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Rhodium(I)/Diene-Catalyzed Addition Reactions of Arylborons with Ketones

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Abstract

Rh(I)/diene-catalyzed addition reactions of arylboroxines/arylboronic acids with unactivated ketones to form tertiary alcohols in good to excellent yields are described. By using C₂-symmetric (3aR,6aR)-3,6-diaryl-1,3a,4,6a-tetrahydropentalenes as ligands, the asymmetric version of such an addition reaction, with up to 68% ee, was also realized.

Over the past decade, transition metal-catalyzed addition reactions of arylborons with aldehydes have been established as attractive transformations for organic synthesis.^{1,2,3,4,5,6} On the other hand, the use of ketones as substrates for transition metal-catalyzed addition reactions of arylborons has largely been limited to activated ketones such as α -keto esters/amides and trifluoromethyl ketones.^{2d,4a,4i,7,8,9,10,11} Unactivated ketones, due to their low reactivity, have only been reported to be suitable substrates under special situations; for example, addition reactions involving boronic acid-bearing ketones¹⁰ or cyclohexenone as substrates,¹¹ NaBPh₄ as reagent,¹² and Ni(0)-catalyzed 1,2-addition reactions of arylboronic acids with unactivated ketones through an oxanickelacycle intermediate process.^{4a,4i} In addition, Korenaga and Sakai recently reported [Rh(COD)OH]₂/electron-poor bisphosphine-catalyzed addition reactions of arylboronic acids with chromone as a side reaction of the 1,4-addition reaction, in which a large excess amount (5 equivalent) of arylboronic acids were needed and low yields (< 48%) were observed.¹³ To date, transition metal-catalyzed addition reactions of arylborons with unactivated ketones have remained largely underexplored.¹⁴

In our laboratory, we are interested in using readily available transition metal complexes for the addition reactions of arylborons with carbonyl-containing compounds.^{15,16,17,18} We have recently documented anionic four-electron donor-based (Type I) palladacycle **1** and **2**,¹⁵ platinumacycle **3**¹⁶ (Figure 1) and [Rh(COD)Cl]₂¹⁷ as catalysts for the addition reaction of arylboronic acids with carbonyl-containing compounds including aldehydes and α -keto esters. During these studies, we attempted to employ unactivated ketones as substrates for the addition reactions. However, our attempts to use transition metal complexes including palladacycles and [Rh(COD)Cl]₂ as catalysts for such addition reactions only led to the observation of fast catalyst decomposition and low conversions.

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Supporting Information Available: General procedures and product characterization of Rh(I)/diene-catalyzed addition reaction of arylborons with ketones.

Recently, based on the consideration that the decomposition of palladacycle catalysts could be minimized by inhibiting the transmetalation process between transition metal catalysts and arylboron compounds, we showed that under the anhydrous condition, Type I palladacycle **2** was indeed very stable and catalyzed the addition reactions of aldehydes with arylboroxines efficiently with an extremely low catalyst loading.¹⁵ We thus surmised that other transition metal catalysts such as Rh(I) catalysts might also be long-lived under the anhydrous condition and might be able to function as efficient catalysts for the addition reactions with unactivated ketones as substrates. Herein, we report our results on using unactivated ketones as substrates, specifically, Rh(I)/diene-catalyzed addition reactions of arylboroxines with unactivated ketones, including an asymmetric version.

Our study began with [Rh(COD)Cl]₂-catalyzed addition reactions with propiophenone as substrate. With untreated, commercially available phenylboronic acid (about 70% as the form of phenylboroxine based on the ¹H NMR analysis) as the reagent, almost no reaction was observed at room temperature, a 51% conversion was observed at elevated temperature (Table 1, entries 1, 2). Lower conversions (from 45% to 20%) were observed with more water, *i.e.*, more amounts of phenylboronic acid, in the reaction system (Table 1, entries 3–5). Significantly, the reaction system turned to black, an indication of catalyst decomposition, was observed after 5 minutes and conversions remained essentially the same even with extended reaction time (entries 1–5, data in parenthesis). In contrast, by using dry base and dry phenylboronic acid (phenylboroxine), we found that although the conversion was low at room temperature, the decomposition of the catalyst was not observed (Table 1, entry 6). Promising catalytic activities were observed at elevated temperature (Table 1, entries 7, 8). Importantly, complete conversion was observed by extending the reaction time (Table 1, entry 9). We also briefly screened the bases and solvents and found that K₂CO₃ was the best base (Table 1, entries 8, 10–12) and toluene was the best solvent (Table 1, entries 8, 13–15).

