



Ni(COD)₂/4-ClC₆H₄COR-catalyzed addition reactions of arylboroxines with aldehydes

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ABSTRACT

Ni(COD)₂/4-ClC₆H₄COR (R = H, CH₃, Ph) was found to be an efficient catalyst system for the addition reactions of arylboroxines with aromatic and aliphatic aldehydes. The catalytically active species for Ni(COD)₂/4-ClC₆H₄COR catalyst systems was likely to be their oxidative addition adducts, 4-RCOC₆H₄-Ni(II)Cl(COD) complexes.

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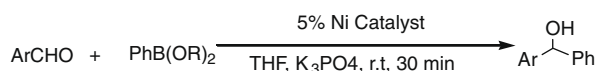
Transition metal-catalyzed addition reactions of organoboron reagents with aldehydes have recently emerged as useful transformations in organic synthesis.^{1–9} Different transition metal catalysts including Rh(I) complexes,^{1,2} Pd(II) complexes,³ Ni(0) complexes⁵ Cu(II) complexes,⁶ Fe(III)⁷ complexes, and more recently Ru(II) complexes⁸ have been reported to catalyze this type of addition reactions. In our laboratory, we have initiated a program to investigate metalcycles, a large family of cyclic organometallic compounds,¹⁰ as catalysts for such addition reactions.^{11,12} In this context, we have recently documented Type I palladacycles/platinacycles as efficient addition reaction catalysts.¹¹ While we were studying Type I palladacycles/platinacycles, we have naturally attempted to include nickel complexes for this purpose. In this Letter, we report that Ni(COD)₂/4-ClC₆H₄COR (R = H, CH₃, Ph) catalyst system could efficiently catalyze the addition reactions of arylboroxines with aldehydes.

We began our study by testing several nickel compounds for the reaction of phenylboronic acid with 4-chlorobenzaldehyde. We found while Ni(PPh₃)₂Br₂, NiBr₂, and NiBr₂/COD did not exhibit activities for the addition reaction (Table 1, entries 1–3), Ni(COD)₂ displayed some activity (Table 1, entry 4). Further testing showed that with phenylboroxine as a reagent, a 57% conversion was observed (Table 1, entry 5). We also found that the addition reaction was very sensitive to water: using K₃PO₄ as received as base led to much lower conversion (Table 1, entry 6). On the other hand, the addition reaction occurred very slowly under anhydrous condition (Table 1, entry 7). We also tested Ni(COD)₂/PCy₃, an efficient catalyst system previously reported by us for the cross-coupling of aryl tosylates and aryl chlorides,¹² but no catalytic activity was observed (Table 1, entry 8). Subsequent screening with other benzaldehydes including activated and deactivated ones surprisingly

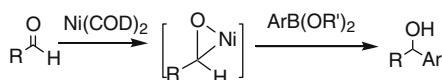
revealed that Ni(COD)₂ was a poor catalyst for all of them (Table 1, entries 9–11, 13, 14) except for 4-bromobenzaldehyde (Table 1, entry 12). These results suggested that the catalytically active species was unlikely to be Ni(COD)₂ itself and excluded the possibility that Ni(COD)₂-catalyzed addition reaction of phenylboroxine with 4-chlorobenzaldehyde proceeded through the mechanism described in previous reports (Scheme 1).⁵

We speculated the possible reason for our observation that only 4-halobenzaldehydes afforded meaningful conversions might be that the interaction of 4-halobenzaldehyde with Ni(COD)₂ generated the catalytically active species, most likely 4-HCOC₆H₄NiX(-COD) (X = Cl, Br). To confirm this speculation, we carried out the following experiments. We first examined the reaction of phenylboroxine with benzaldehyde by adding benzaldehyde to the reaction system of 4-chlorobenzaldehyde with phenylboroxine, a 42% conversion was observed after 1 h (Table 2, entry 1). We next tested to use 5% Ni(COD)₂ and 20% 4-chlorobenzaldehyde as the catalyst system, the reaction also occurred (Table 2, entry 2). These results, which were in contrast with the result that only Ni(COD)₂ being employed as catalyst (Table 1, entry 9), suggested that the reaction of 4-chlorobenzaldehyde with phenylboroxine indeed generated the catalytically active species. As 4-chlorobenzaldehyde itself would react with arylboroxines, using 4-chlorobenzaldehyde for the catalyst generation would complicate the product isolation. We thus examined other aryl chlorides for the generation of catalytically active species. We found *p*-tolyl chloride was ineffective, presumably because it could not undergo oxidative addition with Ni(COD)₂ to generate the catalytically active species (Table 2, entry 3). Gratifyingly, we found 4-chloroacetophenone/Ni(COD)₂ and 4-chlorobenzophenone/Ni(COD)₂ exhibited higher catalytic activity than that of 4-chlorobenzaldehyde/Ni(COD)₂ (Table 2, entries 4, 5). By extending the reaction time to 3 h, excellent conversion was achieved (Table 2, entry 6). Further testing revealed that the use of 10% 4-chlorobenzophenone was sufficient to achieve excellent conversion (Table 2, entries 6–8).

