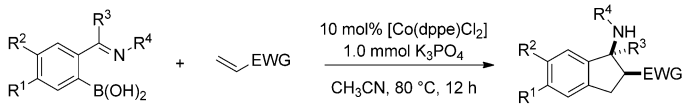
Scheme 3. Proposed mechanism for the cobalt-catalyzed 1,4-addition reaction.

After successfully establishing the 1,4-addition reaction, we applied our methodology to synthesize aminoindanes from *ortho*-iminoarylboronic acids (**7**) and electron-deficient alkenes (**2**). Aminoindanes are valuable intermediates that are found in various biologically active compounds.[17] Previously, metal-catalyzed [3+2]-annulation reactions for the synthesis of indenols[18] and aminoindenes[19] have been successfully demonstrated, but similar reactions for the synthesis of aminoindanes have hardly been studied. In 2006, Takai and co-workers reported a rhenium-catalyzed carbocyclization of imines with acrylates by C–H bond activation that led to the formation of indenes instead of aminoindanes due to facile deamination under the harsh reaction conditions.[20a] Later, by employing allenes as the π-component, they synthesized substituted aminoindanes in high diastereoselectivity.[20b] Recently, Tran and Cramer also reported a rhodium(I)-catalyzed C–H functionalization of unsubstituted ketimines with terminal allenes leading to aminoindanes in a high regio- and diastereoselective manner.[21] These reports, however, required either higher reaction temperatures or an expensive catalyst system. Herein, we present a new and mild cobalt-catalyzed [3+2]-annulation reaction of *ortho*-iminoarylboronic acids with electron-deficient alkenes to give *cis*-1-aminoindane-2-caboxylic acid derivatives in high regio- and diastereoselectivity.

The treatment of *ortho*-iminoarylboronic acid (**7a**) with *tert*-butyl acrylate (**2h**) under a $[Co(dppe)Cl_2]/ZnCl_2/H_2O$ catalytic system afforded the [3+2]-annulation product **8ah** in low yield. To optimize the yield of this [3+2] annulation, the reaction was examined under different cobalt-complex systems (see the Supporting Information). Among these, the use of $[Co(dppe)Cl_2]$ (10 mol%) as the catalyst and K_3PO_4 (1.0 equiv) as the additive in CH_3CN at 80°C was most active, providing *cis*-aminoindane carboxylate ester (**8ah**) in 93% yield with high regio- and diastereoselectivity. The structure of **8ah** was confirmed by its ^1H and ^{13}C NMR spectra and mass data. It was further supported by single-crystal X-ray analysis (see the Supporting Information).[22] Other cobalt catalyst systems, such as $Co(OAc)_2$/dppe and $Co(acac)_2$/dppe in THF/CH_3CN, were also active but gave **8ah** in only 44 and 71% yield, respectively.

To evaluate the scope of the [3+2]-annulation reaction, a variety of *ortho*-iminoarylboronic acids with **2h** was examined (Table 2, Entries 1–7). Thus, *ortho*-iminophenylboronic acids **7b** and **7c**, derived from *para*-methoxy- and *para*-fluoroaniline, provided **8bh** and **8ch** in 94 and 52% yield, respectively (Table 2, Entries 2 and 3). Similarly, other *ortho*-iminoarylboronic acids, such as **7d–f**, participated in the reaction to provide the respective products **8dh–fh** in good yields with high stereoselectivity (Table 2, Entries 3–6). Gratifyingly, *ortho*-ketoiminophenylboronic acid (**7g**) underwent the annulation reaction to give **8gh** in 70% yield (Table 2, Entry 7). To further expand the scope of this protocol, we explored its compatibility with different alkenes (Table 2, Entries 8–14). Similar to the reaction of *tert*-butyl acrylate (**2h**), other acrylates, such as *n*-butyl- (**2a**), methyl- (**2b**), ethyl- (**2c**), and *N*,*N*-diethyl acrylamide (**2d**), underwent the [3+2]-annulation reaction to give the corresponding products in high yields with excellent regio- and diastereoselectivity (Table 2, Entries 8–11). Likewise, **2i–k** also provided **8ai–ak** in 81–96% yield respectively (Table 2, Entries 12–14). It is important to mention that substituted alkenes and cyclic enones did not react togive the 1,4-addition or [3+2]-annulation products (**3** or **8**, respectively) under the standard reaction conditions.

