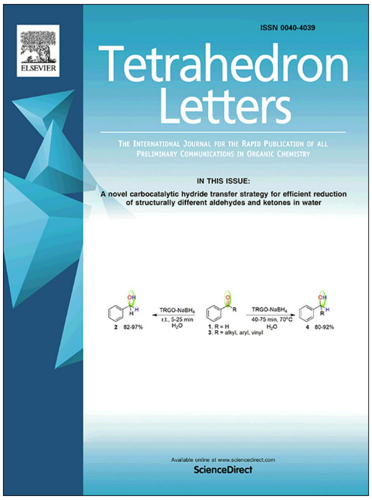

Room Temperature Pd(0)/Ad$_3$P-Catalyzed Coupling Reactions of Aryl Chlorides with Bis(pinacolato)diboron

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Graphical Abstract

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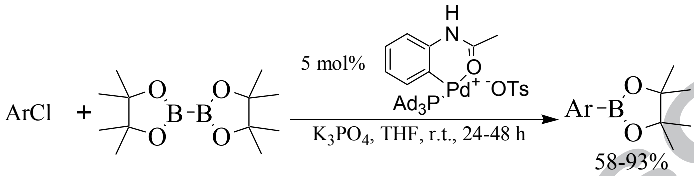

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Room Temperature Pd(0)/Ad$_3$P-Catalyzed Coupling Reactions of Aryl Chlorides with Bis(pinacolato)diboron

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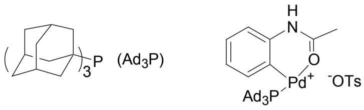
ABSTRACT

Room temperature Pd(0)/Ad$_3$P-catalyzed cross-coupling reactions of aryl chlorides with bis(pinacolato)diboron are described. The Pd(0)/Ad$_3$P catalyst, generated from Ad$_3$P-coordinated acetanilide-based palladacycle complex, proved to be an efficient catalyst system for the Miyaura borylation reactions of a variety of aryl chlorides with bis(pinacolato)diboron. The mild reaction condition, the easy availability of the catalyst and good coupling yields make these reactions potentially useful in organic synthesis.

Introduction

Since Miyaura's first report in 1995,[1] Pd(0)-catalyzed coupling reaction of aryl halides with bis(pinacolato)diboron has become one of the most attractive methods to access arylborates and analogs.[2-4] Aryl iodides/bromides and aryl triflates, which can readily undergo oxidative addition with Pd(0) catalysts, have been the common substrates. By employing bulky, electron-rich ligands including electron-rich phosphines, widely available but less reactive aryl chlorides also became general partners for this type of reaction.[5,6] However, elevated temperatures were generally needed in the reported borylation reactions with aryl chlorides as substrates.

In our laboratory, we have been interested in employing aryl chlorides as reaction partners for transition metal-catalyzed cross-coupling reactions under mild reaction conditions.[7] We have developed a ferrocenylmethylphosphine-containing polymer as unique ligands for room temperature Pd(0)-catalyzed Suzuki cross-coupling reaction of aryl chlorides with arylboronic acids.[7a] We have also documented room temperature Ni(0)/PPh$_3$-catalyzed cross-coupling reaction of aryl chlorides with arylboronic acids.[7b] Our study on these reactions prompted us to considered that Pd(0) catalysts that could readily undergo oxidative addition reaction with aryl chlorides might be able to catalyze the borylation reaction of aryl chlorides with bis(pinacolato)diboron under mild conditions. Recently, tris(1-adamantyl)phosphine (Ad$_3$P), recently reported by Carrow and his coworkers, is an electron-rich trialkylphospine.[8] Ad$_3$P-coordinated acetanilide-based palladacycle complex **1**, which could readily generate 12-electron (Ad$_3$P)Pd(0) species, was found to catalyze the Suzuki cross-coupling reaction of aryl chlorides with arylboronic acids under mild condition,[8] suggesting the oxidative addition reaction of Pd(0)/Ad$_3$P with aryl chlorides readily occurred. We thus reasoned that the borylation reaction of aryl chlorides with bis(pinacolato)diboron might be achieved under mild conditions with Pd(0)/Ad$_3$P as the catalyst. Herein our study on Pd(0)/Ad$_3$P-catalyzed-catalyzed cross-coupling reactions of aryl chlorides with bis(pinacolato)diboron is reported.

