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$Ni(COD)_2/4\text{-}ClC_6H_4COR$-catalyzed addition reactions of arylboroxines with aldehydes

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ABSTRACT

$Ni(COD)_2/4\text{-}ClC_6H_4COR$ (R = H, CH_3, 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 $Ni(COD)_2/4\text{-}ClC_6H_4COR$ catalyst systems was likely to be their oxidative addition adducts, $4\text{-}RCOC_6H_4\text{-}Ni(II)Cl(COD)$ complexes.

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) complexes[5] Cu(II) complexes,[6] Fe(III)[7] complexes, and more recently Ru(II) complexes[8] have been reported to catalyze this type of addition reactions. In our laboratory, we have initiated a program to investigate metalacycles, 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 $(COD)_2/4\text{-}ClC_6H_4COR$ (R = H, CH_3, 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 $Ni(PPh_3)_2Br_2$, $NiBr_2$, and $NiBr_2$/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 K_3PO_4 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 $Ni(COD)_2/PCy_3$, 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 $4\text{-}HCOC_6H_4NiX(\text{-}COD)$ (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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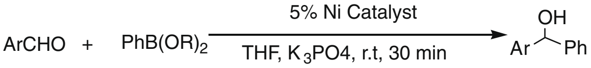
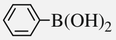
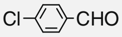
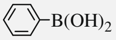
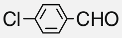
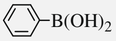
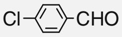
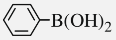
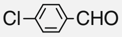
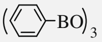
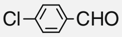
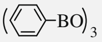
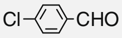
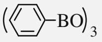
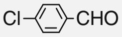
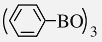
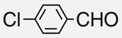
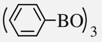
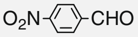
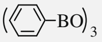
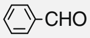
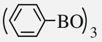
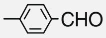
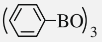
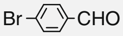
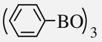
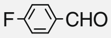
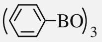
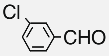
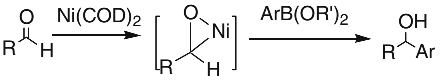
Table 1

Nickel-catalyzed addition reactions of phenylboronic acid/phenylboroxine with benzaldehdyes[a]



Entry	Ni Catalyst	K_3PO_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.

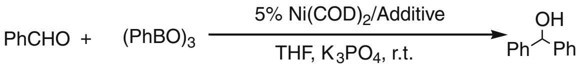
By using 5% $Ni(COD)_2$ and 10% 4-chlorobenzophenone as the catalyst, we examined the addition reaction of other arylboroxines with different aldehydes. Our results are summarized in Table 3. Different aromatic aldehydes including activated and deactivated ones all gave high yields of addition products (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).

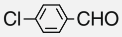
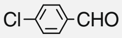
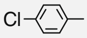
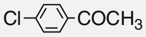
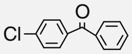
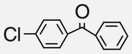
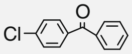
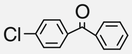
The addition reaction of phenylboroxine with cinnamaldehyde was also tested.[13–15] We found that only 59% conversion was observed after 10 h. As 3,3-diphenylpropanal smoothly underwent addition reaction with phenylboroxine (Table 3, entry 16), the observation of 3,3-diphenylpropanal being obtained as 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-coupling to occur as significant amounts of cross-coupling product was observed.

Table 2

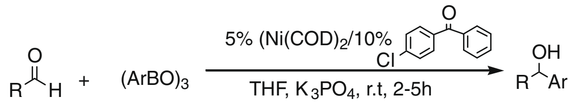
$Ni(COD)_2$/additive-catalyzed addition reactions of phenylboroxine with benzaldehyde[a]

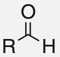
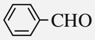
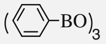
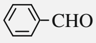
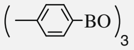
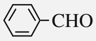
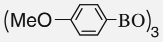
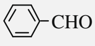
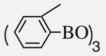
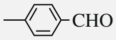
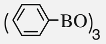
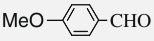
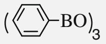
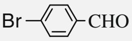
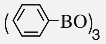
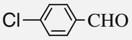
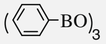
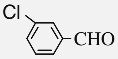
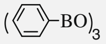
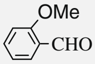
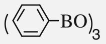
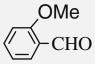
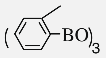
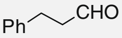
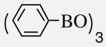
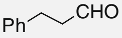
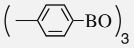
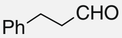
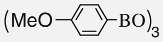
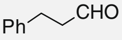
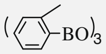
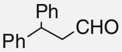
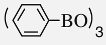
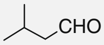
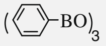
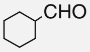
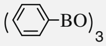


