



Catalytic activity of some palladium complexes of a phosphorus ylide and the structure of a 2-phenylaniline-based palladacycle complex



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ABSTRACT

A six-membered N,C-palladacycle bearing the 2-phenylaniline bidentate ligand (**1**) and three other palladium complexes of a phosphorus ylide (**2**, **3** and **4**) were utilized in Suzuki reactions between phenylboronic acid and a number of aryl bromides and chlorides. The complexes were found to be capable homogeneous catalysts for a variety of substrates, affording the coupled products in good to excellent yields. The structure of compound **1**, determined by X-ray diffraction, is also reported.

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1. Introduction

The palladium-catalyzed Suzuki reaction for the formation of C–C bonds has appeared as an extremely powerful method for the preparation of unsymmetrical biaryls [1–5]. Indeed, various proficient Pd catalyst precursors have been developed in recent years that allow aryl halides to be effectively coupled with aryl boronic acids under aerobic conditions [2,4,5] or even in aqueous solutions [3,5]. For this reason, palladacycles were found to be the most talented catalysts in this regard as they have been extensively studied during the last few decades [6]. They have significant application in organic and organometallic synthesis, chiral recognition and in homogeneous catalysis [7–10]. Since the first report on the use of a palladacycle for the Suzuki reaction [11], a broad diversity of novel palladacycles resulting from the cyclopalladation of phosphines, phosphites, phosphinites, amines, imines, oximes and thioethers have been effectively employed in this reaction [12–17].

The use of nitrogen-based ligands has been reported to demonstrate the catalytic activity in Suzuki and Heck reactions [18–29], which drew our attention to study the catalytic activity of **1** (Fig. 1) in homogenous media. Also, electron-rich, bulky phosphines [30–33] and phosphine oxides [34] have been reported to be successful ligands. Moreover, among the several classes of phosphine ligands described in the literature for Pd-catalyzed Suzuki reactions, we became interested in phosphorus ylide

ligands. Palladacycles **2**, **3** and **4** (Fig. 1) were found to be active precatalysts for Suzuki reactions. However, phosphorus-based ancillary catalysts are frequently air and moisture sensitive, toxic and need an inert atmosphere and gentle reaction conditions.

On the other hand, besides diverse aryl bromides, employing aryl chlorides for this reaction has been a focus because aryl chlorides are cheaper and more accessible than their bromides and iodide counterparts [35]. Therefore, the investigation for novel palladium catalysts has received much attention, mainly for the use of less reactive aryl chlorides as substrates under mild reaction conditions. In continuation of our interest in the development of employing new palladium complexes in C–C bond forming reactions [36,37], we report here the efficiency of palladacycle **1** [38] and some other cyclopalladated phosphorus ylide complexes, **2–4**, in Suzuki C–C cross-coupling reactions for both aryl bromides and chlorides. Furthermore, the detailed structure of **1**, a highly air and moisture stable palladium complex, was determined by X-ray single crystal analysis.

2. Experimental

2.1. Materials and techniques

All chemicals and solvents were purchased from Merck and Aldrich. Complexes **2–4** were prepared by the method reported in our previous work [41]. Conversions were monitored using an Agilent 6890N gas chromatograph equipped with a capillary HP-5⁺ column, based on aryl halides. The column properties were: 30 m length, 0.32 mm in inner diameter and 0.25 µm film thick.

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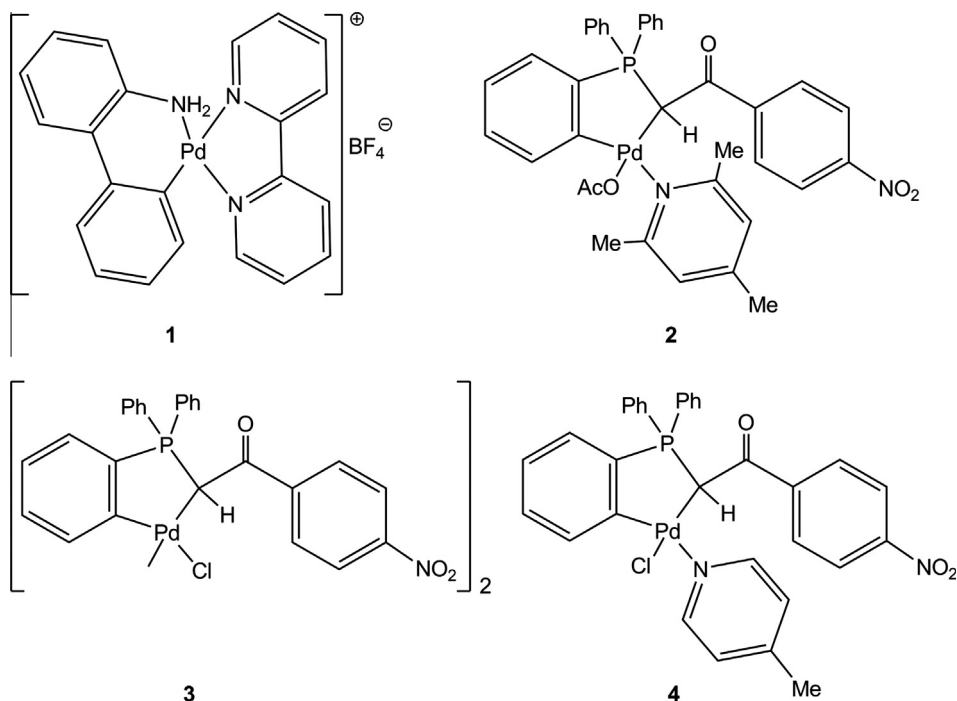