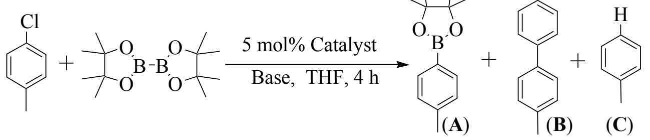


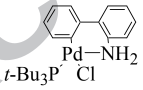
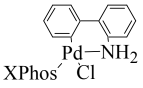
(1)

Figure 1. Tris(1-adamantyl)phosphine (Ad$_3$P) and Ad$_3$P-Coordinated Acetanilide-Based Palladacycle Complex **1**

Our study began with the coupling reaction of *p*-tolyl chloride with bis(pinacolato)diboron by examining different bases with complex **1** as the catalyst and tetrahydrofuran (THF) as the solvent. Our results are listed in Table 1. As KOAc was established to be the base in most of reported borylation reactions,[5,6] KOAc was first tested and a 35% conversion was observed (Table 1, entry 1). Other common inorganic bases were also tested and we found that stronger bases including KOH, K$_3$PO$_4$, K$_2$CO$_3$ and KHCO$_3$ gave higher conversions, but a significant amount of self-cross-coupling reaction product along with a small amount of the deboronated product, *p*-toluene, was observed (Table 1, entries 2-5). KF and NaOAc were found to give slightly lower conversions (Table 1, entries 6-7). The existence of water appeared to lead to faster reactions, but the formation of the deboronated product, *p*-toluene, was observed to be more with more amounts of water (Table 1, entries 8-9). We also examined the reaction with the use of 1:1 to 1:1.5 ratio of $Pd_2(dba)_3$ and Ad_3P as the catalyst and found that catalysts generated from 1:1 to 1:1.5 ratio of $Pd_2(dba)_3$ and Ad_3P were less efficient than complex **1** as lower conversions were observed (Table 1, entries 10-11). Toluene, dioxane and ethanol were also tested as the solvent. A lower conversion was observed with toluene as the solvent and higher conversions along with a significant amount of side product were observed with dioxane and EtOH as the solvent (Table 1, entries 12-14). Varying the amount of the KOAc impacted the reaction and higher conversion was observed with the use of more amounts of KOAc (Table 1 entries 15-17). We also examined the reaction with the use of 2-phenylaniline-based complex **2**[9] or **3**[10] as the catalyst and found that lower conversions were observed (Table 1, entries 18-19). By the lengthening the reaction time, a complete conversion was observed (Table 1, entry 20).

Table 1. Room Temperature Pd(0)/Ad_3P-catalyzed Borylation Reaction of *p*-Tolyl Chloride with Bis(pinacolato)diboron [a]

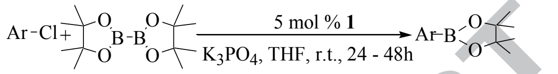


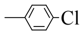
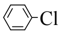
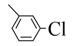
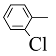
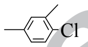
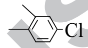
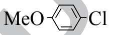
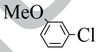
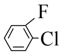
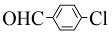
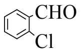
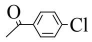
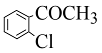
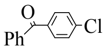
Entry	Base	Catalyst	Solvent	Conversion (%) (**A**:**B**:**C**)[b]
1	KOAc	**1**	THF	35 (100:0: 0)
2	KOH	**1**	THF	96 (31:68: 0)
3	K_3PO_4	**1**	THF	90 (14: 79: 7)
4	K_2CO_3	**1**	THF	85 (12: 88: 0)
5	$KHCO_3$	**1**	THF	56 (52:45:3)
6	KF	**1**	THF	25 (100:0: 0)
7	NaOAc	**1**	THF	28 (100:0: 0)
8	KOAc	**1**	THF	42 (98:0: 2) [c]
9	KOAc (2M)	**1**	THF	90 (72:0:28)[d]
10	KOAc	$Pd_2(dba)_3$/5%Ad_3P	THF	24 (92:0:8)
11	KOAc	$Pd_2(dba)_3$/7.5%Ad_3P	THF	29 (93: 0:7)
12	KOAc	**1**	Toluene	33 (100:0:0)
13	KOAc	**1**	Dioxane	60 (89:0:11)
14	KOAc	**1**	EtOH	71 (69:0:31)
15	KOAc	**1**	THF	27 (100:0:0) [e]
16	KOAc	**1**	THF	41 (100:0:0) [f]
17	KOAc	**1**	THF	50 (100:0:0) [g]
18	KOAc	 (**2**)	THF	23 (99:0:1)[g]
19	KOAc	 (**3**)	THF	31 (100:0:0)[g]
20	KOAc	**1**	THF	99 (100:0:0)[h]

a. Reaction conditions: *p*-tolyl chloride (1.0 equiv.), bis(pinacolato)diboron (3.0 equiv.), **1** (5 mol%), base (3 equiv.), THF (2 mL), room temperature, 4 h. b. Based on GC-MS data or ^1H NMR analysis. c. KOAc was used as received. d. 2M KOAc (aqueous solution) was used. e. 2 equivalents of base was used. f. 4 equivalents of base was used. g. 5 equivalents of base was used. h. Reaction time: 24 h.