Entry	Additive	Amount of additive (%)	Time	Conversion[b] (%)
1		100	1 h	42
2		20	30 min	8
3		20	30 min	0
4		20	30 min	25
5		20	30 min	29
6		20	3 h	99
7		10	3 h	95
8		5	3 h	62

[a] Reaction conditions: aldehyde (0.25 mmol), phenylboroxine (0.5 equiv), THF (1 mL), K_3PO_4 (2 equiv), rt.
[b] Based on ^1H NMR. 5% $Ni(COD)_2$/additive.

Table 3
$Ni(COD)_2$/4-chlorobenzophenone-catalyzed addition reactions of arylboroxines with aldehydes[a]



Entry		$(ArBO_3)$	Yield[b] (%)
1			92
2			96
3			95
4			91
5			94
6			92
7			89
8			94
9			87
10			85
11			94
12			87
13			86
14			93
15			81
16			87.5
17			95
18			95

[a] Reaction conditions: aldehyde (1.0 equiv), phenylboronic acid (0.5 equiv), THF (2 mL), K_3PO_4 (2 equiv), rt for 2–5 h.
[b] Isolated yields.

In summary, we have demonstrated that $Ni(COD)_2$/4-ClC_6H_4COR (R = H, CH_3, Ph) was an efficient catalyst system for the addition reactions of arylboroxines with aromatic and aliphatic aldehydes. Our results suggested that the catalytically active species for the $Ni(COD)_2$/4-ClC_6H_4COR catalyst system was different from that of reported nickel-catalyzed addition reactions of organoborons with aldehydes, in which Ni(0) species was believed to the catalytically active species. The catalytically active species in our $Ni(COD)_2$/4-ClC_6H_4COR catalyst system was likely to be their oxidative addition adducts, 4-$RCOC_6H_4Ni(II)Cl(COD)$ (R = H, CH_3, Ph) complexes. Our future work will be directed to elucidate the mechanistic details of the catalyst system and explore the application of the system to other organoboron species and substrates.

Acknowledgments

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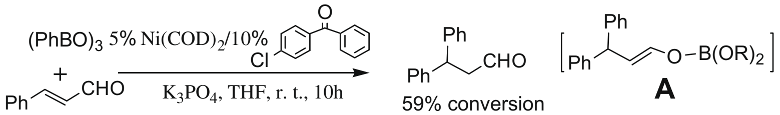
Supplementary data

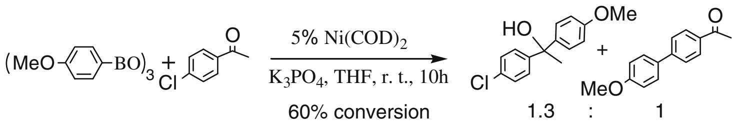
Supplementary data (general procedure of $Ni(COD)_2$/4-ClC_6H_4COR-catalyzed addition reactions and characterizations of the reaction products) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.12.033.

