



Article

Porphyrin *N*-Pincer Pd(II)-Complexes in Water: A Base-Free and Nature-Inspired Protocol for the Oxidative Self-Coupling of Potassium Aryltrifluoroborates in Open-Air

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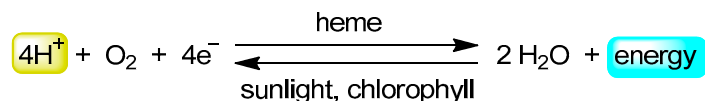
Abstract: Metalloporphyrins (and porphyrins) are well known as pigments of life in nature, since representatives of this group include chlorophylls (Mg-porphyrins) and heme (Fe-porphyrins). Hence, the construction of chemistry based on these substances can be based on the imitation of biological systems. Inspired by nature, in this article we present the preparation of five different porphyrin, *meso*-tetraphenylporphyrin (TPP), *meso*-tetra(*p*-anisyl)porphyrin (TpAP), tetra-sodium *meso*-tetra(*p*-sulfonatophenyl)porphyrin (TSTpSPP), *meso*-tetra(*m*-hydroxyphenyl)porphyrin (TmHPP), and *meso*-tetra(*m*-carboxyphenyl)porphyrin (TmCPP) as well as their *N*-pincer Pd(II)-complexes such as Pd(II)-*meso*-tetraphenylporphyrin (PdTPP), Pd(II)-*meso*-tetra(*p*-anisyl)porphyrin (PdTpAP), Pd(II)-tetrasodium *meso*-tetra(*p*-sulfonatophenyl)porphyrin (PdTSTpSPP), Pd(II)-*meso*-tetra(*m*-hydroxyphenyl)porphyrin (PdTmHPP), and Pd(II)-*meso*-tetra(*m*-carboxyphenyl)porphyrin (PdTmCPP). These porphyrin *N*-pincer Pd(II)-complexes were studied and found to be effective in the base-free self-coupling reactions of potassium aryltrifluoroborates (PATFBs) in water at ambient conditions. The catalysts and the products (symmetrical biaryls) were characterized using their spectral data. The high yields of the biaryls, the bio-mimicking conditions, good substrate feasibility, evading the use of base, easy preparation and handling of catalysts, and the application of aqueous media, all make this protocol very attractive from a sustainability and cost-effective standpoint.

Keywords: porphyrin *N*-pincer Pd(II)-complexes; water; nature-inspired conditions; potassium aryltrifluoroborates; self-coupling; symmetrical biaryls

1. Introduction

Synthetic and natural metalloporphyrins are well-known examples of nitrogen-bridged polycyclic compounds and are largely distributed in nature. Metalloporphyrins display a critical role in numerous biological tasks including oxygen transport, health sustainment, bio-organic transformations, and light-harvesting [1–3]. Metalloporphyrins display vital catalytic significance in the basic reactions of life; for example, as heme (a cofactor of hemoglobin) in oxygen transport [1,4] and as chlorophyll (which is able to convert sunlight to energy) in photosynthesis of plants [4,5] (Scheme 1). Several examples of heme and chlorophylls are displayed in Figure 1. Despite these efficient biochemical, photochemical,

and enzymatic functions, the connectivity and controlled rigidity of metalloporphyrins allow highly ordered arrangements in their crystalline frameworks; for example, metal-organic frameworks (MOFs) encompassing an exciting area of research for over a decade in chemical science and technology disciplines [1,5,6].



Scheme 1. Schematic representation of metalloporphyrin catalyzed basic reactions of life.

