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# Phosphinite- and phosphite-based type I palladacycles as highly active catalysts for addition reactions of arylboronic acids with aldehydes, α,β-unsaturated ketones, α-ketoesters, and aldimines

Ping He, Yong Lu and Qiao-Sheng Hu*

*Department of Chemistry, College of Staten Island and the Graduate Center of the City University of New York, Staten Island, NY 10314, United States*

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**Abstract**—Phosphinite- and phosphite-based type **I** palladacycle-catalyzed additions of arylboronic acids with aldehydes, α,β-unsaturated ketones, α-ketoesters, and aldimines are described. Our study showed that readily available phosphinite- and phosphite-based type **I** palladacycles could possess higher catalytic activity than phosphine-based palladacycles and were highly active, practical catalysts. Our study may pave the road for development of optically active phosphinite- and phosphite-based palladacycles for asymmetric catalysis.

Palladium-catalyzed cross-coupling reactions, for example, the Suzuki coupling, the Stille coupling, the Heck coupling, the Sonogashira coupling, and the amination of aryl halides with amines, etc., have emerged as powerful tools for organic synthesis over the past decades.[1,2] Extensive studies established that there are three key elementary steps in the catalytic cycles of Pd(0)-catalyzed cross-coupling reactions:[1] oxidative addition of Pd(0) with an aryl halide to form Pd(II) complex; transmetalation of the Pd(II) complex with an organometallic reagent to form a diorganopalladate complex; and reductive elimination of the diorganopalladate complex to form the cross-coupling product and regenerate the Pd(0) catalyst (Fig. 1). In our laboratory, we are interested in developing highly active transition metal catalysts and new reactions/processes to further heighten the efficiency of transition metal catalysis.[3–6] Based on our understanding of the generalized mechanism depicted in Figure 1, we envisioned that the individual elementary steps in each catalytic cycle might be controlled. Such a control, especially combined with other bond forming processes, could provide us opportunities to develop new reactions/processes and thus make the already powerful transition metal-catalyzed cross-coupling reactions be even more powerful for organic synthesis. Toward this end, we have recently documented Pd(0)/*t*-Bu$_3$P-catalyzed Suzuki cross-coupling of dihaloarenes with arylboronic acids,[5] a process that relies on the controlling of oxidative addition step. We have also reported Pd-catalyzed reaction of *o*-dihaloarenes and alkynes with hindered Grignard reagents to form substituted fluorenes and indenes,[6] cyclization processes that combines the control of the transmetalation step with sp$^3$ C–H activation.

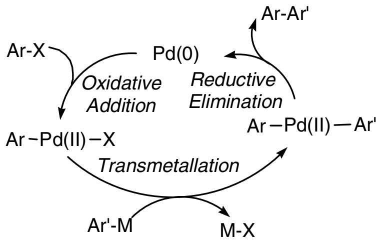

**Figure 1.** Generalized mechanism for Pd-catalyzed cross-coupling reactions.

Our study also included the control of a reductive elimination elementary step. We envisioned that by controlling the reductive elimination process, anionic four-electron donor-based (type **I**) palladacycles,[7,8] rather

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* Corresponding author. Tel.: +1 718 982 3901; fax: +1 718 982 3910; e-mail: qiaohu@mail.csi.cuny.edu

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doi:10.1016/j.tetlet.2007.05.119

