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Palladacycles Derived from Arylphosphinamides for Mild Suzuki-Miyaura Cross-Couplings

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We present a type of palladacyclic complexes derived from arylphosphinamides which can be used as efficient and versatile precatalysts for mild Suzuki-Miyaura cross-coupling. With the presence of 1.0 mol% of palladacycles, a wide variety of aryl bromides and boronic acids could be coupled very efficiently at ambient temperature and under air atmosphere without the need of external supporting ligands. Moreover, the mild conditions also allow for smooth coupling of electron-deficient, i.e., the less stable aryl triflates. In addition to the highly catalytic activity, the palladacyclic complexes can be very easily prepared through a two-step procedure from the readily affordable diphenylphosphinic chloride and exhibit excellent stability toward air and moisture. Due to these prominent properties, the new palladacycles would find practical use in Suzuki-Miyaura couplings.

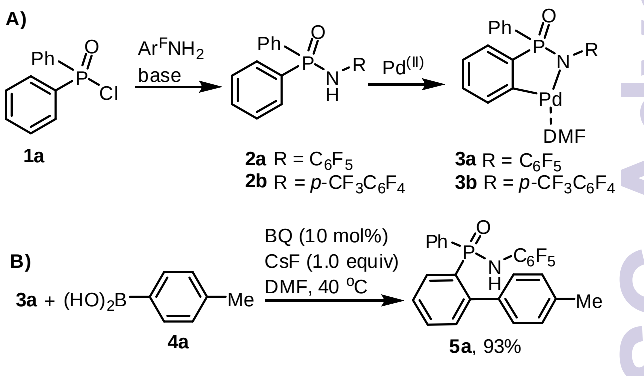
Introduction

Among the transition-metal-catalyzed cross-coupling reaction, the Suzuki-Miyaura cross-coupling has been accepted as the first choice for the creation of C(sp^2)–C(sp^2) bonds.[1] This is attributed to numerous advantages offered by this protocol including the broad functional group tolerance, the abundance of aryl/alkenyl-(pseudo)halides, and the highly stable and low toxic nature of boron reagents. In addition, the boron by-products could also be easily separated from the reaction mixtures. Great academic achievements have been made both with palladium[2] and nickel-catalysts.[3] Moreover, the practicality of a number of catalyst systems in pharmaceutical, agrochemical, and fine chemical industries have also been successfully demonstrated.[4]

Despite these remarkable advances, several challenging issues remain to be overcome. First, the Suzuki-Miyaura couplings are usually performed atelevated temperature. Mild couplings often require the support of expensive ligands such as electron-rich phosphines and *N*-heterocarbenes (NHC).[5,6] The ligand-free couplings under mild conditions are relatively rare.[7] Second, the couplings of thermally instable boronic acids such as polyfluorophenyl[8] and five-membered 2-hetero-aromatic[9] are still problematic although a powerful catalyst system has been reported recently by Buchwald.[10] Third, aryl triflates are attractive electrophiles due to their high reactivity; however, the couplings of such substrates, particularly the electron-deficient derivatives are sometimes troublesome due to the ease of decomposition of substrates.[11] Finally, many catalysts with high catalytic activity are often less stable toward air and moisture, which restricts their practical applications. As such, the development of new catalyst systems aimed at solving these issues is still highly desired in Suzuki-Miyaura coupling.

Results and discussion

In our efforts devoted to the development of new catalyst systems for efficient Suzuki-Miyaura coupling[3e,12] and direct C–H functionalization for the synthesis of phosphorus compounds,[13] we have synthesized a novel palladacyclic



Scheme 1 Preparation of palladium complex **3** and the reaction property.[13a]

