Published in final edited form as:

Tetrahedron Lett. 2007 July 23; 48(30): 5283–5288.

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, New York 10314

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, e. g., 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 an diorganopalladate complex; and reductive elimination of the diorganopalladate complex to form the cross-coupling product and regenerate the Pd(0) catalyst (Figure 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. Towards this end, we have recently documented Pd(0)/*t*-Bu₃P-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 indenenes,⁶ cyclization processes that combines the control of the transmetalation step with *sp*³ C–H activation.

Our study also included the control of reductive elimination elementary step. We envisioned that by controlling the reductive elimination process, anionic four-electron donor-based (Type I) palladacycles,^{7, 8} rather than functioning as cross-coupling catalyst precursors, could catalyze addition reactions of organometallic reagents such as arylboronic acids with carbonyl

Correspondence to: Qiao-Sheng Hu.

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group-containing compounds and analogs (Figure 2). We have demonstrated that phosphine-based Type **I** palladacycles **1–3** 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, i. e., **4–7**,^{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 higher catalytic activity than **3** (Table 1, entries 1, 2, 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 higher catalytic activity than **3**, with phosphite-based palladacycle **7** being the most active one (Table 1, entries 6–9).

Having established that phosphinite-based palladacycles **4, 5** and phosphite-based palladacycle **7** possess 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 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 *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 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 development of optically active phosphinite- and phosphite-based Type **I** palladacycles for asymmetric catalysis.¹⁸ Work toward this direction is actively underway

Supplementary Material

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Acknowledgements

We gratefully thank the NIH (GM69704) for funding. Partial support from PSC-CUNY Research Award Program is also gratefully acknowledged. We also thank Frontier Scientific, Inc. for its generous gifts of arylboronic acids and $\text{Pd}(\text{OAc})_2$.

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Figure 1.
Generalized Mechanism for Pd-Catalyzed Cross-Coupling Reactions

Figure 2.
Cross-Coupling Reactions vs. Addition Reactions for Type I Palladacycle Catalysts

Figure 3.
Phosphinite- and Phosphite-Based Type I Palladacycles

Chart 1.
Phosphine-Based Type I Palladacycles

Table 1Catalyst Comparison^a

Entry	Palladacycle	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), K₃PO₄ (1 equiv), room temperature.

^b Based on ¹H NMR.

Table 2
Phosphinite- and Phosphite-Based Palladacycle-Catalyzed Addition Reactions of Arylboronic Acids with Aldehydes ^a

$$\text{ArB(OH)}_2 + \text{RCHO} \xrightarrow[\text{K}_3\text{PO}_4/\text{Toluene, rt}]{\text{5\% Palladacycle}} \text{Ar}-\text{CH(OH)}-\text{R}$$

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

^aReaction conditions: aldehyde (1.0 equiv), arylboronic acid (1.5–2.0 equiv), K₃PO₄ (1 equiv - 3 equiv), toluene (2 mL), room temperature.

^bIsolated yields (average of two runs).

^c5 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	R ¹	R ²	Palladacycle	Time(h)	Yield(%) ^b
1		Ph	Ph	4	0.5	95
2		Ph	Ph	7	0.5	98
3		Ph	Ph	7	5	96 ^c
4		Ph	Ph	7	0.5	94
5		Ph	Ph	7	0.5	93
6		Ph	Ph	7	0.5	91
7		Ph	Ph	7	1	98
8		Ph	Ph	4	24	92
9		Ph	Ph	7	24	92

^aReaction conditions: ketone (1.0 equiv), arylboronic acid (2.0 equiv), **4** or **7** (5%), K₃PO₄ (1 equiv), toluene (2 mL), room temperature.

^bIsolated yields (average of two runs).

^cReaction was carried out at 4 mmol scale, 1% **7** was used.

Table 4Palladacycles **4/7**-Catalyzed Addition Reactions 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), arylboronic acid (2.0 equiv), K₃PO₄ (3 equiv), toluene (2 mL), room temperature.^b Isolated yields (average of two runs).^c 72% conversion.

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 ₆ H ₅	7	80
2		Bs	C ₆ H ₅	7	90
3		Bs	C ₆ H ₅	4	87
4		Bs	<i>p</i> -MeO-C ₆ H ₄	7	68
5		Bs	<i>p</i> -MeO-C ₆ H ₄	7	79
6		Bs	<i>p</i> -NO ₂ -C ₆ H ₄	7	67 ^c
7		Bs	<i>p</i> -NO ₂ -C ₆ H ₄	7	63 ^c
8		Ts	<i>p</i> -NO ₂ -C ₆ H ₄	7	69 ^c
9		Ts	<i>p</i> -NO ₂ -C ₆ H ₄	7	72 ^c
10		Ph	C ₆ H ₅	4 or 7	0

^aReaction conditions (not optimized): aldehyde (1.0 equiv), arylboronic acid (2.0 equiv), K₃PO₄ (1 equiv), toluene (2 mL), room temperature.

^bIsolated yields (average of two runs).

^c(aryl)(4-nitrophenyl)methanol was also isolated in 21–29% yields.