Fig. 1. Palladacycles employed in Suzuki reactions.

2.2. X-ray crystal structure determination

Crystals suitable for X-ray molecular structure determination of **1** were obtained by the diffusion method for a solution of **1** in acetone/*n*-hexane (1:3 v/v). Intensity data were collected at ambient temperature (295(2) K) using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) on a Bruker APEX-II CCD diffractometer. Data were corrected for absorption using the *SABABS* program [39]. All non-hydrogen atoms were refined anisotropically. The amine H atoms were located in a difference Fourier map and refined freely. All other H atoms were calculated geometrically and refined using a riding/rotating model, with C–H = 0.93–0.96 Å and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or $1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms. The F1, F2 and F3 atoms of the tetrafluoroborate anion were disordered over two orientations (called A and B) with refined occupancies of 0.621(9) and 0.379(9) for the major and minor components, respectively. During the refinement, the geometry of these atoms was restrained to be similar by the *SAME* instruction of *SHELXL-97* [40].

2.3. General protocol for the Suzuki reaction

A round bottom flask was charged with the aryl halide (0.5 mmol), phenylboronic acid (0.75 mmol), base (1.5 or 3 mmol), catalyst (0.01 mmol) and solvent (7 mL), although the amount of the reagents and catalysts was diminished to half when catalysts **2–4** were utilized. The mixtures were heated for the times 2, 4, 8 and 24 h and at the temperatures 85 and 100 °C given in the tables using the bases and catalysts there indicated. The products were characterized by GC.

3. Results and discussion

3.1. Molecular structure of **1**

The single crystal X-ray diffraction study confirmed the details of the structure proposed. Fig. 2 shows the ORTEP plot of compound

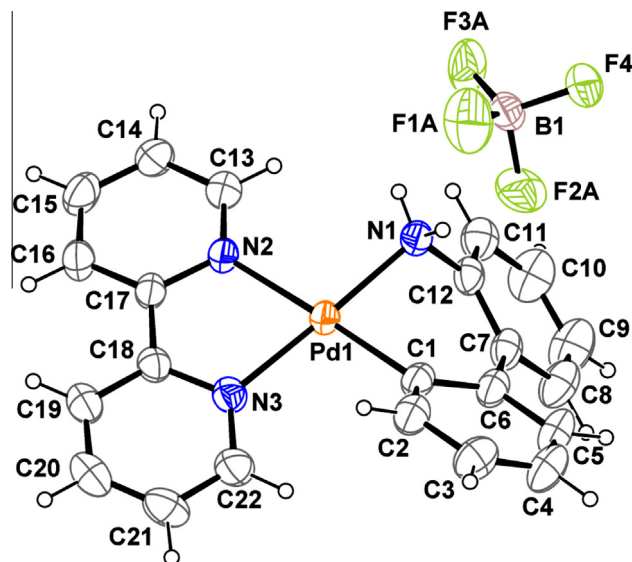


Fig. 2. X-ray molecular structure of **1**, with displacement ellipsoids drawn at the 50% probability level. Only the major components of the disordered fluorine atoms are shown.

Table 1
Selected bond distances (Å) and angles (°) for **1**.

