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

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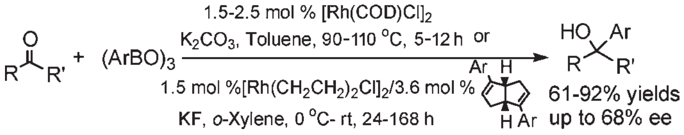
ABSTRACT



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 *C*$_2$-symmetric (3a*R*,6a*R*)-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.[1−6] 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,7−11] 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 ketones[10] or cyclohexenone as substrates,[11] NaBPh$_4$ as the reagent,[12] and Ni(0)-catalyzed 1,2-addition reactions of arylboronic acids with unactivated ketones through an oxanickelacycle intermediate process.[4a,i] In addition, Korennaga and Sakai

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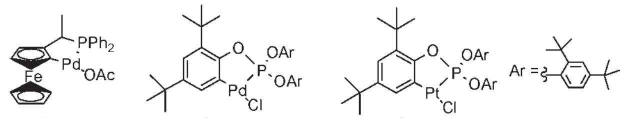
recently reported $[Rh(COD)OH]_2$/electron-poor bisphosphine-catalyzed addition reactions of arylboronic acids with chromone as a side reaction of the 1,4-addition reaction, in which a large excess amount (5 equiv) of arylboronic acids were needed and low yields ($<48\%$) were observed.[13] To date, transition-metal-catalyzed addition reactions of aryborons 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.[15−18] We have recently documented anionic four-electron donor-based (Type I) palladacycle **1** and **2**,[15] platinacycle **3**[16] (Figure 1), and $[Rh(COD)Cl]_2$[17] 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.



1 **2** **3**

Figure 1. Type I metalacycles.

Recently, based on the consideration that the decomposition of palladacycle catalysts could be minimized by inhibiting the transmetalation process between transition metal catalysts and aryboron 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 conditions 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 the substrate. With untreated, commercially available phenylboronic acid (~70% as the form of phenylboroxine based on the ^1H NMR analysis) as the reagent, almost no reaction was observed at rt, 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, after 5 min, and conversions remained essentially the same even with an extended reaction time (entries 1−5, data in parentheses). In contrast, by using a dry base and dry phenylboronic acid (phenylboroxine), we found that although the conversion was low at rt, 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 K_2CO_3 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 the catalyst, toluene as the solvent, and K_2CO_3 as the 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 -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, entries 14−23). Among the 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 (3a*R*,6a*R*)-3,6-diaryl-1,3a,4,6a-tetrahydropentalenes (**6**) (Figure 2) as the ligands.[19,20] We found that the Rh(I)/chiral diene **6**-catalyzed addition reaction occurred smoothly to afford the

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(9) For examples with other activated ketones as substrates: (a) Jumde, V. R.; Facchetti, S.; Iuliano, A. *Tetrahedron: Asymmetry* **2010**, *21*, 2775–2781. (b) Martina, S. L. X.; Jagt, R. B. C.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Chem. Commun.* **2006**, 4093–4095. Also see ref 2d.

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(14) During the preparation of this manuscript, Korennaga and Sakai reported $[Rh(COD)OH]_2$/electron-poor bisphosphine BFPY-catalyzed addition reactions of arylboronic acids with unactivated ketones, with one example of asymmetric addition in 38% ee: Korenaga, T.; Ko, A.; Uotani, K.; Tanaka, Y.; Sakai, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 10703–10706.

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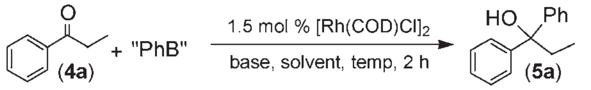
(18) (a) Liao, Y.-X.; Hu, Q.-S. *J. Org. Chem.* **2011**, *76*, 7602–7607. (b) Xing, C.-H.; Hu, Q.-S. *Tetrahedron Lett.* **2010**, *51*, 924–927. (c) Liu, T.-P.; Liao, Y.-X.; Xing, C.-H.; Hu, Q.-S. *Org. Lett.* **2011**, *13*, 2452–2455. (d) Liao, Y.-X.; Xing, C.-H.; Israel, M.; Hu, Q.-S. *Org. Lett.* **2011**, *13*, 2058–2061.