References and notes

1. For recent reviews on Rh(I)-catalyzed addition reactions of arylboronic acids with carbonyl containing compounds: (a) Glorius, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3364–3366; (b) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829–2844; (c) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169–196. and references cited therein.
2. Selected examples of Rh(I)-catalyzed 1,2-addition of arylboronic acids with aldehydes: (a) Xing, C.-H.; Liu, T.-P.; Zheng, J. R.; Ng, J.; Eposito, M.; Hu, Q.-S. *Tetrahedron Lett.* **2009**, *50*, 4953–4957; (b) Trindade, A. F.; Gois, P. M. P.; Veiros, L. F.; Andre, V.; Duarte, M. T.; Afonso, C. A. M.; Caddick, S.; Cloke, F. G. N. *J. Org. Chem.* **2008**, *73*, 4076–4086; (c) Tuerkmen, H.; Denizalti, S.; Oezdemir, I.; Cetinkaya, E.; Cetinkaya, B. *J. Organomet. Chem.* **2008**, *693*, 425–434; (d) Gois, P. M. P.; Trindade, A. F.; Veiros, L. F.; Andre, V.; Duarte, M. T.; Afonso, C. A. M.; Caddick, S.; Cloke, F. G. N. *Angew. Chem., Int. Ed.* **2007**, *46*, 5750–5753; (e) Jagt, R. B. C.; Toullec, P. Y.; Schudde, E. P.; De Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *J. Comb. Chem.* **2007**, *9*, 407–414; (f) Kilincarslan, R.; Yigit, M.; Ozdemir, I.; Cetinkaya, E.; Cetinkaya, B. J. *Heterocycl. Chem.* **2007**, *44*, 69–73; (g) Yigit, M.; Oezdemir, I.; Cetinkaya, E.; Cetinkaya, B. *Transition Met. Chem.* **2007**, *32*, 536–540; (h) Arao, T.; Suzuki, K.; Kondo, K.; Aoyama, T. *Synthesis* **2006**, 3809–3814; (i) Yan, C.; Zeng, X.; Zhang, W.; Luo, M. *J. Organomet. Chem.* **2006**, *691*, 3391–3396; (j) Suzuki, K.; Ishii, S.; Kondo, K.; Aoyama, T. *Synlett* **2006**, 648–650; (k) Ozdemir, I.; Yigit, M.; Cetinkaya, E.; Cetinkaya, B. *Heterocycles* **2006**, *68*, 1371–1379; (l) Suzuki, K.; Kondo, K.; Aoyama, T. *Synthesis* **2006**, 1360–1364; (m) Duan, H. F.; Xie, J.-H.; Shi, W.-J.; Zhang, Q.; Zhou, Q.-L. *Org. Lett.* **2006**, *8*, 1479–1481; (n) Jagt, R. B. C.; Toullec, P. Y.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Org. Biomol. Chem.* **2006**, *4*, 773–775; (o) Chen, J.; Zhang, X.; Feng, Q.; Luo, M. *J. Organomet. Chem.* **2006**, *691*, 470–474; (p) Oezdemir, I.; Guerbuez, N.; Seckin, T.; Cetinkaya, B. *Heteroat. Chem.* **2005**, *16*, 461–465; (q) Yigit, M.; Ozdemir, I.; Cetinkaya, E.; Cetinkaya, B. *Appl. Organomet. Chem.* **2005**, *19*, 633–638; (r)



Scheme 2. $Ni(COD)_2$/4-Chlorobenzophenone-catalyzed addition reactions of phenylboroxine with cinnamaldehyde.



Scheme 3. $Ni(COD)_2$-catalyzed addition reactions of 4-methoxyphenylboroxine with 4-chloroacetophenone.

Oezdemir, I.; Guerbuez, N.; Goek, Y.; Cetinkaya, B.; Cetinkaya, E. *Transition Met. Chem.* **2005**, *30*, 367–371; (s) Son, S. U.; Kim, S. B.; Reingold, J. A.; Carpenter, G. B.; Sweigart, D. A. *J. Am. Chem. Soc.* **2005**, *127*, 12238–12239; (t) Zhang, W.; Qin, Y.; Zhang, S.; Luo, M. *ARKIVOC* **2005**, *14*, 39–48; (u) Focken, T.; Rudolph, J.; Bolm, C. *Synthesis* **2005**, 429–436; (v) Huang, R.; Shaughnessy, K. H. *Chem. Commun.* **2005**, 4484–4486; (w) Ozdemir, I.; Demir, S.; Cetinkaya, B. *J. Mol. Catal. A: Chem.* **2004**, *215*, 45–48; (x) Imlinger, N.; Mayr, M.; Wang, D.; Wurst, K.; Buchmeiser, M. R. *Adv. Synth. Catal.* **2004**, *346*, 1836–1843; (y) Moreau, C.; Hague, C.; Weller, A. S.; Frost, C. G. *Tetrahedron Lett.* **2001**, *42*, 6957–6960; (z) Pourbaix, C.; Carreaux, F.; Carboni, B. *Org. Lett.* **2001**, *3*, 803–805; Batey, R. A.; Thadani, A. N.; Smil, D. V. *Org. Lett.* **1999**, *1*, 1683–1686.