With [Rh(COD)Cl]₂ as catalyst, toluene as solvent and K₂CO₃ as base, a number of arylboroxines and different types of ketones were examined for the addition reaction, and our results are summarized in Table 2. Unactivated alkyl aryl ketones and benzophenone reacted with arylboroxines that bear electron-donating and electron-withdrawing groups to give corresponding tertiary alcohols in good to excellent yields (Table 2, entries 1–13). In addition, aliphatic ketones including both cyclic and acyclic ones were also suitable substrates and tertiary alcohols were obtained in high yields (Table 2, entry 14–23). Among different ketones examined, cyclic aliphatic ketones are more reactive than acyclic ones for such addition reactions.

We have also preliminarily examined the asymmetric version of this addition reaction by using (3*aR*,6*aR*)-3,6-diaryl-1,3*a*,4,6*a*-tetrahydropentalenes (**6**) (Figure 2) as the ligands.^{19,20} We found Rh(I)/chiral diene **6**-catalyzed addition reaction occurred smoothly to afford the product with moderate enantioselectivities, and **6c** was observed to be most enantioselective ligand among **6** (Table 3, entries 1–4). Significantly, we found Rh(I)/chiral diene **6**, especially Rh(I)/chiral diene **6c**, exhibited much higher catalytic activities than [Rh(COD)Cl]₂ as evidenced by the fact that Rh(I)/chiral diene **6**-catalyzed addition reaction occurred smoothly even at room temperature (Table 5, entries 4–5). The high catalytic activity also permitted the use of commercially available *p*-tolylboronic acid, (77% in *p*-tolylboroxine form based on ¹H NMR analysis) or with water as the additive for the addition reaction (Table 5, entries 4, 6–7). Further examination revealed that base can only affect the reaction rate but not the enantioselectivity (Table 3, entries 7–9). The use of *o*-xylene slightly improved the enantioselectivity comparing to toluene and benzene (Table 3, entries 9–12). By using **6c** as the ligand, KF as the base and *o*-xylene as the solvent,²¹ several ketones and arylboronic acids (72–79% in arylboroxine form based on ¹H NMR analysis)

were also examined, up to 68% ee was obtained (Table 4). To our knowledge, this is the highest enantioselectivity reported so far for transition metal-catalyzed intermolecular addition reactions of arylborons with unactivated ketones.²²

In summary, based on the consideration that Rh(I) catalysts might be long-lived under an anhydrous condition, we demonstrated that [Rh(COD)Cl]₂-catalyzed addition reactions of ketones with arylborons efficiently occurred under an anhydrous condition. By using optically active (3*aR*,6*aR*)-3,6-diaryl-1,3*a*,4,6*a*-tetrahydropentalenes as the ligand, the asymmetric version of this addition reaction was realized and up to 68% ee was obtained. In addition, Rh(I)/(3*aR*,6*aR*)-3,6-diaryl-1,3*a*,4,6*a*-tetrahydropentalene complexes were found to exhibit higher catalytic activity than [Rh(COD)Cl]₂. Our study provided a general catalyst system for the addition reaction of arylborons with unactivated ketones. Our study also paved the road for us to explore other transition metal catalysts for such addition reactions,²³ and to develop highly enantioselective catalysts to access optically active tertiary alcohols.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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22. (a) A 36% ee was reported for Ni(0)-catalyzed addition reaction of 4-(trifluoromethyl)acetophenone with a phenylborate, see Ref. 4a. (b) A 38% ee was reported for

Rh(I)/electron-poor bisphosphine (*R*)-BFPY-catalyzed addition reaction of acetophenone with phenylboronic acid, see Ref. 14.