Pd1–C1	2.007 (3)
Pd1–N1	2.054 (2)
Pd1–N3	2.061 (2)
Pd1–N2	2.125 (2)
N1–Pd1–N3	177.89 (10)
C1–Pd1–N2	177.83 (10)
C1–Pd1–N1	82.92 (11)
C1–Pd1–N3	99.18 (10)
N1–Pd1–N2	99.21 (10)
N3–Pd1–N2	78.68 (8)

Table 2
Crystallographic data and structure refinement details for **1**.

Empirical formula	C ₂₂ H ₁₈ N ₃ Pd·BF ₄
Formula weight	517.60
T (K)	295
Radiation (k, Å)	Mo K α (0.71073)
Crystal system	Orthorhombic
Space group	<i>Pbca</i>
<i>a</i> (Å)	10.4380 (19)
<i>b</i> (Å)	19.695 (4)
<i>c</i> (Å)	20.790 (4)
<i>V</i> (Å ³)	4273.9 (14)
<i>Z</i>	8
<i>D</i> _{calc} (Mg/m ³)	1.609
μ (mm ⁻¹)	0.92
Crystal size (mm ³)	0.13 × 0.09 × 0.05
No. of reflections measured	40765
No. of independent reflections	3876
No. of restraints/parameters	3/316
<i>R</i> [<i>F</i> ² > 2(<i>F</i> ²)]	0.026
<i>wR</i> (<i>F</i> ²)	0.073
<i>R</i> _{int}	0.037
<i>S</i>	1.02

1. Selected bond distances and angles are listed in Table 1; crystallographic data and parameters concerning the data collection and structure solution and refinement are summarized in Table 2.

The asymmetric unit of **1** consists of a complex cation and a tetrafluoroborate anion rotationally disordered over two orientations. The palladium metal exhibits a slightly distorted square-planar geometry (maximum displacement 0.007(3) Å for atom C1), as indicated by the angles subtended by the ligands at the Pd(II) centre, varying from 78.68(8)° to 99.21(10)° and from 177.83(10)° to 177.89(10)°. The summation of the bond angles around the palladium is 359.99°. The metal protrudes by 0.0018(2) Å from the mean coordination plane. The Pd1–C1 bond distance (2.007(3) Å) is similar to that found in a related orthopalladated complex [38], and the Pd1–N3 distance also falls in the common range found for this bond. In contrast to that observed in a related Pd complex containing the 2,2′-bipyridine ligand [41], the Pd1–N1 (2.054(2) Å) bond length is significantly shorter than the Pd1–N2 (2.125(2) Å) distance. The dihedral angles formed by the aromatic rings of the biphenyl and bipyridine ligands are 31.20(9)° and 12.08(9)°, respectively. The six-membered chelate ring assumes a half-chair conformation, with the atoms Pd1 and N1 displaced by 0.8029(2) and 0.512(3) Å, respectively, from opposite sides of the C1/C6/C7/C12 mean plane. The five-membered chelate ring adopts a flattened envelope conformation, with the atom N3 displaced by 0.172(2) Å from the Pd1/N2/C17/C18 mean plane (maximum deviation 0.002(2) Å for atom C17). As illustrated in Fig. 3, in the crystal the cations and anions are linked into a three-dimensional network by N–H⋯O and C–H⋯O hydrogen bonds.