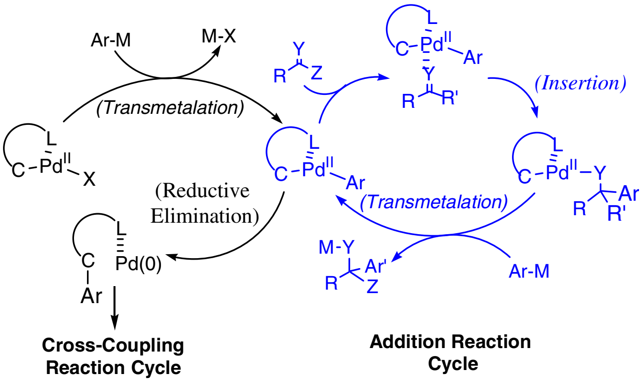


**Figure 2.** Cross-coupling reactions versus addition reactions for type **I** palladacycle catalysts.

than functioning as cross-coupling catalyst precursors, could catalyze addition reactions of organometallic reagents such as arylboronic acids with carbonyl group-containing compounds and analogs (Fig. 2). We have demonstrated that phosphine-based type **I** palladacycles **1–3** (Chart 1) were indeed effective catalysts for addition reactions of arylboronic acids with α,β-unsaturated ketones, aldehydes, and α-ketoesters.[9] Although palladacycle **3** was found to be a very efficient catalyst for such addition reactions, it was prepared from non-commercially available phosphine precursor. In addition, as the catalytic activity of a type **I** palladacycle is expected to be influenced by the steric and electronic nature of palladium-bound aromatic part and the P-ligand part, we envisioned that phosphine-based palladacycle **3** may not be the one with the highest catalytic activity and type **I** palladacycles with other Pd-bound aromatic parts and P-ligand part might possess higher catalytic activity than that of **3**. These considerations prompted us to examine palladacycles derived from readily available and more π-acidic phosphinites and phosphites, that is, **4–7** (Fig. 3),[10,11] for addition reactions of arylboronic acids with carbonyl group-containing compounds. In this Letter, we report that phosphinite- and phosphite-based palladacycles could indeed be more active than phosphine-based palladacycle **3**, and are highly efficient catalysts for the addition reactions of arylboronic acids with aldehydes, α-ketoesters, α,β-unsaturated ketones, and aldimines.

We began our study by comparing the catalytic activities of phosphinite-based palladacycles **4**, **5** and phosphite-based palladacycles **6**, **7** with that of phosphine-based palladacycle **3**, under the reaction conditions we previously established (toluene as the solvent and $K_3PO_4$ as the base).[9] The room temperature addition of phenylboronic acid with 2-nitrobenzaldehyde was first studied and our results are listed in Table 1.[12] We found that palladacycles **4**, **5**, and **7** exhibited a higher catalytic activity than **3** (Table 1, entries 1–3, 5, and 6). Lower catalytic activity was observed for phosphite-based palladacycle **6** (Table 1, entry 4), suggesting that the steric hindrance of Pd-bound aromatic part also plays an important role for the catalytic activity of palladacycles. We have further employed less reactive 2-methoxybenzaldehyde as substrates and palladacycles **4**, **5**, and **7** again exhibited a higher catalytic activity than **3**, with phosphite-based palladacycle **7** being the most active one (Table 1, entries 6–9).

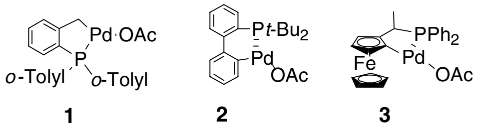


**Chart 1.** Phosphine-based type **I** palladacycles.

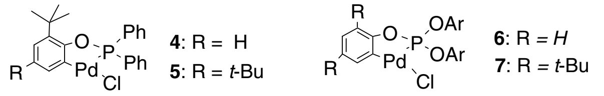
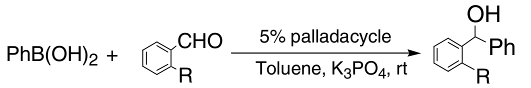


**Figure 3.** Phosphinite- and phosphite-based type **I** palladacycles.

**Table 1.** Catalyst comparison[a]



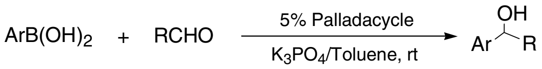
| Entry | Palladacyde | R | Reaction time | Conversion[b] (%) |
|---|---|---|---|---|
| 1 | **3** | $NO_2$ | 30 min | 88 |
| 2 | **4** | $NO_2$ | 30 min | 100 |
| 3 | **5** | $NO_2$ | 30 min | 100 |
| 4 | **6** | $NO_2$ | 30 min | 49 |
| 5 | **7** | $NO_2$ | 30 min | 100 |
| 6 | **3** | $OCH_3$ | 4 h | 26 |
| 7 | **4** | $OCH_3$ | 4 h | 72 |
| 8 | **5** | $OCH_3$ | 4 h | 59 |
| 9 | **7** | $OCH_3$ | 4 h | 83 |

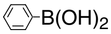
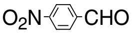
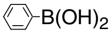
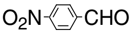
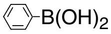
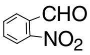
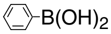
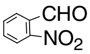
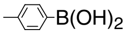
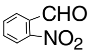
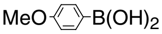
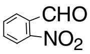
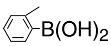
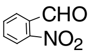
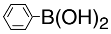
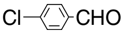
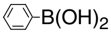
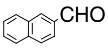
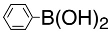
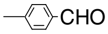
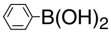
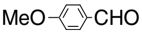
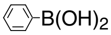
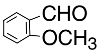
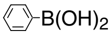
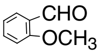
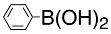
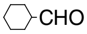
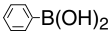
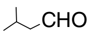
[a] Reaction conditions: aldehyde (1.0 equiv), phenylboronic acid (2.0 equiv), toluene (2 mL), $K_3PO_4$ (1 equiv), room temperature.
[b] Based on $^1$H NMR.