With complex **1** as the catalyst, THF as the solvent and KOAc as the base, we next examined room temperature Pd(0)/Ad_3P-catalyzed borylation reactions of a number of aryl chlorides. Our results are summarized in Table 2. As shown in Table 2, complex **1** proved to be an efficient catalyst for both activated and deactivated aryl chlorides, including those with *ortho*-, *meta*- and *para*-substituents. Complete conversions and good isolated yields were observed for all aryl chlorides employed. Electron-poor (activated) aryl chlorides were more reactive than electron-rich aryl chlorides, and reactions involving them as the coupling partner required shorter reaction time to go to completion (Table 2, entry 10-14).

Table 2. Room Temperature Complex **1**-Catalyzed Borylation Reaction of Aryl Chlorides with Bis(Pinacolato)diboron [a]

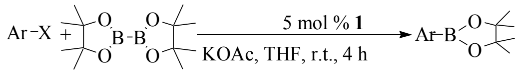


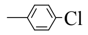
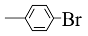
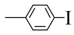
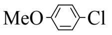
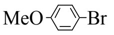
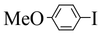
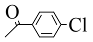
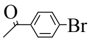
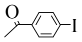
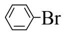
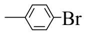
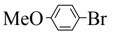
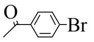
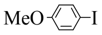
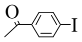
Entry	Ar-Cl		Yield(%)[b]
1		(**1a**)	88
2		(**1b**)	85
3		(**1c**)	87
4		(**1d**)	81
5		(**1e**)	88
6		(**1f**)	90
7		(**1g**)	93
8		(**1h**)	92
9		(**1i**)	80
10		(**1j**)	82[c]
11		(**1k**)	58
12		(**1l**)	85[c]
13		(**1m**)	70
14		(**1n**)	90

a. Reaction conditions: aryl chlorides (0.2 mmol), bis(pinacolato)diboron (3 equiv.), KOAc (4-5 equiv.), THF (1 mL), room temperature. b. Isolated yields. c. Reaction condition: 12 h.

We have also carried out the study of the borylation reaction of aryl iodides, aryl bromides and aryl chlorides with bis(pinacolato)diboron. We found under the same reaction condition, the reaction of aryl iodides occurred much slower than aryl chlorides and aryl bromides (Table 3). As aryl iodides have been established to readily undergo oxidative addition with Pd(0) catalysts,[11,12] the low conversion suggested that the transmetalation step might likely be the rate-determining step for the borylation reaction of aryl iodides with bis(pinacolato)diboron.[12] We found by lengthening the reaction time and using 4 equivalents of base, aryl bromides underwent the borylation reaction smoothly, yielding the desired product in excellent yields (Table 3, entries 10-13). By using aqueous solution of KOAc and extending the reaction time, high yields were also obtained with aryl iodides as the substrates (Table 3, entries 14-15).

Table 3. Room Temperature Complex **1**-Catalyzed Borylation Reaction of Aryl Halides with Bis(pinacolato)diboron [a]

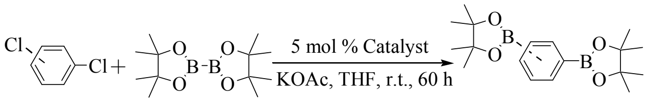


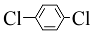
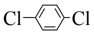
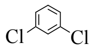
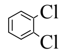
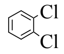
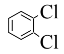
Entry	Ar-X	Conversion (%)[b]
1		33
2		72
3		11
4		24
5		70
6		7
7		52
8		55
9		7
10		90[c,d]
11		92[c,d]
12		93[c,d]
13		95[c,d]
14		95[c,e]
15		91[c,e]

a. Reaction conditions: aryl halides (0.2 mmol), bis(pinacolato)diboron (3 equiv.), KOAc (3 equiv.), THF (1 mL), room temperature. b. Based on ^{1}H NMR. c.Isolated yields.d. Reaction condition: KOAc (5 equiv.), rt, 24 h. e. Reaction condition: KOAc (2 M, 5 equiv.), rt, 48 h.