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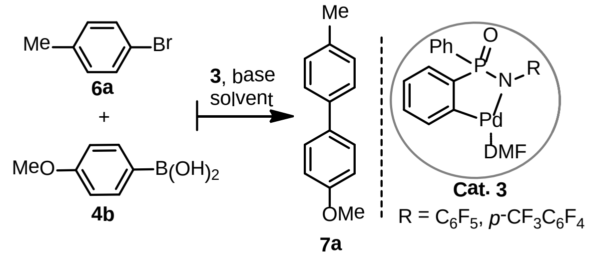
complex **3** from the readily available diphenylphosphinic chloride**1a** and polyfluoroaniline (Scheme 1A).[13a] Structural characterization showed that the complexes involved a molecule of DMF solvent. A control experiment revealed that the reaction of stoichiometric amount of **3a** with boronic acid **4a** led to the formation of *ortho*-arylated product **5a** in 93% yield under mild conditions (Scheme 1B). These observations indicated that the transmetalation of **3a** with boronic acid **4a** and the followed reductive elimination, the last two steps of the Suzuki-Miyaura cross-coupling cycle, could readily proceed.

On the basis of this initial result, we conceived that, if the oxidative addition between the Pd(0) generated from the palladium complexes **3** and an aryl (pseudo)halide takes place facilely, the new palladacycle **3** can be used as a promising precatalyst for mild Suzuki-Miyaura cross-coupling. Taking this consideration in mind, we evaluated the catalytic efficiency of **3a** using 4-bromotoluene **6a** and 4-methoxyphenyl boronic acid **4b** as a model reaction (Table 1). Although the reaction was less effective or ineffective in a range of aprotic polar solvents (entries 1–5), we found that complete conversion as well as high yield of the coupled product **7a** could be obtained when the reaction was performed in non-polar toluene (entry 6) and several alcoholic solvents such as *t*BuOH, *i*PrOH, and EtOH (entries 7–9) with 1 mol% loading of **3a** in the presence of K_2CO_3 as base at 40 °C. Next, the most readily affordable EtOH was chosen as solvent to further examine the efficacy of the complex. It was found that the reaction proceeded very well at ambient temperature (entries 10 and 11). Moreover, an array of bases (entries 11–15) was also compatible for mild couplings except for Li_2CO_3 (entry 13). Notably, the coupling could complete rapidly within two hours when K_3PO_4 was used as base (entry 15). The reaction also proceeded efficiently in an aqueous medium although the yield was slightly diminished (entry 16). In addition, the palladacycle **3b** displayed an equally good catalytic activity to **3a** (entry 17). These results indicate that the phosphinamide-based palladacycles are active precatalysts for mild Suzuki-Miyaura reaction. Most importantly, the complexes tolerate various solvents and bases. These features represent the important advantages of a catalyst since for transition-metal-catalyzed cross-couplings, it is often observed that a catalyst which is effective under a set of conditions would become ineffective even by a minor change of the parameters such as solvent, base, or ligand.[14]

It is also noteworthy that the catalytic activity of the palladacycles was entirely maintained after by storing the complex in a flask for over 8 months under an ambient atmosphere (entries 18 and 19). Moreover, almost identical yield (92%) was obtained when the reaction was scaled up to 10 mmol. These results unambiguously exemplified that the complexes **3** exhibit excellent stability against the erosion of lab atmosphere. Finally, the catalyst can be very easily prepared via a two-step procedure from inexpensive diphenylphosphinic chloride **1a** and do not need further activation with electron-rich or sterically bulk ligands. As a result, the stability and cheapness may be added bonus of the complexes **3** for practical applications.

Thus, an comprehensive evaluation on various reaction parameters through the model reaction demonstated that the phosphinamide-derived palladacycles **3** could serve as a practical precatalyst for mild Suzuki-Miyaura cross-couplings. Next, to examine the generality, a rich range of arylbromides were subjected to react with an array of aryl boronic acids under the standard conditions (Table 1, entry 15). The reactions proceeded very well for both coupling partners decorated by electron-neutral, -rich, and -deficient substitutents (Table 2, **7a**–**7n**). In most cases, excellent yields could be obtained for a wide variety of combiantions of aryl bromides with boronic acids. Moreover, almost identical reaction efficiency was observed under nitrogen and air atmosphere. In addition, the ring-fused aromatic bromide could be coupled smoothly under the conditions (**7o**–**7r**). Notably, the 2,6-disubstituted aryl bromides were also viable substrates (**7s** and **7t**) although a 2 mol% catalyst loading and a slightly elevated temperature were needed for these sterically hindered compounds. Of note, the coupling occurred exclusively at the bromide position for 1-bromo-4-chlorobenzene (**7l**–**7n**). These results indicate that