Having established that phosphinite-based palladacycles **4**, **5** and phosphite-based palladacycle **7** possess a higher catalytic activity than phosphine-based palladacycle **3**, we next briefly examined the addition of arylboronic acids with aldehydes, α,β-unsaturated ketones, and α-ketoesters by employing palladacycles **4**, **5**, and **7** as catalysts. Our results are listed in Tables 2–4, respectively. We found palladacycles **4**, **5**, and **7** in general were highly active catalysts for these addition reactions. High yields were observed for tested aldehydes including aromatic and aliphatic ones (Table 2),[12,13] α,β-unsaturated ketones including cyclic and acyclic ones (Table 3),[14] and α-ketoesters (Table 4).[15] In terms of substrate reactivity, α,β-unsaturated ketones were found to be the most reactive, with aldehydes being next and α-ketoesters the least reactive, a trend similar to what was observed in our study with palladacycle **3** as catalyst.

We have also examined the addition reaction of arylboronic acids with aldimines and our results are listed in Table 5.[16,17] We found **4** and **7** were also effective catalysts for *N*-Ts- and *N*-Bs-containing aldimines in general. We found that when aldimines derived from

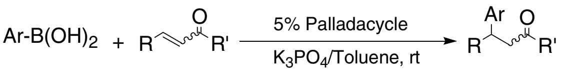
**Table 2.** Phosphinite- and phosphite-based palladacycle-catalyzed addition reactions of arylboronic acids with aldehydes[a]

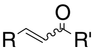
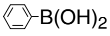
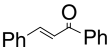
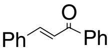
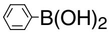
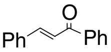
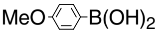
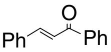


| Entry | $ArB(OH)_2$ | RCHO | Palladacycle | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 |  |  | **7** | 1 | 94 |
| 2 |  |  | **7** | 5 | 86[c] |
| 3 |  |  | **5** | 0.5 | 91 |
| 4 |  |  | **7** | 0.5 | 94 |
| 5 |  |  | **7** | 0.5 | 92 |
| 6 |  |  | **7** | 0.5 | 93 |
| 7 |  |  | **7** | 0.5 | 92 |
| 8 |  |  | **7** | 48 | 88 |
| 9 |  |  | **7** | 36 | 84 |
| 10 |  |  | **7** | 48 | 91 |
| 11 |  |  | **7** | 48 | 90 |
| 12 |  |  | **4** | 14 | 93 |
| 13 |  |  | **7** | 10 | 90 |
| 14 |  |  | **7** | 48 | 93 |
| 15 |  |  | **7** | 48 | 90 |

[a] Reaction conditions: aldehyde (1.0 equiv), arylboronic acid (1.5–2.0 equiv), $K_3PO_4$ (1–3 equiv), toluene (2 mL), room temperature.
[b] Isolated yields (average of two runs).
[c] 5 mmol scale, 1% **7** was used.

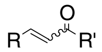
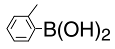
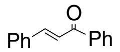
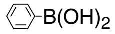
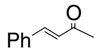
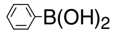
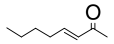
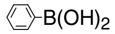
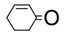
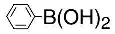
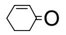
**Table 3.** Palladacycles **4**/**7**-catalyzed 1,4-addition of arylboronic acids with α,β-unsaturated ketones[a]



| Entry | $ArB(OH)_2$ |  | Palladacycle | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 |  |  | **4** | 0.5 | 95 |
| 2 |  |  | **7** | 0.5 | 98 |
| 3 |  |  | **7** | 5 | 96[c] |
| 4 |  |  | **7** | 0.5 | 94 |

(continued on next page)

**Table 3** (*continued*)

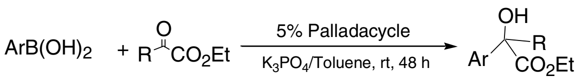
| Entry | ArB(OH)$_2$ |  | Palladacycle | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|
| 5 |  |  | **7** | 0.5 | 93 |
| 6 |  |  | **7** | 0.5 | 91 |
| 7 |  |  | **7** | 1 | 98 |
| 8 |  |  | **4** | 24 | 92 |
| 9 |  |  | **7** | 24 | 92 |

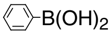
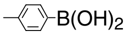
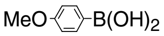
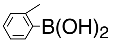
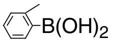
[a] Reaction conditions: ketone (1.0 equiv), arylboronic acid (2.0 equiv), **4** or **7** (5%), $K_3PO_4$ (1 equiv), toluene (2 mL), room temperature.