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Table 1Nickel-catalyzed addition reactions of phenylboronic acid/phenylboroxine with benzaldehydes^a

Entry	Ni Catalyst	K ₃ PO ₄	PhB(OR) ₂	ArCHO	Conversion ^b (%)
1	Ni(PPh ₃)Br ₂	A or B			0 ^c
2	NiBr ₂	A or B			0 ^c
3	NiBr ₂ + 2 COD	A or B			0 ^c
4	Ni(COD) ₂	B			10 ^{c,d}
5	Ni(COD) ₂	B			57
6	Ni(COD) ₂	A			27 ^e
7	Ni(COD) ₂	C			8
8	Ni(COD) ₂ /PCy ₃	B			0
9	Ni(COD) ₂	B			0
10	Ni(COD) ₂	B			<5 ^c
11	Ni(COD) ₂	B			<1 ^f
12	Ni(COD) ₂	B			25 ^g
13	Ni(COD) ₂	B			0
14	Ni(COD) ₂	B			0

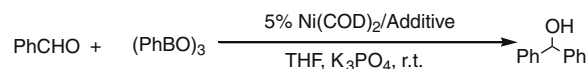
^a Based on ¹H NMR.^b Based on ¹H NMR.^c Reaction time 10 h.^d A ratio of 60:40 of addition product:cross-coupling product was observed.^e A ratio of 81:19 of addition product:cross-coupling product was observed.^f Reaction time 3 h.^g A ratio of 82:18 of addition product:cross-coupling product was observed.**Scheme 1.** Reported mechanism for Ni(COD)₂-catalyzed addition reactions of organoboron reagents with aldehydes.

By using 5% Ni(COD)₂ and 10% 4-chlorobenzophenone as the catalyst, we examined the addition reaction of other arylboroxines with different aldehydes. Our results are summarized in Table 3. Different aromatic aldehydes including activated and deactivated ones all gave high yields of addition products (Table 3, entries 1–9). *Ortho*-substituted *o*-methoxybenzaldehyde was also tested and was found to be an excellent substrate (Table 3, entries 10–11). We have further examined the addition reaction with aliphatic aldehydes as substrates and found that they were also excellent substrates (Table 3, entries 12–17).

The addition reaction of phenylboroxine with cinnamaldehyde was also tested.^{13–15} We found that only 59% conversion was observed after 10 h. As 3,3-diphenylpropanal smoothly underwent addition reaction with phenylboroxine (Table 3, entry 16), the observation of 3,3-diphenylpropanal being obtained as the product suggested that 3,3-diphenylpropanal was likely formed from **A** during the reaction workup (Scheme 2).

We also tested the addition reaction of 4-methoxyphenylboroxine with 4-chloroacetophenone. We found that the addition went very slowly, with only 60% conversion being observed after 10 h (Scheme 3). The slower addition reaction permitted more cross-cou-

pling to occur as significant amounts of cross-coupling product was observed.

Table 2Ni(COD)₂/additive-catalyzed addition reactions of phenylboroxine with benzaldehyde^a

Entry	Additive	Amount of additive (%)	Time	Conversion ^b (%)
1		100	1 h	42
2		20	30 min	8
3		20	30 min	0
4		20	30 min	25
5		20	30 min	29
6		20	3 h	99
7		10	3 h	95
8		5	3 h	62

^a Reaction conditions: aldehyde (0.25 mmol), phenylboroxine (0.5 equiv), THF (1 mL), K₃PO₄ (2 equiv), rt.^b Based on ¹H NMR. 5% Ni(COD)₂/additive.

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