Table 1 Evaluation of the catalytic activity of palladacycles **3**[a]



Entry	Cat. (mol%)	Base	Solvent	T (h)	T (°C)	Yield (%)[b]
1	**3a** (0.5)	K_2CO_3	DMF	18	40	53
2	**3a** (1.0)	K_2CO_3	DMF	18	40	66
3	**3a** (1.0)	K_2CO_3	dioxane	18	40	40
4	**3a** (1.0)	K_2CO_3	MeCN	18	40	24
5	**3a** (1.0)	K_2CO_3	THF	18	40	5
6	**3a** (1.0)	K_2CO_3	toluene	18	40	90
7	**3a** (1.0)	K_2CO_3	*t*BuOH	18	40	84
8	**3a** (1.0)	K_2CO_3	*i*PrOH	18	40	83
9	**3a** (1.0)	K_2CO_3	EtOH	18	40	90
10[c]	**3a** (1.0)	K_2CO_3	EtOH	18	rt	87
11	**3a** (1.0)	K_2CO_3	EtOH	24	rt	90
12	**3a** (1.0)	Na_2CO_3	EtOH	24	rt	90
13	**3a** (1.0)	Li_2CO_3	EtOH	24	rt	40
14	**3a** (1.0)	CsF	EtOH	24	rt	94
15	**3a** (1.0)	**K_3PO_4**	**EtOH**	**2**	**rt**	**94**
16[d]	**3a** (1.0)	K_3PO_4	EtOH/H_2O	2	rt	71
17	**3b** (1.0)	K_3PO_4	EtOH	2	rt	94
18[e]	**3a** (1.0)	K_3PO_4	EtOH	2	rt	96
19[e,f]	**3a** (1.0)	K_3PO_4	EtOH	2	rt	93

[a] The reaction conditions are: **6a** (0.5 mmol), **4b** (0.75 mmol, 1.5 equiv), **3** (1 mol%), base (1.5 mmol, 3.0 equiv) in solvent (3 mL) under nitrogen atmosphere. [b] Isolated yield. [c] rt stands for the ambient temperature ranging from 20 to 25 °C. [d] EtOH/H_2O = 1:1 in volume. [e] The reaction was run under air atmosphere. [f] The reaction was carried out by storing **3a** in a flask for over 8 months.

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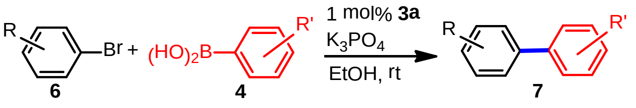
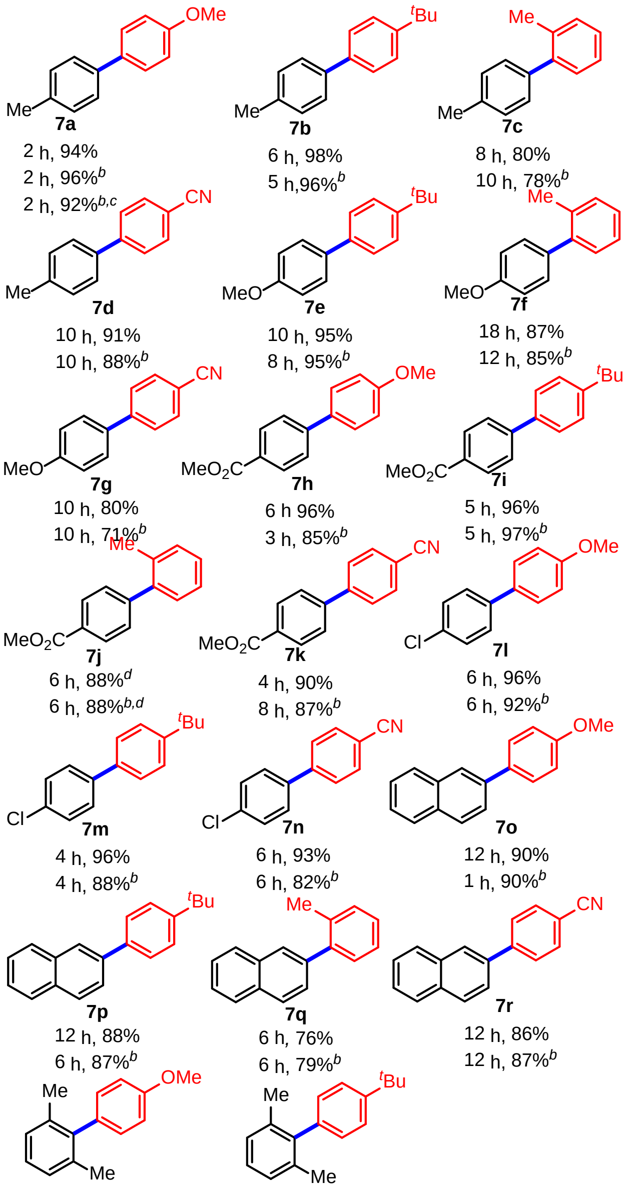
Table 2 The substrate scope of aryl bromides and boronic acids[a]