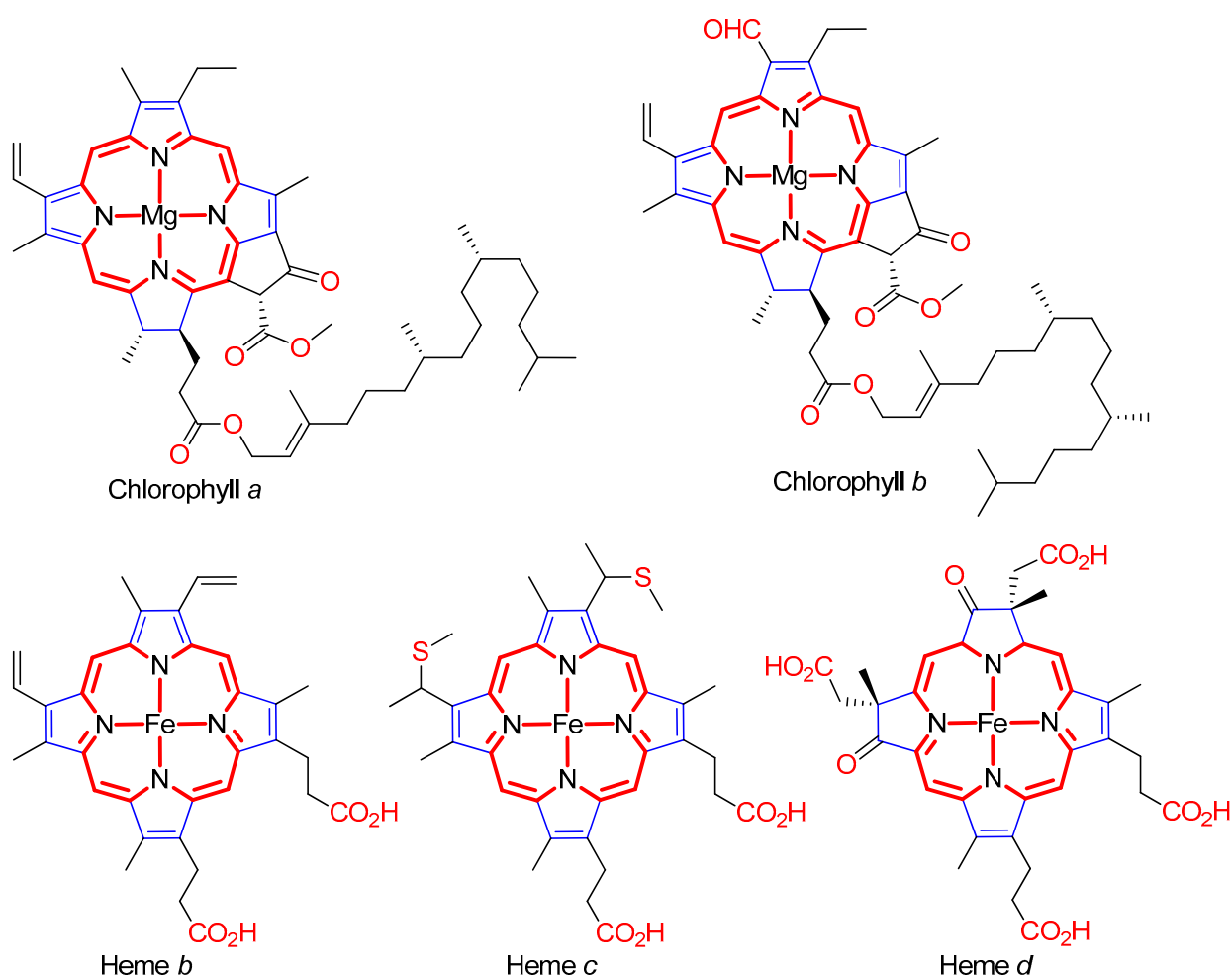


Figure 1. Structures of some metalloporphyrins which demonstrates the life on earth.

Besides the biological-catalytic functions of metalloporphyrins, their aptness to a large number of organic transformations as effective catalysts is well-documented [2,7] and is due to the wide selection of metal-ions that can form complexes with porphyrins [2]. The metalloporphyrins have been reported for their catalytic efficiency in cross-coupling reactions [2,8–12], epoxidations of alkenes [7,13,14], oxidation of alcohols/thiols/benzylic groups/aldehydes [15–17], cycloaddition reactions [18,19], reductions of multiple bonds [20,21], aziridinations of olefins [22,23], and olefin cyclopropanations [24,25]. These metalloporphyrins have also been reported as effective catalysts in large scale organic transformations [7] which is an additional benefit together with their inherent safeness and biomimicking properties [2,12]. Hence, the application of metalloporphyrins as catalysts in further organic reactions is interesting and imitates organic reactions of nature.