3. (a) Chuzel, O.; Alexander Roesch, A.; Jean-Pierre Genet, J.-P.; Darses, S. *J. Org. Chem.* **2008**, *73*, 7800–7802; (b) Mora, G.; Darses, S.; Genet, J.-P. *Adv. Synth. Catal.* **2007**, *349*, 1180–1184; (c) Imlinger, N.; Wurst, K.; Buchmeiser, M. R. *J. Organomet. Chem.* **2005**, *690*, 4433–4440; (d) Pucheault, M.; Darses, S.; Genet, J.-P. *J. Am. Chem. Soc.* **2004**, *126*, 15356–15357.
4. For Palladium(II)-catalyzed 1,2-addition of arylboronic acids with aldehydes: (a) Yamamoto, T.; Iizuka, M.; Takenaka, H.; Ohta, T.; Ito, Y. *J. Organomet. Chem.* **2009**, *694*, 1325–1332; (b) Yu, A.; Cheng, B.; Wu, Y.; Li, J.; Wei, K. *Tetrahedron Lett.* **2008**, *49*, 5405–5407; (c) Kuriyama, M.; Shimazawa, R.; Shirai, R. *J. Org. Chem.* **2008**, *73*, 1597–1600; (d) Qin, C.; Wu, H.; Cheng, J.; Chen, X.; Liu, M.; Zhang, W.; Su, W.; Ding, J. *J. Org. Chem.* **2008**, *73*, 4102–4107; (e) Nishikata, T.; Kiyomura, S.; Yamamoto, Y.; Miyaura, N. *Synlett* **2008**, 2487–2490; (f) Francesco, I. N.; Wagner, A.; Colobert, F. *Eur. J. Org. Chem.* **2008**, *34*, 5692–5695; (g) Kuriyama, M.; Shimazawa, R.; Enomoto, T.; Shirai, R. *J. Org. Chem.* **2008**, *73*, 6939–6942; (h) Liu, G.; Lu, X. *Tetrahedron* **2008**, *64*, 7324–7330; (i) Lin, S.; Lu, X. *J. Org. Chem.* **2007**, *72*, 9757–9760; (j) Novodomska, A.; Dudicova, M.; Leroux, F. R.; Colobert, F. *Tetrahedron: Asymmetry* **2007**, *18*, 1628–1634; (k) Qin, C.; Wu, H.; Cheng, J.; Chen, X.; Liu, M.; Zhang, W.; Su, W.; Ding, J. *J. Org. Chem.* **2007**, *72*, 4102–4107; (l) Liu, G.; Lu, X. *J. Am. Chem. Soc.* **2006**, *128*, 16504–16505; (m) Suzuki, K.; Arao, T.; Ishii, S.; Maeda, Y.; Kondo, K.; Aoyama, T. *Tetrahedron Lett.* **2006**, *47*, 5789–5792; (n) Yamamoto, T.; Ohta, T.; Ito, Y. *Org. Lett.* **2005**, *7*, 4153–4155; Also see: (o) Gibson, S.; Foster, D. F.; Eastham, G. R.; Tooze, R. P.; Cole-Hamilton, D. J. *Chem. Commun.* **2001**, 779–780.
5. For nickel-catalyzed 1,2-addition of arylboronic acids/borates with aldehydes: (a) Bouffard, J.; Itami, K. *Org. Lett.* **2009**, *11*, 4410–4413; (b) Zhou, L.; Du, X.; He, R.; Ci, Z.; Bao, M. *Tetrahedron Lett.* **2009**, *50*, 406–408; (c) Yamamoto, K.; Tsurumi, K.; Sakurai, f.; Kondo, K.; Aoyama, T. *Synthesis* **2008**, 3585–3590; (d) Arao, T.; Kondo, K.; Aoyama, T. *Tetrahedron Lett.* **2007**, *48*, 4115–4117; (e) Takahashi, G.; Shirakawa, E.; Tsuchimoto, T.; Kawakami, Y. *Chem. Commun.* **2005**, 1459–1461; (f) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2005**, *7*, 4689–4691.
6. For copper-catalyzed 1,2-addition of arylboronic acids with aldehydes: (a) Zheng, H.; Zhang, Q.; Chen, J.; Liu, M.; Cheng, S.; Ding, J.; Wu, H.; Su, W. *J. Org. Chem.* **2009**, *74*, 943–945; (b) Tomita, D.; Kanai, M.; Shibasaki, M. *Chem. Asian J.* **2006**, *1*, 161–166.
7. For iron-catalyzed 1,2-addition of arylboronic acids with aldehydes: Zou, T.; Pi, S.-S.; Li, J.-H. *Org. Lett.* **2009**, *11*, 453–456.