23. Preliminary study showed that palladacycle **2** and platina-cyclohexadiene **3** also catalyzed the addition reaction of phenylboroxine with cyclohexanone, affording the addition products in 71% and 45% yield (5 mol % catalyst loading, 90 °C, 10 h), respectively.

Figure 1.
Type I Metalacycles

6a: Ar = Ph

6b: Ar = 4-*t*-BuC₆H₄

6c: Ar = 4-CF₃C₆H₅

6d: Ar = 3,5-(CF₃)C₆H₃

Figure 2.
(3a*R*,6a*R*)-3,6-Diaryl-1,3a,4,6a-tetrahydropentalenes

Table 1

[Rh(COD)Cl]₂-Catalyzed Addition Reaction of Phenylboron Reagents with Propiophenone^a

entry	"PhB"	base	solvent	temp(°C)	conv(%) ^b
1	PhB(OH) ₂	K ₂ CO ₃	Toluene	rt	0 (1) ^c
2	PhB(OH) ₂	K ₂ CO ₃	Toluene	90	51(52) ^{d,e}
3	PhB(OH) ₂	K ₂ CO ₃	Toluene	90	47(53) ^{d,e,f}
4	PhB(OH) ₂	K ₂ CO ₃	Toluene	90	42(47) ^{d,e,g}
5	(PhBO) ₃	K ₂ CO ₃	Toluene	90	20(25) ^{d,e,h}
6	(PhBO) ₃	K ₂ CO ₃	Toluene	rt	7
7	(PhBO) ₃	K ₂ CO ₃	Toluene	60	25
8	(PhBO) ₃	K ₂ CO ₃	Toluene	90	79
9	(PhBO) ₃	K ₂ CO ₃	Toluene	90	99 ⁱ
10	(PhBO) ₃	KF	Toluene	90	70
11	(PhBO) ₃	K ₃ PO ₄	Toluene	90	77
12	(PhBO) ₃	Cs ₂ CO ₃	Toluene	90	32
13	(PhBO) ₃	K ₂ CO ₃	THF	70	7
14	(PhBO) ₃	K ₂ CO ₃	CH ₂ ClCH ₂ Cl	90	3
15	(PhBO) ₃	K ₂ CO ₃	Dioxane	90	25

^aReaction conditions: propiophenone (0.25 mmol), "PhB" (2 equiv), base (3 equiv), solvent (1 mL), 1.5 mol % of [Rh(COD)Cl]₂, 2 h;

^bBased on GC-MS analysis;

^cReaction time: 20 h.

^dCatalyst decomposition was observed after 5 minute.

^eIn parenthesis: yield with the reaction time of 5 h.

^f1 equiv of H₂O was added.

g_2 equiv of H_2O was added.

h_6 equiv of H_2O was added.

i Reaction time: 5 h.

Table 2[Rh(COD)Cl]₂-Catalyzed Addition Reactions of Aryl-boroxines with Unactivated Ketones

$\text{R}-\text{C}(=\text{O})-\text{R}' + (\text{ArBO})_3 \xrightarrow[\text{K}_2\text{CO}_3, \text{Toluene}, 90-110^\circ\text{C}, 5-12 \text{ h}]{1.5-2.5 \text{ mol } \% [\text{Rh}(\text{COD})\text{Cl}]_2} \text{HO}-\text{C}(\text{Ar})(\text{R})(\text{R}')$				
entry	RCOR'	(ArBO) ₃	product	yield(%) ^b
1	(4a)	₃	5a	88
2	4a	₃	5b	92
3	4a	₃	5c	90
4	4a	₃	5d	87
5	4a	₃	5e	80
6	(4b)	₃	5f	82
7	(4c)	₃	5g	90
8	4c	₃	5h	86
9	(4d)	₃	5i	88
10	4d	₃	5j	90
11	(4e)	₃	5k	80
12	4e	₃	5l	85
13	4e	₃	5m	88