Self-coupling is an important strategy among the existing procedures for symmetrical biaryl synthesis and is a straightforward and convenient process [26]. This method avoids the requirement of two different substrates that are normally required in cross-coupling procedures [27]. Aryldiazonium salts [26,28,29], aryl halides [26,30–32], arylboronic acids [26,27,33–35], arylboronates [26,35–43], arylmagnesium compounds [26,44,45], aryllithium compounds [26,46,47], arylmercury salts [26,48,49], aryl mesylates [26,50–52], aryl tosylates [26,52], aryl triflates [26,52,53], arylsilanes [26,54,55], arylcarboxylic acids [26,56,57], and tetraarylborates [58–61] are the substrates used for this self-coupling process. In this connection, aryl halides, arylcarboxylic acids, arylboronic acids, arylsilanes, and arylboronates seem to be stable substrates [26,27]. Among these self-couplings, the couplings of arylcarboxylic acids, arylsilanes, and aryl halides require harsh conditions like oxidants, high temperature, and co-catalysts [26,27], but the self-coupling of arylboron substrates can be performed at room temperature (rt) and (or) using mild conditions [26,27,33–43]. The application of aryltrifluoroborates in self-coupling reactions is underdeveloped despite the high stability, fair water solubility, and good reactivity of these substrates [10,39–43].

The catalysts based on transition-metals such as Pd [26,27,33–39,41,43], Au [40,62–64], Cu [42,65–68], Rh [69], Ru [70], and Fe [71] have been reported for the self-coupling transformations of arylboron compounds but most of the Au, Cu, Rh, Ru, and Fe-based reactions suffer from drawbacks such as the requirement of an external oxidant, a base, organic solvent, low product yields, formation of by-products, and high temperature [26,27]. The Pd-promoted methods, on the other hand, can be performed at rt using mild reaction conditions in a safer solvent such as water [27]. Hence, we undertook the development of a new Pd-based protocol for the synthesis of biaryl using a self-coupling strategy, and found *N*-pincer Pd(II)-porphyrin complexes as efficient catalysts for this purpose in water, employing PATFBs as attractive substrates. The present protocol using water as reaction media (which is nature's preferred solvent instead of flammable, volatile, and toxic organic solvents [72]), together with metalloporphyrins as catalysts (which are the catalysts of several significant functions in biology), at ambient conditions in open-air can become a nature mimicking protocol for the synthesis of symmetrical biaryls.

2. Results and Discussion

The porphyrins, **TPP**, **TpAP**, **TSTpSPP**, **TmHPP**, and **TmCPP**, and their *N*-pincer Pd(II)-complexes, **PdTPP**, **PdTpAP**, **PdTSTpSPP**, **PdTmHPP**, and **PdTmCPP** (Figure 2) were synthesized according to our previous reports [2,10–12] (Sections 3.1.2 and 3.1.3). The characterization data of these compounds were revealed in our published data [10].