7a 2 h, 94%; 2 h, 96%[b]; 2 h, 92%[b,c]

7b 6 h, 98%; 5 h,96%[b]

7c 8 h, 80%; 10 h, 78%[b]

7d 10 h, 91%; 10 h, 88%[b]

7e 10 h, 95%; 8 h, 95%[b]

7f 18 h, 87%; 12 h, 85%[b]

7g 10 h, 80%; 10 h, 71%[b]

7h 6 h 96%; 3 h, 85%[b]

7i 5 h, 96%; 5 h, 97%[b]

7j 6 h, 88%[d]; 6 h, 88%[b,d]

7k 4 h, 90%; 8 h, 87%[b]

7l 6 h, 96%; 6 h, 92%[b]

7m 4 h, 96%; 4 h, 88%[b]

7n 6 h, 93%; 6 h, 82%[b]

7o 12 h, 90%; 1 h, 90%[b]

7p 12 h, 88%; 6 h, 87%[b]

7q 6 h, 76%; 6 h, 79%[b]

7r 12 h, 86%; 12 h, 87%[b]

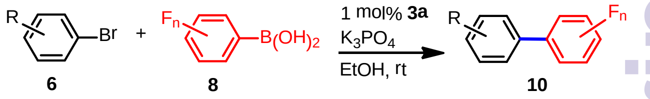
7s 12 h, 80%[e]

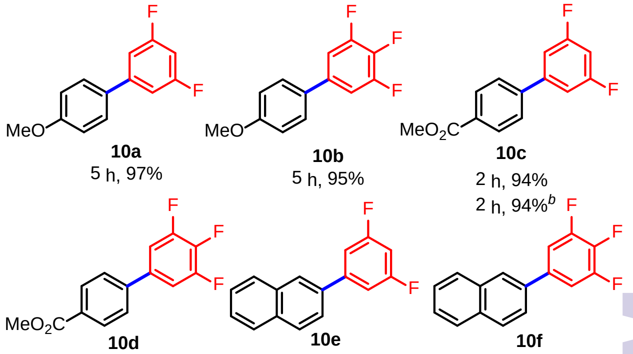
7t 12 h, 79%[e,f]

[a] The reaction conditions: **6** (0.5 mmol), **4** (0.75 mmol, 1.5 equiv), **3a** (1 mol%), K$_3$PO$_4$ (1.5 mmol, 3.0 equiv) in EtOH (3 mL) at rt under nitrogen; isolated yield; the reaction time was not optimized. [b] The reactions were performed under air atmosphere. [c] **6a** (10 mmol), **4b** (15 mmol, 1.5 equiv), **3a** (1 mol%), K$_3$PO$_4$ (30 mmol, 3.0 equiv) in EtOH (60 mL) at rt for 1.5 h. [d] The methyl ester group of the product was partially exchanged to ethyl ester. [e] The reaction was run with the presence of 2 mol% **3a** at 50 $^{\circ}$C under nitrogen atmosphere. [f] The yield was determined based on the ^{1}H-NMR spectroscopic analysis due to the contamination of a small amount of inseparable by-product from the homocoupling of boronic acid.

the precatalyst was less effective for the inert aryl chlorides.

