



Rh(I)/diene-catalyzed addition reactions of aryl/alkenylboronic acids with aldehydes

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ARTICLE INFO

Article history:

Received 10 April 2009

Revised 20 May 2009

Accepted 1 June 2009

Available online 17 June 2009

ABSTRACT

[Rh(COD)Cl]₂-catalyzed addition reactions of arylboronic acids with aldehydes, with low Rh(I) catalyst loading, are described. We also found that the reaction of arylboronic acids with α,β -unsaturated aldehydes greatly depends on the solvent and the steric hindrance of the reagents/substrates.

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In 1998, Miyaura reported Rh(I)/bisphosphine-catalyzed addition reactions of aryl/alkenylboronic acids with aldehydes,¹ which marked an important step of transition metal-catalyzed such addition reactions.^{2–10} Subsequent study from the same group showed that Rh(I)/*t*-Bu₃P (1:1 ratio) possess much higher catalytic activity than Rh(I)/bisphosphine catalysts,² suggesting that bulky, monodentate ligands would be superior ligands. Since then, a number of Rh(I) catalysts derived from monodentate ligands have been developed.^{3,4} In our laboratory, we are interested in developing highly active/efficient catalysts for such addition reactions. We have recently documented metalacycle-catalyzed addition reactions of arylboronic acids with carbonyl-containing compounds.⁷ In our studies, we demonstrated that the catalytic activity of the metalacycles could be tuned by varying the Lewis acidity of the metal center, including employing less electron-donating ligands and softer metal.⁷ We surmised that such Lewis acidity tuning strategy might also be suitable to develop highly active Rh(I) catalysts with unprecedented catalytic activities.

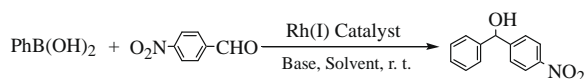
Dienes have recently been reported as efficient ligands in Rh(I)-catalyzed addition reaction of arylboronic acids with α,β -unsaturated ketones/esters/aldehydes.^{11,12} Importantly, Rh(I)/diene catalysts exhibited higher catalytic activity than Rh(I)/phosphines including Rh(I)/bisphosphine catalysts. We speculated that such catalytic activity increase might in part be due to the less electron-donating ability of the dienes, which could make the Rh(I) center more Lewis acidic. We thus envisioned that Rh(I)/diene catalysts could be highly active catalyst systems for the addition of arylboronic acids with aldehydes. In this Letter, we report on the Rh(I)/diene-catalyzed addition reactions of arylboronic acids with aldehydes, with low Rh(I) catalyst loading, and a highly efficient tandem reaction sequence of arylboronic acids with α,β -unsaturated aldehydes.¹³

Our study began with the addition reaction of phenylboronic acid with 4-nitrobenzaldehyde by using chloro(1,5-cyclooctadiene)rhodium(I) dimer ([Rh(I)(COD)Cl]₂) (**1**), chloronorbomadiene-rhodium dimer ([Rh(I)(NBD)Cl]₂) (**2**), and [Rh(I)(CH₂CH₂)₂Cl]₂ (**3**) as catalysts (Table 1). We first tested KOH and KF, two bases that have been previously used for this type of addition reactions with other ligands for Rh(I).^{2,4k} We found that with [Rh(COD)Cl]₂ as catalyst, a low conversion was observed for KF/toluene–H₂O, and varied conversions depending on the amount of the base used were observed for KOH/dioxane, with 1 equiv of KOH affording the best result (Table 1, entries 1–4). Screening other bases/solvents showed that K₃PO₄/THF was an excellent solvent/base combination (Table 1, entries 5–15). [Rh(I)(NBD)Cl]₂ (**2**) and [Rh(I)(CH₂CH₂)₂Cl]₂ (**3**) exhibited less efficiency than **1** (Table 1, entries 16–20). Further study revealed that the existence of water in the reaction system can accelerate the reaction (Table 1, entries 21 and 22). We have lowered the amount of [Rh(COD)Cl]₂ to 0.1% for the addition reaction. Once again, K₃PO₄ was observed as the best base.