Initially, potassium 4-methoxyphenyltrifluoroborate (**1a**) was found to participate in self-coupling to give 98% of biaryl, **2a** (in 15 min) using 0.1 mol% of **PdTSTpSPP**, 4 mL of water at rt in open-air (entry 1, Table 1). This transformation using **PdTPP**, **PdTpAP**, **PdTmHPP**, and **PdTmCPP**, each with 0.1 mol% in 4 mL 1:1, vol:vol mixture of water and DMF was observed to provide **2a** in 21%, 39%, 58%, and 67% in 4h and indicated that the catalyst, **PdTSTpSPP** was highly suitable for the self-coupling of **1a** (entries 2–5, Table 1). Further, the catalyst loading studies, using 0.07 mol%, 0.05 mol%, and 0.03 mol% showed the formation of **2a** in 98%, 98%, and 82% in 15 min, 15 min and 60 min (entries 6–8, Table 1), suggesting the requirement of 0.05 mol% **PdTSTpSPP** as catalyst for the self-coupling of **1a**. The investigations using other arylboron compounds such as, 4-methoxyphenylboronic acid (**2**), neopentylglycol, and pinacol esters of 4-methoxyphenylboronic acid (**3** and **4**) and the diethanolamine derivative of 4-methoxyphenylboronic acid (**5**) showed 92%, 14%, 17%, and 73% yields of **2a** (entries 9–12, Table 1), indicating that potassium 4-methoxyphenyltrifluoroborate (**1a**) is the best substrate for the current self-coupling process. This may be due to the high water solubility of the aryltrifluoroborates.

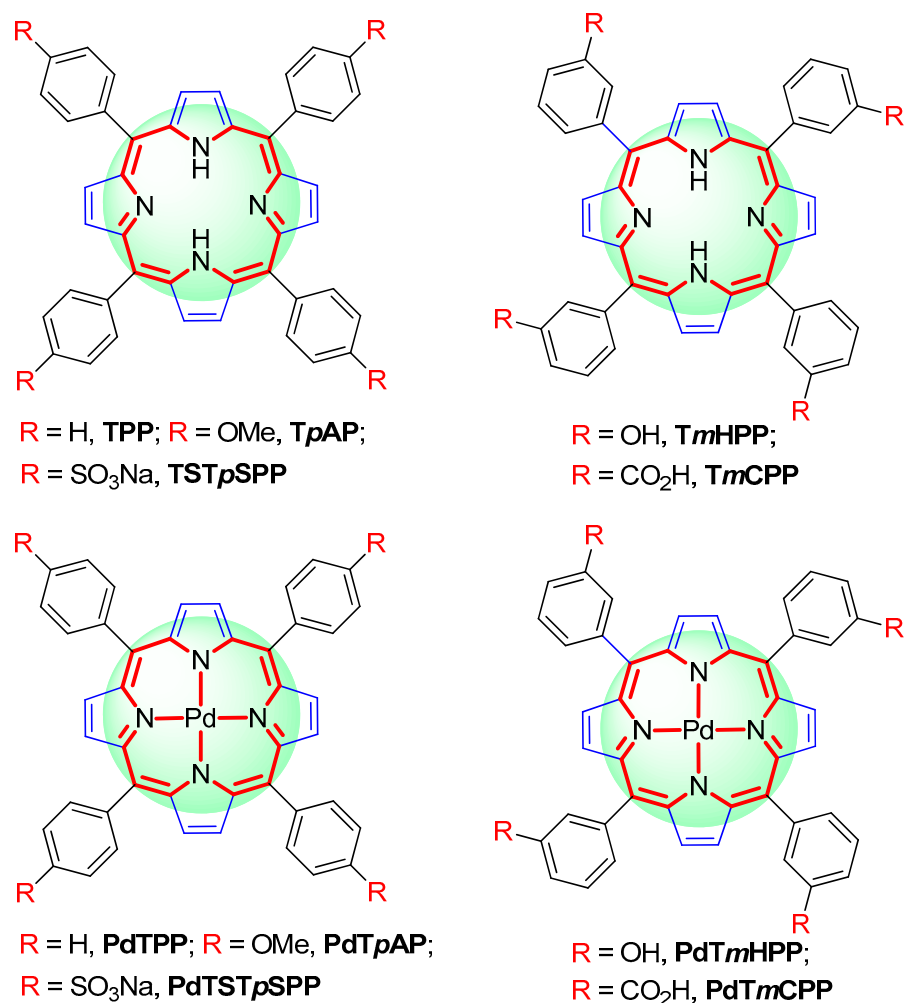
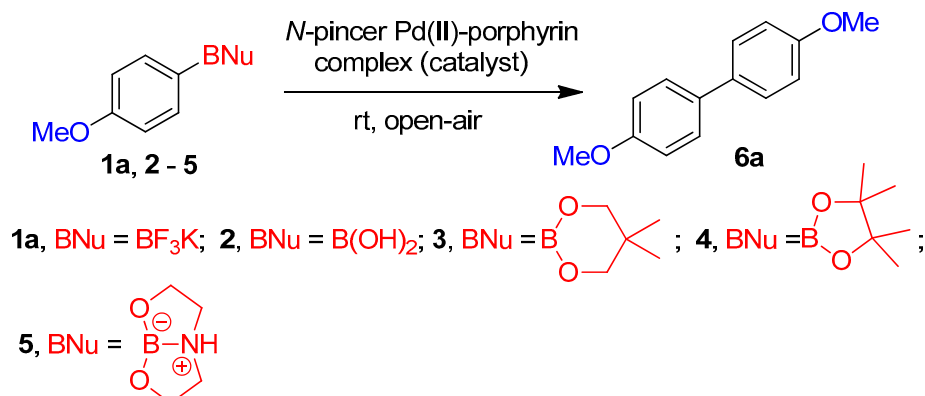