[b] Isolated yields (average of two runs).

[c] The reaction was carried out at a 4 mmol scale, 1% **7** was used.

**Table 4.** Palladacycles **4**/**7**-catalyzed 1,4-addition of arylboronic acids with α-ketoesters[a]



| Entry | ArB(OH)$_2$ | R | Palladacycle | Yield[b] (%) |
|---|---|---|---|---|
| 1 |  | Ph | **4** | 83 |
| 2 |  | Ph | **7** | 68[c] |
| 3 |  | Ph | **7** | 94 |
| 4 |  | Ph | **7** | 92 |
| 5 |  | $CH_3$ | **7** | 60 |

[a] Reaction conditions (not optimized): α-ketoester (1.0 equiv), arylboranic acid (2.0 equiv), $K_3PO_4$ (3 equiv), toluene (2 mL), room temperature.

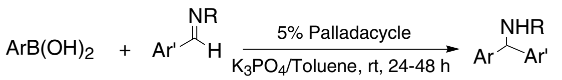
[b] Isolated yields (average of two runs).

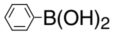
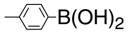
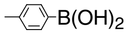
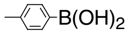
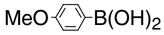
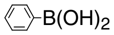
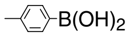
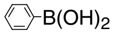
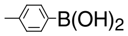
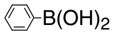
[c] 72% conversion.

*p*-nitrobenzaldehyde were used as substrates, (4-nitrophenyl)phenylmethanol was isolated in 21–29% yields (Table 5, entries 6–9), suggesting that the aldimines likely underwent hydrolysis during the reaction. We also found that the aldimine derived from aniline and benzaldehyde was not reactive, with either **4** or **7** as catalyst.

In summary, we have demonstrated that readily available phosphinite- and phosphite-based type **I** palladacycles **4**, **5**, and **7** exhibited a higher catalytic activity than that of phosphine-based type **I** palladacycle **3**, and were highly active catalysts for the addition reactions of arylboronic acids with aldehydes, α,β-unsaturated ketones, α-ketoesters, and aldimines. Our study may pave the road for the development of optically active phosphinite- and phosphite-based type **I** palladacycles for asymmetric catalysis.[18] Work toward this direction is actively underway.

**Table 5.** Palladacycles **4**/**7**-catalyzed addition reactions of arylboronic acids with aldimines[a]



| Entry | ArB(OH)$_2$ | R | Ar′ | Palladacycle | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 |  | Bs | $C_6H_5$ | **7** | 80 |
| 2 |  | Bs | $C_6H_5$ | **7** | 90 |
| 3 |  | Bs | $C_6H_5$ | **4** | 87 |
| 4 |  | Bs | *p*-MeO–$C_6H_4$ | **7** | 68 |
| 5 |  | Bs | *p*-MeO–$C_6H_4$ | **7** | 79 |
| 6 |  | Bs | *p*-$NO_2$–$C_6H_4$ | **7** | 67[c] |
| 7 |  | Bs | *p*-$NO_2$–$C_6H_4$ | **7** | 63[c] |
| 8 |  | Ts | *p*-$NO_2$–$C_6H_4$ | **7** | 69[c] |
| 9 |  | Ts | *p*-$NO_2$–$C_6H_4$ | **7** | 72[c] |
| 10 |  | Ph | $C_6H_5$ | **4** or **7** | 0 |

[a] Reaction conditions (not optimized): aldehyde (1.0 equiv), arylboronic acid (2.0 equiv), $K_3PO_4$ (1 equiv), toluene (2 mL), room temperature.

[b] Isolated yields (average of two runs).

[c] (Aryl)(4-nitrophenyl)methanol was also isolated in 21–29% yields.

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## Supplementary data

General procedures and product characterization for palladacycle-catalyzed addition reactions. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.05.119.

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