Table 2. Results of the cobalt-catalyzed [3+2] annulation of *o*-iminoarylboronic acids **7** with acrylates **2**.[a]

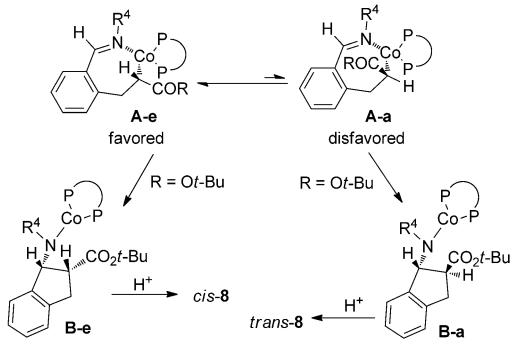


7 2 *cis*-**8**

	R^1	R^2	R^3	R^4	EWG	Yield [%][b]
1	H	H	H	*p*-tolyl (**7a**)	CO_2tBu (**2h**)	93 (**8ah**)
2	H	H	H	4-$MeOC_6H_4$ (**7b**)	CO_2tBu (**2h**)	91 (**8bh**)
3	H	H	H	4-FC_6H_4 (**7c**)	CO_2tBu (**2h**)	52 (**8ch**)
4	H	H	H	Me (**7d**)	CO_2tBu (**2h**)	87 (**8dh**)
5	H	H	H	*n*-butyl (**7e**)	CO_2tBu (**2h**)	74 (**8eh**)
6	-O-CH_2-O-		H	*p*-tolyl (**7f**)	CO_2tBu (**2h**)	69 (**8fh**)
7	H	H	Me	4-$MeOC_6H_4$ (**7g**)	CO_2tBu (**2h**)	70 (**8gh**)
8	H	H	H	*p*-tolyl (**7a**)	CO_2nBu (**2a**)	95 (**8aa**)
9	H	H	H	*p*-tolyl (**7a**)	CO_2Me (**2b**)	85 (**8ab**)
10	H	H	H	*p*-tolyl (**7a**)	CO_2Et (**2c**)	92 (**8ac**)
11	H	H	H	*p*-tolyl (**7a**)	$CONEt_2$ (**2d**)	59 (**8ad**)
12	H	H	H	*p*-tolyl (**7a**)	CO_2Cy (**2i**)	94 (**8ai**)
13	H	H	H	*p*-tolyl (**7a**)	CO_2-2-naphthyl (**2j**)	81 (**8aj**)
14	H	H	H	*p*-tolyl (**7a**)	CO_2-PMB[c] (**2k**)	96 (**8ak**)

[a] Reactions were carried out by using an *ortho*-iminoarylboronic acid **7** (0.30 mmol), an activated alkene **2** (0.20 mmol), $[Co(dppe)Cl_2]$ (0.020 mmol, 10.0 mol%), K_3PO_4 (0.20 mmol, 1.0 equiv) in MeCN (2.0 mL) at 80°C for 12 h under N_2. [b] Isolated yields. [c] PMB = *para*-methoxybenzyl.

The diastereochemical outcome of this [3+2]-annulation reaction, which produces exclusively the *cis*-**8** rather than *trans*-**8** product, can be predicted on the basis of the model shown in Scheme 4, involving *ortho*-iminoarylboronic acid



Scheme 4. Proposed stereochemical model for the cobalt-catalyzed [3+2]-annulation reaction.

(**7**) and acrylate (**2h**) as the substrates. The 1,4-addition reaction of **7** with **2a** in the presence of $[Co(dppe)Cl_2]$ is expected to give the seven-membered intermediate **A**, of which there are two conformers: **A-e** with the ester group (COOR) at the equatorial position, and **A-a** with the ester group located at the axial position. Conformer **A-e** is much more favorable than **A-a** because the latter will encounter the strong non-bonding interaction of the ester group with the aromatic rings of the imine moiety, the dppe ligand, and others. Further intramolecular addition of the carbon–cobalt bond to the C=N double bond in **A-e** and **A-a** is expected to give *cis*-**8** and *trans*-**8**, respectively. The formation of **A-a** is much less favorable, thus we observed only the *cis* [3+2]-addition products in this type of reaction.

In summary, we have successfully demonstrated a cobalt-catalyzed 1,4-addition reaction of organoboronic acids to activated alkenes. Various types of activated alkenes, including acrylates, acrylonitrile, acrylamide, and enones, were compatible with this reaction. Furthermore, a [3+2]-annulation reaction to synthesize various *cis*-aminoindane carboxylic acid derivatives was also demonstrated. The observation of a Michael-type product and a Heck-type product in the reactions that use a $[Co(dppe)Cl_2]/ZnCl_2$ or $[Ni(dppe)Br_2]/ZnCl_2$ catalyst system, respectively, clearly reveals that the nature of the metal complex plays a crucial role in the addition reaction of organoboronic acids with alkenes. Further applications of the reaction in the asymmetric synthesis are also underway.

Acknowledgements

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Keywords: annulation · 1,4-addition · alkenes · aminoindanes · cobalt · boron

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[22] CCDC-904574 (**8ah**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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