Figure 2. Chemical structures of porphyrins and their *N*-pincer Pd(II)-complexes (catalysts).

The applicability of this nature-inspired procedure has also been studied using a variety of aryltrifluoroborates (**1a–1u**). The PATFBs with electron-releasing functionalities (ERFs) such as -OMe, -Me, -Br, -OH, -SMe, and -^{*t*}Bu at *p*-, *m*- and *o*-positions delivered excellent yields (88–98%) of the self-coupling products, **6a–6f**, **6l**, **6m** and **6p** with high turnover number (TON) (1760–1960) and turnover frequency (TOF) (2347–7840) values (entries 1–6,12,13,16, Table 2). Electron withdrawing functionalities (EWFs) containing PATFBs at all the *p*-, *m*-, and *o*-positions were found as the best substrates to give 91–99% of self-coupled products, **6g–6k**, **6n**, **6o**, and **6q** with large values of TON as 1820–1980 and TOF as 3680–11880 (entries 7–11,14,15,17, Table 2). Unsubstituted PATFB such as **1r** and potassium salts of heteroaryltrifluoroborates, **1s–1u** also provided excellent isolated yields of self-coupled products under *N*-pincer Pd(II)-porphyrin, **PdTSTpSPP** catalyzed reactions in water with excellent yields (86–96%) of products, **6r** and **6s–6u** with TON, 1720–1920 and TOF, 1720–7680 (entries 18–21, Table 2). This study revealed that the current **PdTSTpSPP** catalyzed self-coupling of PATFBs shows a large substrate scope irrespective of position and nature of the functional groups. The structures of all the symmetrical biaryls were confirmed using their ¹H NMR, ¹³C NMR and mass (LCMS) spectral data (Section 3.2) and the copies of the ¹H NMR and ¹³C NMR spectra has been provided at Supplementary Materials with this article.

Table 1. Search for the catalyst and nucleophile ¹.

Entry	Arylboron Compound	Catalyst (mol%)	Solvent (mL)	Time (min)	Isolated Yield (%)
1	1a	PdTSTpSPP (0.1)	Water (4)	15	98
2	1a	PdTPP (0.1)	Water (2) + DMF (2)	240	21
3	1a	PdTpAP (0.1)	Water (2) + DMF (2)	240	39
4	1a	PdTmHPP (0.1)	Water (2) + DMF (2)	240	58
5	1a	PdTmCPP (0.1)	Water (2) + DMF (2)	240	67
6	1a	PdTSTpSPP (0.07)	Water	15	98
7	1a	PdTSTpSPP (0.05)	Water	15	98
8	1a	PdTSTpSPP (0.03)	Water	60	82
9	2	PdTSTpSPP (0.05)	Water	15	92
10	3	PdTSTpSPP (0.05)	Water (2) + DMF (2)	180	14
11	4	PdTSTpSPP (0.05)	Water (2) + DMF (2)	180	17
12	5	PdTSTpSPP (0.05)	Water	60	73

¹ Arylboron substrate (1 mmol) and 4 mL of solvent were used and the reactions conducted in open-air at rt.