$\text{R}-\text{C}(=\text{O})-\text{R}' + (\text{ArBO})_3 \xrightarrow[\text{K}_2\text{CO}_3, \text{Toluene}, 90-110^\circ\text{C}, 5-12\text{ h}]{1.5-2.5\text{ mol \% } [\text{Rh}(\text{COD})\text{Cl}]_2} \text{HO}-\text{C}(\text{Ar})(\text{R})(\text{R}')$				
entry	RCOR'	(ArBO) ₃	product	yield(%) ^b
14	(4f)		5n	91
15	4f		5o	90
16	4f		5p	88
17	4f		5q	86
18	(4g)		5r	82
19	(4h)		5s	80
20	(4i)		5t	81
21	(4j)		5u	84
22	(4k)		5v	83
23	4k		5w	87

^a Reaction conditions: ketone (0.25 mmol), arylboroxine (0.17 mol), K₂CO₃ (3 equiv), toluene (1 mL), catalyst (1.5–2.5 mol %), 90–110 °C, 5–12 h;

^b Isolated yield;

^c Reaction temperature: 70 °C, 24 h.

Table 3

Rh(I)/Chiral Diene **6**-Catalyzed Addition Reaction of *p*-Tolylboronic Acid with Propiophenone^a

entry	diene	base	solvent	temp(°C)	time(h)	yield(%) ^b	ee ^c
1	6a	K ₂ CO ₃	Toluene	60	48	87	16
2	6b	K ₂ CO ₃	Toluene	60	48	88	25
3	6c	K ₂ CO ₃	Toluene	60	20	87	34
4	6d	K ₂ CO ₃	Toluene	rt	38	86	11 ^d
5	6c	K ₂ CO ₃	Toluene	rt	106	86	40
6	6c	K ₂ CO ₃	Toluene	rt	42	89	40 ^d
7	6c	K ₂ CO ₃	Toluene	rt	38	88	40 ^e
8	6c	K ₃ PO ₄	Toluene	rt	38	70	40 ^e
9	6c	KF	Toluene	rt	30	89	40 ^e
10	6c	KF	Benzene	rt	30	85	36 ^e
11	6c	KF	<i>o</i> -Xylene	rt	30	88	41 ^d
12	6c	KF	<i>o</i> -Xylene	rt	30	87	41 ^e

^a Reaction conditions: ketone (0.125 mmol), *p*-tolylboroxine (0.083 mmol, equal to 2 equiv of *p*-tolylboronic acid), base (3 equiv), toluene(1 mL), [Rh(CH₂CH₂Cl)₂Cl]₂ (2.5 mol %), ligand (6 mol %).

^b Isolated yield.

^c Determined by HPLC analysis (chiral OD column).

^d *p*-Tolylboronic acid was used.

^e 2 equiv of H₂O was added.

Table 4Rh(I)/Chiral diene **6c**-Catalyzed Addition Reactions of Arylboronic Acids with Ketones^a

$\text{R}-\text{C}(=\text{O})-\text{R}' + \text{ArB}(\text{OH})_2 \xrightarrow[\text{KF, } o\text{-Xylene, rt, 24 h}]{1.5 \text{ mol \% } [\text{Rh}(\text{CH}_2\text{CH}_2)_2\text{Cl}]_2 / 3.6 \text{ mol \% } \mathbf{6c}} \text{R}-\text{C}(\text{OH})(\text{Ar})-\text{R}'$				
entry	ketone	ArB(OH) ₂	yield(%) ^b	ee ^c
1	(4a)		83	47 ^d
2	4a		85	39
3	(4f)		81	36
4	4f		80	68 ^d
5	4f		84	43
6	4f		84	49 ^e
7	(4g)		83	56

^aReaction conditions: ketone (0.25 mmol), arylboronic acid (2 equiv), KF (3 equiv), *o*-xylene (1 mL), [Rh(CH₂CH₂)₂Cl]₂ (1.5 mol %), **6c** (3.6 mol %);^bIsolated yield; e.^cDetermined by HPLC analysis (Chiral OD Column);^d5 mol % Rh(I)/6 mol % **6c** at 0 °C for 7 days.^eReaction at 60 °C.