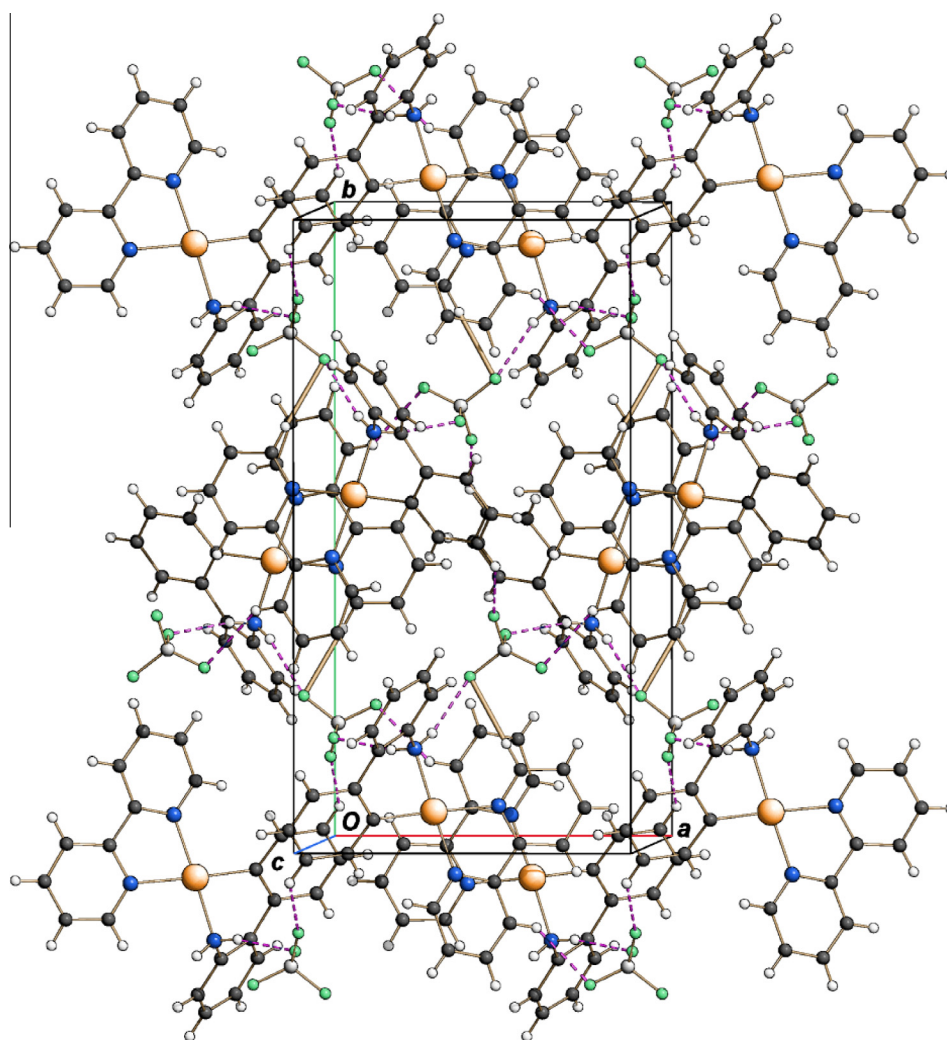


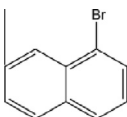
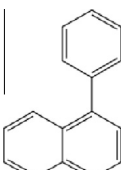
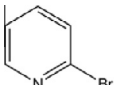
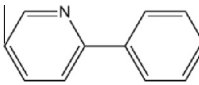
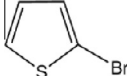
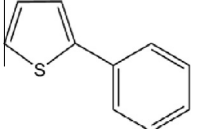
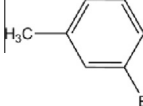
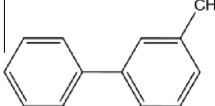
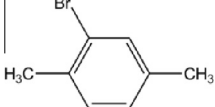
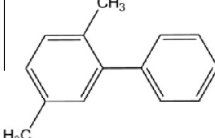
Fig. 3. Packing diagram of **1**. Dashed lines represent the hydrogen bonding interactions. The minor components of the disordered fluorine atoms are omitted.

3.2. Suzuki reaction for aryl bromides

The catalytic applicability of Pd(II) complexes **1** and **2** was evaluated for the Suzuki reaction for aryl bromides. The efficiency of **1** in the Suzuki reactions of a variety of aryl bromides and chlorides with phenylboronic acid was compared with the palladacyclic complexes bearing phosphorus ylide. The optimized reaction conditions obtained in our previous investigation [36] were utilized within this work. However, because of the low to moderate yields of the reactions using **1** as catalyst, the reaction time and temperature were increased to 2 h and 85 °C. The couplings took place with **1** and **2** employing Na₂CO₃ as a base for neutral substrates and K₃PO₄·3H₂O for electron-deficient and rich substrates. Table 3 summarizes our results for the Suzuki reactions. Complex **1**

showed promising catalytic activity in the reactions of 1-bromonaphthalene (entry 1) and 3-bromotoluene (entry 7) with phenylboronic acid. In spite of using 0.02 mmol of **1** and 3 mmol of K₃PO₄·3H₂O, the coupling of 2-bromo-1, 4-dimethylbenzene was poor (entry 9). **1** Showed low and moderate catalytic activities in the reactions of 2-bromopyridine and 2-bromothiophene with phenylboronic acid, respectively (entries 3 and 5). The rate of coupling for each of these reactions was higher than that observed when complex **2** was used (entries 4 and 6). Generally, **2** was found to be more effective than **1** in all reactions, especially in the couplings of less reactive aryl bromides with phenylboronic acid at low catalyst loading (entries 8 and 10). This distinction may be due to the stability of the five membered ring of the palladacycle in **2** and/or the enhanced solubility of the reagents and reduction

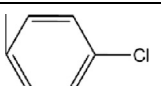
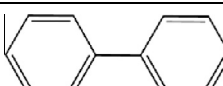
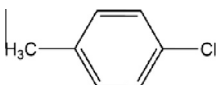
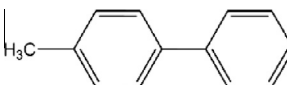
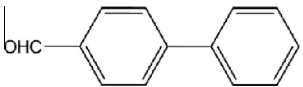
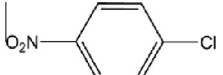
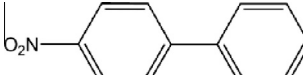
Table 3
The Suzuki reaction of aryl bromides with phenylboronic acid^a.