With [Rh(COD)Cl]₂ as catalyst and K₃PO₄ as base, we have examined a number of aromatic aldehydes and arylboronic acids for the addition reaction. We found that the reaction went smoothly with 0.025–0.05% [Rh(COD)Cl]₂ as catalyst (Table 2, entries 1–10). Aliphatic aldehydes have been reported to be less effective substrates in Rh(I)-catalyzed addition reaction of arylboronic acids with aldehydes due to the tendency of aliphatic aldehydes to undergo Aldol reaction under the reaction condition. It was of interest to us to see whether the Rh(I)/diene system could effect the reaction with this type of substrate. We were pleased to find that the addition with aliphatic aldehydes as substrates proceeded well with high isolated yields (Table 2, entries 11–17). To our knowledge, the 0.025% loading of **1** represented the lowest Rh(I) loading in the addition reaction of arylboronic acids with aldehydes. We have also tested vinylboronic acids as nucleophiles for the addition and found that vinylboronic acids were less reactive than arylboronic acids and higher catalyst loading was required for the reaction (Table 2, entries 18 and 19).

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Table 1
Rh(I)/diene-catalyzed addition reactions of phenylboronic acid with 4-nitrobenzaldehyde ^a



Entry	Rh(I) Cat.	Catalyst loading (%)	Solvent	Base	Time (h)	Conver. ^b (%)
1	1	1	Toluene	KF (2 equiv)	0.5	18
2	1	1	Dioxane	KOH (0.5 equiv)	0.5	66
3	1	1	Dioxane	KOH (1 equiv)	0.5	87
4	1	1	Dioxane	KOH (3 equiv)	0.5	12
5	1	1	Dioxane	K ₃ PO ₄ (2 equiv)	0.5	99
6	1	1	THF	K ₃ PO ₄ (2 equiv)	0.5	99
7	1	1	THF	K ₃ PO ₄ (2 equiv)	0.25	91
8	1	1	Dioxane	K ₃ PO ₄ (2 equiv)	0.25	85
9	1	1	THF	KOH (2 equiv)	0.25	41
10	1	1	THF	K ₂ CO ₃	0.25	43
11	1	1	THF	Na ₂ CO ₃	0.25	16
12	1	1	THF	KF	0.25	34
13	1	1	THF	KOAc	0.25	10
14	1	1	THF	NaOH	0.25	<2
15	1	1	THF	Cs ₂ CO ₃	0.25	55
16	2	1	Dioxane	KOH (2 equiv)	0.25	80
17	2	2	THF	KF (2 equiv)	0.25	34
18	2	2	Toluene	KF (2 equiv)	0.25	0
19	2	2	THF	K ₃ PO ₄ (2 equiv)	0.25	91
20	3	1	THF	K ₃ PO ₄ (2 equiv)	1	0
21	1	1	THF	K ₃ PO ₄ (5.5 M, 2 equiv)	0.25	99
22	2	1	THF	K ₃ PO ₄ (5.5 M, 2 equiv)	1	92
23	1	0.1	THF	K ₃ PO ₄ (5.5 M, 3 equiv)	0.5	81
24	1	0.1	THF/H ₂ O (10:1)	KOH (2 equiv)	0.5	42
25	1	0.1	Dioxane/H ₂ O (10:1)	KOH (2 equiv)	0.5	25

^a Reaction conditions: aldehyde (0.5 mol), phenylboronic acid (0.75 mmol), THF (2 mL), base (0.5–3.0 equiv), rt.

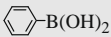
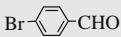
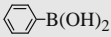

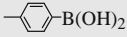

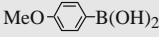

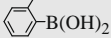

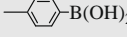

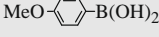

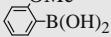

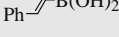
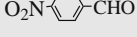
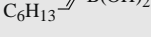
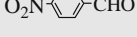
^b Conversion based on ¹H NMR.

Table 2
[Rh(COD)Cl]₂-catalyzed addition reactions of aryl/alkenylboronic acids with aldehydes ^a



Entry	ArB(OH) ₂	RCHO	Cat. loading	Time (h)	Yield ^b (%)
1			0.025	10	96
2			0.025	15	97
3			0.05	19	82
4			0.05	16	83
5			0.05	16	90
6			0.05	19	89
7			0.05	19	84
8			0.05	17	87
9			0.05	17	93

Table 2 (continued)

Entry	ArB(OH) ₂	RCHO	Cat. loading	Time (h)	Yield ^b (%)
10			0.05	10	91
11			0.05	19	83
12			0.05	16	91
13			0.05	16	92
14			0.05	16	93
15			0.05	17	82
16			0.05	17	86
17			0.05	17	87
18			0.25	16	86
19			0.25	16	44

^a Reaction conditions: aldehyde (1.0 equiv), boronic acid (1.5 equiv), THF (4 mL), K₃PO₄ (5.0 M, 3.0 equiv), rt.

^b Isolated yields.