Table 3 The coupling of polyfluorophenyl boronic acids[a]





10a 5 h, 97%

10b 5 h, 95%

10c 2 h, 94%; 2 h, 94%[b]

10d 2 h, 96%

10e 5 h, 93%

10f 2 h, 94%

[a] The reaction conditions were: **6** (0.5 mmol), **8** (0.75 mmol, 1.5 equiv), **3a** (1 mol%), K$_3$PO$_4$ (1.5 mmol, 3.0 equiv) in EtOH (3 mL) at rt for 2–5 h under air atmosphere; isolated yield; the reaction time was not optimized. [b] The reactions were performed under nitrogen atmosphere.

Nevertheless, the results provide a useful way for the othogonal modification of multihalogen-substituted benzenes.

Having demonstrated the highly catalytic activity of **3a** for coupling aryl bromides with a range of common phenyl boronic acids, we examined its catalytic efficiency for coupling the polyfluorophenyl (**8**) (Table 3) and 2-heterocyclicboronic acids (**9**) (Table 4). As mentioned, the coupling of these two types of nucleophiles remains problematic under most of the conventional conditions. Here, we found that while the reaction was ineffective for the more electron-deficient 2,6-difluorophenyl boronic acid presumably due to the fast protodeboronation, complete conversion as well as excellent yields were observed for the reaction of 3,5-difluoro and 3,4,5-trifluorophenyl boronic acids. The electron-rich (**10a** and **10b**), deficient (**10c** and **10d**), and the ring-fused (**10e** and **10f**) aryl bromides were compatible. In addition, a range of *O*- and *S*-containing 2-heteroaromatic boronic acids were also viable substrates (**11a–11r** in Table 4). Although the catalytic activity was somewhat decreased for 2-heterocyclic boronic acids as compared with the common aryl brononic acids, high to excellent yields could be obtained by performing the reaction with the presence of 2 mol% of **3a** or by elevating the reaction temperature to 50 $^{\circ}$C under nitrogen atmosphere. Moreover, a broad variety of functional groups such as methoxy, ester, aldehyde, nitro, and chloride groups were well tolerated. Unfortunately, a preliminary trial showed that the conditions were ineffective for a *N*-Boc protected indol-2-yl boronic acid. The reasons await detailed investigation.

Next, we investigated the reaction of the aryl triflate electrophiles (Table 5). Among the transition-metal-catalyzed cross-couplings of phenolic derivatives, the aryl triflates are attactive substrates due to the high reactivity. However, their instability

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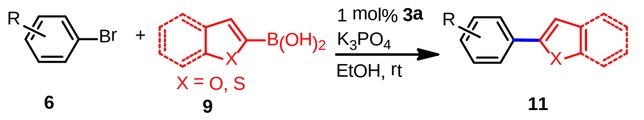
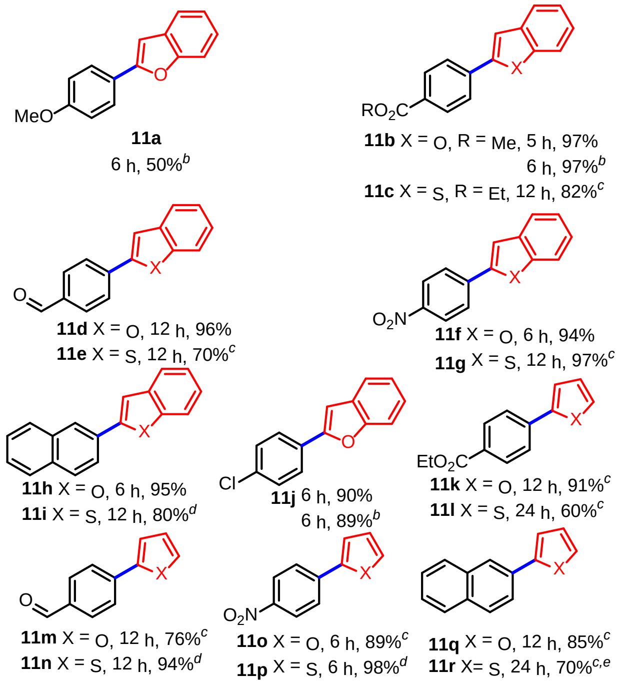
Table 4 The coupling of 2-heterocyclic boronic acids[a]