We also studied the hetero-coupling reaction of PATFBs, **1a** and **1r** (each with 0.5 mmol) under the present conditions, and observed the formation of self-coupling products **6a** and **6r** along with the hetero-coupling product **7**, in 19%, 21%, and 57% yields in 15 min (Scheme 2). This study indicated that the developed method shows some selectivity in the formation of hetero-coupling products over self-couplings, and hence a detailed investigation may be undertaken towards a complete understanding of the hetero-couplings of arylboron compounds using metalloporphyrin-based catalysts.

The plausible mechanistic futures of PdTSTpSPP catalyzed self-coupling of PATFBs is sketched in Scheme 3 based on previous reports [10–12,27,39,73]. The reduction-dissociation process of PdTSTpSPP delivers the Pd(0)-porphyrin intermediate **A** [10–12]. The Pd(0)-porphyrin species **A** is involved in oxidative addition with PATFB **1** and atmospheric oxygen to give Pd(II)-species **B**, which is on transmetalation with **1** gives the diarylPd(II) intermediate **C** [27,39,73]. Intermediate **C** forms symmetrical biaryl **6** and Pd(0)-porphyrin active catalytic principal **A** on reductive elimination.

Table 2. Substrate feasibility study ¹.

Entry	Aryltrifluoroborate (1)	Time (min)	Product (6)	Yield (%) ²	TON	TOF
1	 1a	15	6a	98	1960	7840
2	 1b	25	6b	94	1880	4512
3	 1c	25	6c	92	1840	4416

Table 2. Cont.

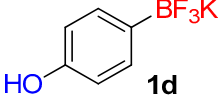
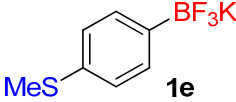
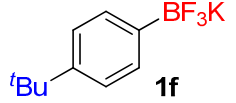
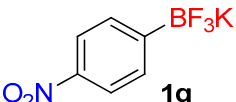
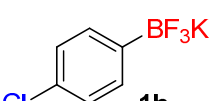
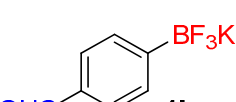
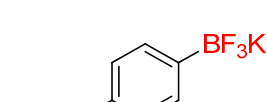
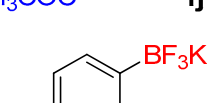
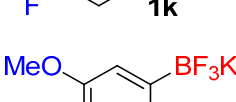
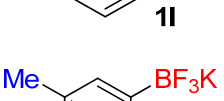
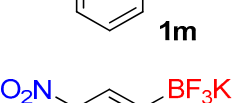
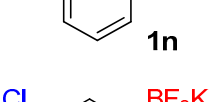
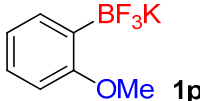
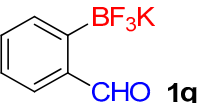
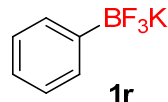
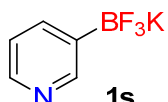
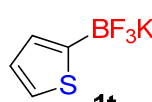
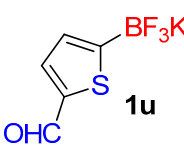
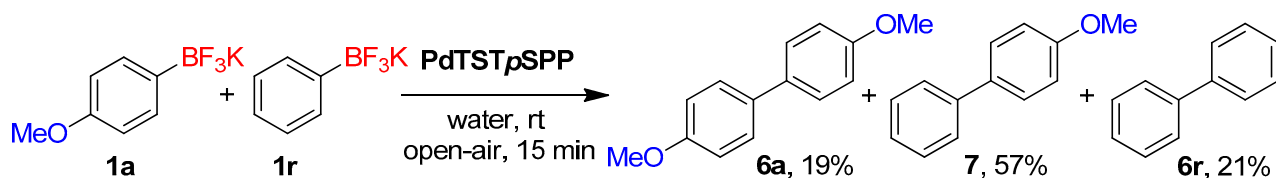
Entry	Aryltrifluoroborate (1)	Time (min)	Product (6)	Yield (%) ²	TON	TOF
4	 1d	35	6d	89	1780	3051
5	 1e	20	6e	94	1880	5640
6	 1f	20	6f	94	1880	5640
7	 1g	10	6g	99	1980	11,880
8	 1h	15	6h	97	1940	7760
9	 1i	10	6i	99	1980	11,880
10	 1j	20	6j	97	1940	5820
11	 1k	10	6k	98	1960	11,760
12	 1l	30	6l	93	1860	3720
13	 1m	30	6m	88	1760	3520
14	 1n	20	6n	95	1900	5700
15	 1o	30	6o	92	1840	3680