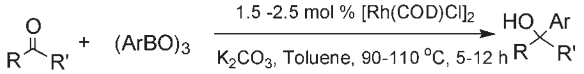
Table 1. [Rh(COD)Cl]$_2$-Catalyzed Addition Reaction of Phenylboron Reagents with Propiophenone[a]

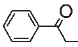
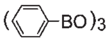
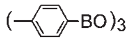
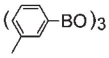
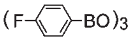
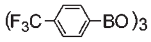
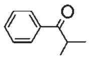
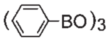
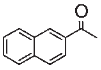
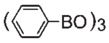
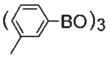
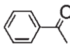
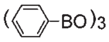
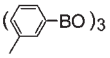
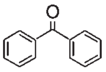
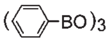
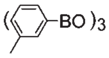
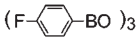
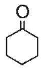
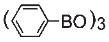
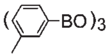
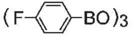
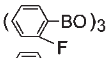
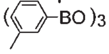
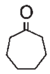
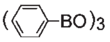
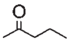
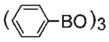
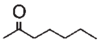
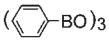
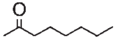
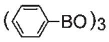
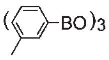


entry	"PhB"	base	solvent	temp (°C)	conv (%)[b]
1	$PhB(OH)_2$	K_2CO_3	Toluene	rt	0 (1)[c]
2	$PhB(OH)_2$	K_2CO_3	Toluene	90	51(52)[d,e]
3	$PhB(OH)_2$	K_2CO_3	Toluene	90	47(53)[d,e,f]
4	$PhB(OH)_2$	K_2CO_3	Toluene	90	42(47)[d,e,g]
5	$(PhBO)_3$	K_2CO_3	Toluene	90	20(25)[d,e,h]
6	$(PhBO)_3$	K_2CO_3	Toluene	rt	7
7	$(PhBO)_3$	K_2CO_3	Toluene	60	25
8	$(PhBO)_3$	K_2CO_3	Toluene	90	79
9	$(PhBO)_3$	K_2CO_3	Toluene	90	99[i]
10	$(PhBO)_3$	KF	Toluene	90	70
11	$(PhBO)_3$	K3PO4	Toluene	90	77
12	$(PhBO)_3$	Cs_2CO_3	Toluene	90	32
13	$(PhBO)_3$	K_2CO_3	THF	70	7
14	$(PhBO)_3$	K_2CO_3	CH_2ClCH_2Cl	90	3
15	$(PhBO)_3$	K_2CO_3	Dioxane	90	25

[a] Reaction conditions: propiophenone (0.25 mmol), "PhB" (2 equiv), base (3 equiv), solvent (1 mL), 1.5 mol % of [Rh(COD)Cl]$_2$, 2 h. [b] Based on GC-MS analysis. [c] Reaction time: 20 h. [d] Catalyst decomposition was observed after 5 min. [e] In parentheses: yield with the reaction time of 5 h. [f] 1 equiv of H_2O was added. [g] 2 equiv of H_2O were added. [h] 6 equiv of H_2O were added. [i] Reaction time: 5 h.

Table 2. [Rh(COD)Cl]$_2$-Catalyzed Addition Reactions of Arylboroxines with Unactivated Ketones[a]



entry	RCOR'	$(ArBO)_3$	product	yield(%)[b]
1	 (4a)		**5a**	88
2	**4a**		**5b**	92
3	**4a**		**5c**	90
4	**4a**		**5d**	87
5	**4a**		**5e**	80
6	 (4b)		**5f**	82
7	 (4c)		**5g**	90
8	**4c**		**5h**	86
9	 (4d)		**5i**	88
10	**4d**		**5j**	90
11	 (4e)		**5k**	80
12	**4e**		**5l**	85
13	**4e**		**5m**	88
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), K_2CO_3 (3 equiv), toluene (1 mL), catalyst (1.5–2.5 mol %), 90–110 °C, 5–12 h. [b] Isolated yield.

product with moderate enantioselectivities, and **6c** was observed to be the 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 the Rh(I)/chiral diene **6**-catalyzed addition reaction occurred smoothly even at rt (Table 3, entries 4–5). The high catalytic activity also permitted the use of commercially available *p*-tolylboronic acid (77% in *p*-tolylboroxine form based on ^{1}H NMR analysis) or of water as the additive for the addition reaction (Table 3, 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 compared 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 ^{1}H NMR analysis) were also examined, and 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 aryborons with unactivated ketones.[22]

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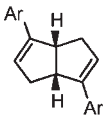
(19) For recent reviews on chiral olefin ligands: (a) Feng, C.-G.; Xu, M.-H.; Lin, G.-Q. *Synlett* **2011**, 1345–1356. (b) Shintani, R.; Hayashi, T. *Aldrichimica Acta* **2009**, *42*, 31–38. (c) Defieber, C.; Grutzmacher, H.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4482–4502. (d) Johnson, J. B.; Rovis, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 840–871. (e) Glorius, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3364–3366.