11a 6 h, 50%[b]

11b X = O, R = Me, 5 h, 97%
6 h, 97%[b]

11c X = S, R = Et, 12 h, 82%[c]

11d X = O, 12 h, 96%
11e X = S, 12 h, 70%[c]

11f X = O, 6 h, 94%
11g X = S, 12 h, 97%[c]

11h X = O, 6 h, 95%
11i X = S, 12 h, 80%[d]

11j 6 h, 90%
6 h, 89%[b]

11k X = O, 12 h, 91%[c]
11l X = S, 24 h, 60%[c]

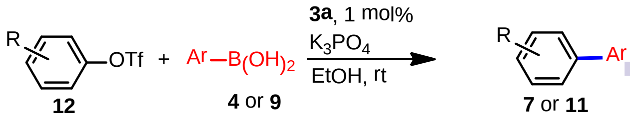
11m X = O, 12 h, 76%[c]
11n X = S, 12 h, 94%[d]

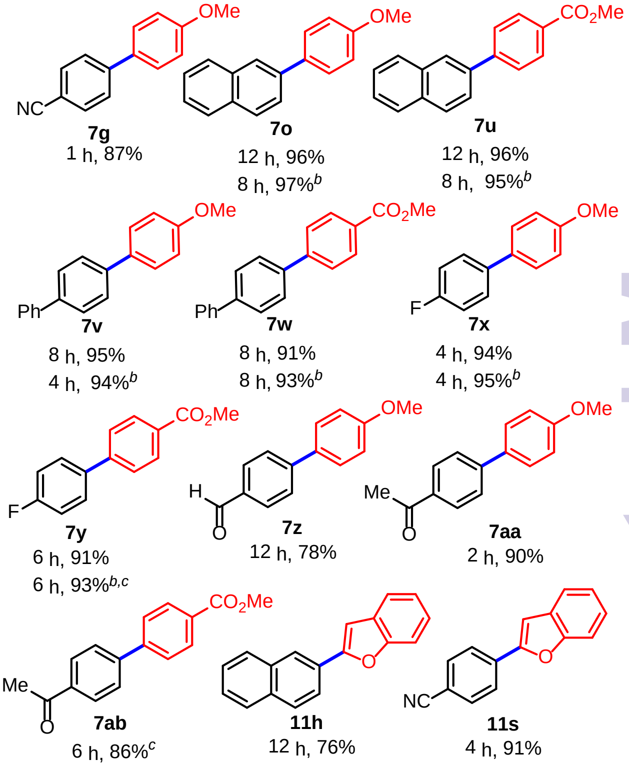
11o X = O, 6 h, 89%[c]
11p X = S, 6 h, 98%[d]

11q X = O, 12 h, 85%[c]
11r X= S, 24 h, 70%[c,e]

[a] The reaction conditions were: **6** (0.5 mmol), **9** (0.75 mmol, 1.5 equiv), **3a** (1 mol%), K_3PO_4 (1.5 mmol, 3.0 equiv) in EtOH (3 mL) at rt for 5–24 h under nitrogen atmosphere; isolated yield; the reaction time was not optimized. [b] The reactions were performed under air atmosphere. [c] The ractions were performed in the presence of 2 mol% of **3a** at 50 °C. Under these conditions, the methyl ester group in methyl 4-bromobenzoate substrate was exchanged to ethyl ester in the products **11c**, **11k**, and **11l**. [d] The reactions were performed in the presence of 2 mol% of **3a** at 50 °C in DMF solvent. [e] Cs_2CO_3 instead of K_3PO_4 was used as base in DMF at 50 °C.