Entry	Aryl bromide	Catalyst	Base	Product	Yield (%)
1		1	Na ₂ CO ₃		90.6
2		2			99
3		1	Na ₂ CO ₃		26.5
4		2			85.1
5		1	Na ₂ CO ₃		58.3
6		2			96.3
7		1	K ₃ PO ₄ ·3H ₂ O		82.2
8		2			90.3
9		1 ^b	K ₃ PO ₄ ·3H ₂ O		19.6
10		2			91.1

^a Reaction conditions: aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst (0.01 mmol), base (1.5 mmol), MeOH (7 ml), 2 h, 85 °C.

^b Catalyst (0.02 mmol), base (3 mmol).

Table 4
Suzuki reactions of aryl chlorides with phenylboronic acid.^a

Entry	Aryl chloride	Catalyst	Base	T (°C)	t (h)	Product	Yield (%)
1		1	Na ₂ CO ₃	100	8		33.6
2		2		85	2		47.5
3		3		85	4		60.4
4		4		85	4		48.9
5		1	K ₃ PO ₄ ·3H ₂ O	100	8		19
6		2		85	4		35.8
7		3		85	4		9.3
8		4		85	4		1.9
9		1 ^b	K ₃ PO ₄ ·3H ₂ O	100	24		73.8
10		2		85	4		71
11		3		85	4		75.7
12		4		85	4		76.5
13		2	K ₃ PO ₄ ·3H ₂ O	85	4		50.6
14		3		85	4		67.8

^a Reaction conditions: aryl chloride (0.5 mmol), phenylboronic acid (0.75 mmol), catalyst (0.01 mmol), base (1.5 mmol), MeOH (7 ml).

^b Catalyst (0.02 mmol).

of Pd(II) to Pd(0), thus providing a simpler mechanism to the catalytic cycle.

3.3. Suzuki reaction for aryl chlorides

The catalytic performance of the Pd(II) complexes **1–4** was also tested in the Suzuki reaction for a representative range of aryl chlorides with phenylboronic acid. The results are given in Table 4. As the catalyst **1** did not show high reactivity in the reactions of aryl bromides (Table 3), the reaction time and temperature in Suzuki reactions of less reactive aryl chlorides utilizing **1** were both increased. The reactions of chlorobenzene (entry 1) and 4-chlorotoluene (entry 5) applying **1** as a catalyst gave low product rates. In the presence of **2**, chlorobenzene was coupled with phenylboronic acid to give a moderate yield of biphenyl (entry 2). To obtain higher yields, the reaction time of other reactions employing **2–4** was elevated to 4 h. In spite of doubling the reaction time, the reactions of chlorobenzene using **3** and **4** were slightly difficult (entries 3 and 4). Complexes **2–4** were found to be less active in the coupling of 4-chlorotoluene and phenylboronic acid (entries 6–8). Complex **1** was able to activate 4-chlorobenzaldehyde but a much longer reaction time and higher temperature were required (entry 9). As can be seen in Table 4, complexes **2–4** gave a relatively high yield of the product in the reaction of 4-chlorobenzaldehyde with phenylboronic acid (entries 10–12). In contrast to the literature reports and expectations, the reactions of 4-nitrochlorobenzene employing **2** and **3** failed to give high yields (entries 13 and 14).

4. Conclusion

The identity of complex **1** has been confirmed by an X-ray structure analysis. Catalytic studies revealed that complex **1** is relatively active in Suzuki reactions with aryl bromides. It is of interest that the phosphorus ylide derived palladacycles **2–4** were found to be more efficient for the Suzuki reactions of a representative range of aryl halides with phenylboronic acid. Presently, further efforts to extend the applications of these types of palladacycles to other palladium catalyzed reactions (e.g., Sonogashira, Stille) are in progress in our laboratory.

Acknowledgments

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Appendix A. Supplementary data

CCDC 892995 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via <http://>

www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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