(20) (a) Wang, Z.-Q.; Feng, C.-G.; Xu, M.-H.; Lin, G.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336–5337. (b) Wang, Z.-Q.; Feng, C.-G.; Zhang, S.-S.; Xu, M.-H.; Lin, G.-Q. *Angew. Chem., Int. Ed.* **2010**, *49*, 5780–5783.

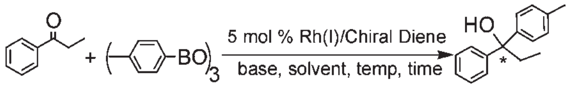
(21) For an example of Rh(I)-catalyzed addition reactions of arylboronic acids with aldehydes with KF as the base: Duan, H.-F.; Xie, J.-H.; Shi, W.-J.; Zhang, Q.; Zhou, Q.-L. *Org. Lett.* **2006**, *8*, 1479–1481.



6a: Ar = Ph
6b: Ar = 4-*t*-BuC$_6$H$_4$
6c: Ar = 4-CF$_3$C$_6$H$_4$
6d: Ar = 3,5-(CF$_3$)2C$_6$H$_3$

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

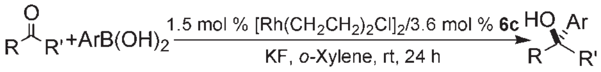
Table 3. Rh(I)/Chiral Diene **6**-Catalyzed Addition Reaction of *p*-Tolylboronic Acid with Propiophenone[a]

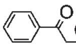
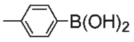
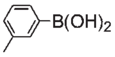
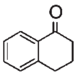
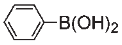
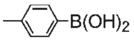
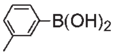
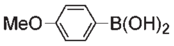
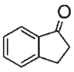
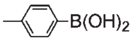


entry	diene	base	solvent	temp(°C)	time(h)	yield(%)[b]	ee(%)[c]
1	**6a**	K_2CO_3	Toluene	60	48	87	16
2	**6b**	K_2CO_3	Toluene	60	48	88	25
3	**6c**	K_2CO_3	Toluene	60	20	87	34
4	**6d**	K_2CO_3	Toluene	rt	38	86	11[d]
5	**6c**	K_2CO_3	Toluene	rt	106	86	40
6	**6c**	K_2CO_3	Toluene	rt	42	89	40[d]
7	**6c**	K_2CO_3	Toluene	rt	38	88	40[e]
8	**6c**	K_3PO_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	*o*-Xylene	rt	30	88	41[d]
12	**6c**	KF	*o*-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(CH$_2$CH$_2$)$_2$Cl]$_2$ (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 H$_2$O were added.

Table 4. Rh(I)/Chiral Diene **6c**-Catalyzed Addition Reactions of Arylboronic Acids with Ketones[a]



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

[a] Reaction conditions: ketone (0.25 mmol), arylboronic acid (2 equiv), KF (3 equiv), *o*-xylene (1 mL), [Rh(CH$_2$CH$_2$)$_2$Cl]$_2$ (1.5 mol %), **6c** (3.6 mol %). [b] Isolated yield. [c] Determined by HPLC analysis (Chiral OD Column). [d] 5 mol % Rh(I)/6 mol % **6c** at 0 °C for 7 days. [e] Reaction at 60 °C.

In summary, based on the consideration that Rh(I) catalysts might be long-lived under anhydrous conditions, we demonstrated that [Rh(COD)Cl]$_2$-catalyzed addition reactions of ketones with arylborons efficiently occurred under anhydrous conditions. By using optically active (3a*R*,6a*R*)-3,6-diaryl-1,3a,4,6a-tetrahydropentalenes as the ligand, the asymmetric version of this addition reaction was realized and up to 68% ee was obtained. In addition, Rh(I)/(3a*R*,6a*R*)-3,6-diaryl-1,3a,4,6a-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.

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Supporting Information Available. General procedures and product characterization of Rh(I)/diene-catalyzed addition reaction of arylborons with ketones. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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(22) A 36% ee was reported for the Ni(0)-catalyzed addition reaction of 4-(trifluoromethyl)acetophenone with a phenylborate; see ref 4a. (b) A 38% ee was reported for the Rh(I)/electron-poor bisphosphine (*R*)-BFPY-catalyzed addition reaction of acetonaphthenone with phenylboronic acid; see ref 14.

(23) A preliminary study showed that palladacycle **2** and platinacycle **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.