Table 2. Cont.

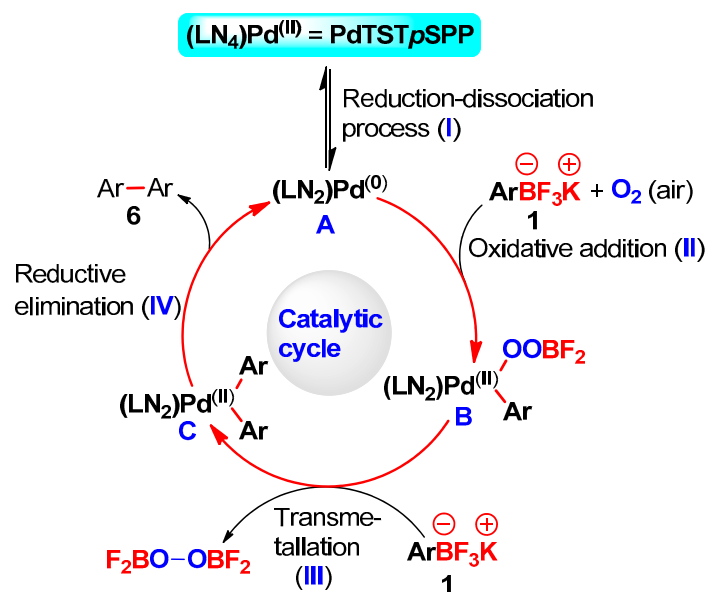
Entry	Aryltrifluoroborate (1)	Time (min)	Product (6)	Yield (%) ²	TON	TOF
16	 1p	45	6p	88	1760	2347
17	 1q	40	6q	91	1820	2730
18	 1r	15	6r	96	1920	7680
19	 1s	60	6s	91	1820	1820
20	 1t	60	6t	86	1720	1720
21	 1u	50	6u	90	1800	2160

¹ Conditions: PATFB (1 mmol), water (4 mL) at ambient conditions in open-air. ² Isolated yield.



Scheme 2. Study of PdTSTpSPP catalyzed hetero-coupling of PATFBs.

A comparison of reported self-coupling procedures of aryltrifluoroborates [39–43] is shown in Table 3 and evidences the clear merits of the present nature-mimicking method over the reported protocols using Pd NPs/Te-Dps [39], Au nanoclusters:poly(*N*-vinyl-2-pyrrolidone) [40], Pd(OAc)₂–electrolysis [41], Cu(OAc)₂–ultra sound [42], and Pd NPs@Al(OH)₃ [43] which require organic solvent [41], base/additive [39–43], heating [39–43], long process time [39,40,42,43] or suffer from low biaryl yield with some aryltrifluoroborates [39–43]. Hence, the present *N*-pincer Pd(II)-porphyrin catalyzed process is advantageous over the reported aryltrifluoroborate self-couplings. In view of global sustainability, the elimination/decrease of the application of volatile organics, the use of benign/nature-mimicking catalysts, and conducting the chemical reactions at ambient conditions can make a significant contribution [74–78].