The observation of aliphatic aldehydes as excellent substrates for this reaction prompted us to carry out studies to understand the reactivities of different aldehydes for this reaction. We tested the addition reaction with phenylboronic acid as the nucleophile. Our results are listed in Table 3. We found that *p*-nitrobenzaldehyde, which bears an electron-withdrawing substituent, exhibited higher reactivity than *p*-methylbenzaldehyde, which bears an electron-donating group (Table 3, entry 1). Aliphatic aldehydes such as hexanal and 3-methylbutanal showed a similar reactivity as *p*-methylbenzaldehyde (Table 3, entries 1–5). Interestingly, 3-phenylpropanal exhibited a higher reactivity than hexanal, 3-methylbutanal, or *p*-methylbenzaldehyde (Table 3, entries 2, 4, and 5). In addition, 3,3-diphenylpropanal showed a higher reactivity than 3-phenylpropanal (Table 3, entry 6). These results might suggest that the phenyl group participated in the addition reaction.


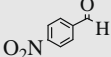


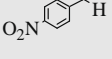







We have also employed [Rh(COD)Cl]₂ as the catalyst for the addition reaction of arylboronic acids with α,β-unsaturated aldehydes.^{12,14} We found that the reaction outcome was dependent on the solvent used and on the steric hindrance of substrates/reagents. With MeOH as solvent, the addition reaction occurred in a 1,4-addition fashion and 3,3-diphenylpropanal was observed in high yield (Table 4, entry 1), which was consistent with the previous observation.¹² With THF as solvent, the 1,4-addition followed by 1,2-addition occurred and alcohols were observed in good to high yields (Table 4). With 2-substituted phenylboronic acids as nucleophiles, we observed that crotonaldehyde gave tandem reaction products in good yields, but cinnamaldehyde gave a mixture of 1,2-addition products and 1,4-addition followed by 1,2-addition products, suggesting that the initial addition was dependent on the steric hindrance of the substrates and reagents.

In summary, we have demonstrated that [Rh(COD)Cl]₂ was a highly efficient catalyst for the addition reactions of arylboronic acids with aldehydes, with low Rh(I) catalyst loading. We also

found that the reaction of arylboronic acids with α,β-unsaturated aldehydes greatly depends on the solvent and the steric hindrance of the reagents/substrates. Our future work will be directed to determine the scope and limitation of Rh(I)/diene-catalyzed addition reactions and to develop the asymmetric version of these processes.

Table 3

Competitive addition reaction of phenylboronic acid with aromatic aldehydes and aliphatic aldehydes^a

Entry	Reaction		Ratio of A:B ^b
	R ₁ CHO	R ₂ CHO	
1			1:7.3
2			1:2.2
3			3.1:1
4			1:2.4
5			1:2.5
6			1.2:1

^a Reaction conditions: phenylboronic acid (1.0 equiv), aldehydes (1.0 equiv each), THF (2 mL), K₃PO₄ (5 M, aqueous solution, 3.0 equiv), room temperature, 18 h.

^b Ratio based on ¹H NMR.

Table 4
Tandem reactions catalyzed by [Rh(COD)Cl]₂^a

Entry	ArB(OH) ₂	Reaction		Solvent	Yield ^b (%)
		ArB(OH) ₂ + R-CH=CH-CHO	→ Ar-CH(OH)-CH ₂ -Ar		
1				MeOH	98 ^c
2				THF	86
3				THF	73
4				THF	80
5				THF	^d
6				THF	^e
7				THF	80
8				THF	86
9				THF	78
10				THF	55
11				THF	81 ^f

^a Reaction conditions: aldehyde (1.0 equiv), arylboronic acid (3.0 equiv), solvent (6 mL), K₃PO₄ (5 M aqueous solution, 6.0 equiv), room temperature.

^b Isolated yields.

^c Conversion based on ¹H NMR.

^d A mixture of 1,2-addition allylic alcohol and 1,4-addition followed by 1,2-addition was observed, in a ratio of 0.67:1.

^e A mixture of 1,2-addition allylic alcohol and 1,4-addition followed by 1,2-addition was observed, in a ratio of 4.6:1.

^f 0.25% [Rh(COD)Cl]₂ was used.

Acknowledgments

We gratefully thank the NSF (CHE0719311) for funding. Partial support from PSC-CUNY Research Award Program is also gratefully acknowledged. We also thank Frontier Scientific, Inc. for its generous gifts of arylboronic acids.

Supplementary data

General procedure of Rh(I)/diene-catalyzed addition reactions and characterizations of the reaction products are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.06.074.

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