Table 5 The coupling of aryl triflates[a]





7g 1 h, 87%

7o 12 h, 96%
8 h, 97%[b]

7u 12 h, 96%
8 h, 95%[b]

7v 8 h, 95%
4 h, 94%[b]

7w 8 h, 91%
8 h, 93%[b]

7x 4 h, 94%
4 h, 95%[b]

7y 6 h, 91%
6 h, 93%[b,c]

7z 12 h, 78%

7aa 2 h, 90%

7ab 6 h, 86%[c]

11h 12 h, 76%

11s 4 h, 91%

[a] The reaction conditions were: Aryl triflates **12** (0.5 mmol), boronic acids **4** or **9** (0.75 mmol, 1.5 equiv), **3a** (1 mol%), K_3PO_4 (1.5 mmol, 3.0 equiv) in EtOH (3 mL) at rt for 1–12 h under nitrogen atmosphere; isolated yield; the reaction time was not optimized. [b] Yields were obtained under air atmosphere. [c] The methyl ester group of the product was partially exchanged to ethyl ester.

makes this reaction troublesome. Especially, the decomposition of electron-deficient aryl triflates is often occured when protic solvents such as water or alcohols are used, although a heterogeneous Pd/C-catalyzed effective coupling of electron-deficient aryl triflates in aqueous media has been reported.[7a] Here, we demonstrated that with the presence of 1 mol% of **3a**, a wide array of electron-deficient aryl triflates underwent smooth coupling with various boronic acids including electron-rich and deficient, as well as 2-heterocyclic boronic acids to afford the coupled products in high to excellent yield at room temperature and under nitrogen or air atmosphere.

Concerning the catalytic mechanism of the cyclic palladium complexes **3**, it should proceed via a conventional $Pd^{(0)}$ to $Pd^{(II)}$ cycle since palladium black was observed during the reaction, although analysis by transmission-electron-microscopy (TEM) did not provide clear evidence to confirm the formation of palladium nanoparticles. In addition, the arylated product **5a** (Scheme 1) could also be detected. These results together with our previous reports[13a] indicates that the generation of $Pd^{(0)}$ may proceed through the transmetallation of palladacycle **3** and boronic acids followed by the reductive elimination of $Pd^{(II)}$.

Conclusions

In conclusion, we have demonstrated that the unprecedented palladacycles derived from phosphinamide are a type of practical precatalysts for mild Suzuki-Miyaura cross-coupling of aryl bromides and triflates attributed to their prominent overall performance such as high activity, easy preparation, excellent stability, and broad compatibility for various reaction parameters.

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wide variety of electrophiles and nucleophiles could be cross-coupled efficiently with the presence of 1 mol% of pallacycles at ambient temperature and under air atmosphere. More important implications beyond this work are that the results presented herein would provide useful clues for further design of new catalysts and development of new reactions. Some of these works are currently underway in our lab.

Experimental Section

General procedure for cross-coupling under nitrogen atmosphere:

To a Schlenk tube equipped with a magnetic bar was charged solid aryl bromide or triflate (0.5 mmol), boronic acid (0.75 mmol), **3a** (1 mol%), anhydrous K_3PO_4 (1.5 mmol). The tube was then evacuated under vacuum and backfilled with N_2. EtOH (3.0 mL) was injected *via* syringe (the aryl bromide or triflate (0.5 mmol) was also added at this stage if it is liquid). The reaction mixture was stirred at rt or 50 ^{o}C until the arylbromidesor triflates had disappeared as monitored by TLC. The reaction mixture was poured into water (30 mL) and then extracted with CH_2Cl_2 (20 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated to dryness. Thecrude material was purified by flash chromatography on silica gel using a mixture of hexane and CH_2Cl_2 as eluents to give the desired cross-coupled product.

Acknowledgements

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Table of Content

We present the arylphosphinamide-derived palladacyclic complexes (See Scheme) which could be used as efficient and versatile precatalysts for mild Suzuki-Miyaura cross-coupling.