We have also examined the coupling reaction of dichlorobenzenes with bis(pinacolato)diboron. We found that the reaction of 1,4-dichlorobenzene with 1 equivalent of bis(pinacolato)diboron generated 4-chlorophenylborate and 1,4-phenyldiborate in a ratio of 61:39. By using more amounts of bis(pinacolato)diboron, we found that the borylation reaction of 1,4-dichlorobenzene and 1,3-dichlorobenzene afforded phenyldiborates in good yields (Table 4, entries 2 and 3). The reaction of 1,2-dichlorobenzene with bis(pinacolato)diboron was also carried out, 1,2-phenyldiborate was obtained in a moderate yield,[13] along with a significant amounts of 2-chlorophenylborate (Table 4, entry 4). Complexes **2** and **3** were also employed as catalysts for the reaction. No desired product was observed with complex **2** as the catalyst (Table 4, entry 5). 1,2-Phenyldiborate was obtained in 26% yield, along with 13% of 2-chlorophenylborate, with complex **3** as the catalyst (Table 4, entry 6). These results suggested that complex **1** was an useful catalyst for the room temperature cross-coupling reaction of aryl dichlorides with bis(pinacolato)diboron to access aryldiborates.

Scheme 4. Room Temperature Complex **1**-Catalyzed Borylation Reaction of Aryl Dichlorides with Bis(pinacolato)diboron [a]



Entry	Ar-X	Catalyst	Yield (%)[b]
1		**1**	73[c]
2		**1**	84
3		**1**	77
4		**1**	36[d]
5		**2**	0
6		**3**	26[e,f]

a. Reaction conditions: aryl halides (0.2 mmol), bis(pinacolato)diboron (6 equiv.), K_3PO_4 (10 equiv.), THF (1 ml), room temperature. b. Isolated yields. c. Conversion based on ^{1}H NMR. The ratio of 4-chlorophenylborate to 1,4-phenyldiborate was 61: 39. d. 18% of monochloroborate was observed. e. 13% of monochloroborate was observed. f. Reaction time: 48 h.

Compared to other reported Pd(0) catalyst systems for the coupling reaction of aryl chlorides with bis(pinacolato)diboron, *e.g.*, Pd(0)/Buchwald's biphenylphosphines,[5t, 6a] Pd(0)/PCy_3,[5y] which required elevated reaction temperature and/or additional amounts of ligands, complex **1** catalyzed the reaction efficiently at room temperature. Considering the easy availability and air-stability of complex **1**, even the requirements of the slightly higher catalyst loading or longer reaction time would still favorably place complex **1** into one of useful catalysts.

Summary

We have demonstrated that Ad_3P-coordinated acetanilide-based palladacycle complex **1** was an excellent catalyst for room temperature borylation reactions of readily available aryl chlorides with bis(pinacolato)diboron. Complex **1** represents a general transition metal catalyst system that can catalyze the Miyaura borylation reaction of aryl chlorides with bis(pinacolato)diboron at room temperature. The mild reaction condition, the easy availability of the catalyst systems, and excellent coupling yields make Pd(0)/Ad_3P catalyst system potentially useful in organic synthesis.

Experimental Section

General Procedure for Complex 1-Catalyzed Cross-Coupling Reactions of Aryl Chlorides with Bis(pinacolato)diboron: In a glovebox with an N_2 atmosphere, to a vial containing bis(pinacolato)diboron (0.6 mmol, 3 equiv.), complex **1** (8.5 mg, 0.01 mmol, 0.05 equiv.), potassium acetate (78.5 mg, 0.8 mmol, 4 equiv.), THF (1 mL), was added aryl chloride (0.2 mmol, 1 equiv.). The mixture was allowed to react at room temperature for 24-48 h. After quenching with water, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine and then evaporated under vacuum. Flash chromatography on silica gel Flash chromatography on silica gel (hexane : ethyl acetate = 100 : 0 to 85 : 15) yielded the product.

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Supporting Information Available: Experimental procedure and data for Pd(0)/Ad_3P-catalyzed coupling of aryl chlorides with bis(pinacolato)diboron.

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Highlights

- First general Pd(0) catalyst for room temperature Miyaura borylation of aryl chlorides
- Broad substrate scope
- Mild reaction condition
- High yields