8. Yamamoto, Y.; Kurihara, K.; Miyaura, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 4414–4416.
9. Jia, X.; Fang, L.; Lin, A.; Pan, Y.; Zhu, C. *Synlett* **2009**, 495–499.
10. Recent reviews of metalacycles: (a) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527–2572; (b) Beletskaya, I. P.; Cheprakov, A. V. *J. Organomet. Chem.* **2004**, *689*, 4055–4082; (c) Bedford, R. B. *Chem. Commun.* **2003**, 1787–1796; (d) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. E. *Chem. Rev.* **1986**, *86*, 451–489.
11. (a) Liao, Y.-X.; Xing, C.-H.; He, P.; Hu, Q.-S. *Org. Lett.* **2008**, *10*, 2509–2512; (b) He, P.; Lu, Y.; Dong, C.-G.; Hu, Q.-S. *Org. Lett.* **2007**, *9*, 343–346; (c) He, P.; Lu, Y.; Hu, Q.-S. *Tetrahedron Lett.* **2007**, *48*, 5283–5288.
12. (a) Bedford, R. B.; Betham, M.; Charmant, J. P. H.; Haddow, M. F. A.; Orpen, G.; Pilarski, L. T.; Coles, S. J.; Hursthouse, M. B. *Organometallics* **2007**, *26*, 6346–6353; Also see: (b) Gibson, S.; Foster, D. F.; Eastham, G. R.; Tooze, R. P.; Cole-Hamilton, D. J. *Chem. Commun.* **2001**, 779–780.
13. (a) Tang, Z.-Y.; Hu, Q.-S. *J. Am. Chem. Soc.* **2004**, *126*, 3058–3059; (b) Tang, Z.-Y.; Hu, Q.-S. *J. Org. Chem.* **2006**, *71*, 2167–2169; (c) Tang, Z.-Y.; Hu, Q.-S. *Adv. Synth. Catal.* **2004**, *346*, 1635–16367.
14. For Rh(I)-catalyzed 1,4-addition reactions of arylboronic acids with α, β-unsaturated aldehydes: (a) Nishimura, T.; Nagaosa, M.; Hayashi, T. *Chem. Lett.* **2008**, *37*, 860–861; (b) Wuitschik, G.; Rogers-Evans, M.; Mueller, K.; Fischer, H.; Wagner, B.; Schuler, F.; Polonnchuk, L.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7736–7739; (c) Douglas, T. M.; Le Notre, J.; Brayshaw, S. K.; Frost, C. G.; Weller, Andrew S. *Chem. Commun.* **2006**, 3408–3410; (d) Fujita, N.; Motokura, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Jitsukawa, K.; Kaneda, K. *Tetrahedron Lett.* **2006**, *47*, 5083–5087; (e) Trenkle, W. C.; Barkin, J. L.; Son, S. U.; Sweigart, D. A. *Organometallics* **2006**, *25*, 3548–3551; (f) Paquin, J.-F.; Defieber, C.; Stephenson, C. R. J.; Carreira, E. M. *J. Am. Chem. Soc.* **2005**, *127*, 10850–10851; (g) Hayashi, T.; Tokunaga, N.; Okamoto, K.; Shintani, R. *Chem. Lett.* **2005**, *34*, 1480–1481; (h) Itooka, R.; Iguchi, Y.; Miyaura, N. *J. Org. Chem.* **2003**, *68*, 6000–6004; (i) Paquin, J.-F.; Stephenson, C. R. J.; Defieber, C.; Carreira, E. M. *Org. Lett.* **2005**, *7*, 3821–3824.
15. For Pd-catalyzed 1,4-additions of arylboronic acids with α, β-unsaturated aldehydes: (a) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Tetrahedron Lett.* **2007**, *48*, 4007–4010; (b) Lin, S.; Lu, X. *Tetrahedron Lett.* **2006**, *47*, 7167–7170; (c) Lu, X.; Lin, S. *J. Org. Chem.* **2005**, *70*, 9651–9653; (d) Gini, F.; Hessen, B.; Minnaard, A. J. *Org. Lett.* **2005**, *7*, 5309–5312; (e) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, *23*, 4317–4324; (f) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2768–2770.