Scheme 3. Proposed mechanism of PdTSTpSPP catalyzed self-coupling of PATFBs.

Table 3. Comparison of self-couplings of aryltrifluoroborates.

Entry	Catalyst	Solvent	Base/Additive	Temp.	Time (h)	Yield (%)	Ref.
1	Pd NPs/Te-Dps ¹	Water	Tris-HCl buffer	100 °C	10–24	60–87	[39]
2	Au nanoclusters;poly(<i>N</i> -vinyl-2-pyrrolidone)	Water	pH 6.86 buffer	47 °C	24	14–quant.	[40]
3	Pd(OAc) ₂ –electrolysis	DMF	<i>p</i> -Benzoquinone	80 °C	0.24–0.40	41–99	[41]
4	Cu(OAc) ₂ –ultra sound	Aq. EtOH	Dowex polymer support	Ultrasound	6	0–98	[42]
5	Pd NPs@Al(OH) ₃	Water	KOAc, Ag ₂ O	50 °C	16–48	42–98	[43]
6	PdTSTpSPP	Water	-	rt	0.17–1.0	86–99	Present

¹ Pd NPs/Te-Dps; Pd nanoparticles stabilized with Dps protein of *Thermosynechoccus elongatus* bacterium.

3. Materials, Methods and Characterization Data

3.1. Materials and Methods

3.1.1. General

The chemical substances utilized in the present homocoupling of PABs were purchased from Spectrochem (Mumbai, India), Alfa Aesar (Haverhill, MA, USA), Merck (Burlington, MA, USA), AVRA (Hyderabad, India), Sigma-Aldrich (St. Louis, MO, USA), and TCI (Tokyo, Japan). Porphyrins and Pd(II)-porphyrin complexes were made from literature reports [2,10,79]. Pyrrole was directly purified by distillation before its use. Silica gel coated thin layer chromatography (TLC) (Merck, Burlington, MA, USA, silica gel-60 F₂₅₄) was employed to confirm the progress of the self-couplings. Silica gel-packed glass-columns were employed to produce the pure symmetrical biaryls using an eluent of a mixture of EtOAc and hexanes. The Bruker Avance 400/100 MHz NMR spectrometer (Billerica, MA, USA) was employed to record the ¹H and ¹³C-NMR spectra and molecular mass was recorded with a Thermo LCQ Max LCMS (Dreieich, Germany).

3.1.2. Synthesis of Porphyrins

TPP: Propanoic acid (180 mL) at 140 °C was added to 75 mL of pyrrole and 8.37 g of benzaldehyde, and the mixture was heated for 1h at 140 °C. The reaction contents were cooled to rt then 110 mL of EtOH was added and stirred at rt for 1 h. The reaction mixture was filtered and the filtrate evaporated in vacuo. Finally, the residue obtained was

used to purify the TPP using neutral alumina-packed-column chromatography (CC) with eluent CHCl_3 .

TpAP, TmHPP, and TmCPP: Propionic acid (180 mL) was added to 7.30 g of its anhydride and heated for 5 min at 140 °C. Then, 5.00 g of pyrrole (distilled), and 80 mmol of *p*-anisaldehyde/*m*-hydroxybenzaldehyde/*m*-formylbenzoic acid were added, stirred at 140 °C for 1 h and the mixture cooled to rt. Then 100 mL of EtOH was added, stirred at rt for 1 h, and filtered. The obtained residue was dried in vacuo and subjected to neutral alumina-packed-CC with eluent CHCl_3 to obtain the pure porphyrins, **TpAP**, **TmHPP**, and **TmCPP**.

TSTpSPP: TPP (5 gr) in conc. H_2SO_4 (60 mL) was heated at 60 °C 16 h and cooled to rt with 12 mL of added ice-cold water. The obtained green colored solution was adjusted to pH between 9–10 using an aqueous solution of saturated NaHCO_3 . The mixture was evaporated in vacuo and thoroughly washed using 2×25 mL of CH_2Cl_2 . A solid precipitate obtained on the addition of 20 mL of MeOH:acetone (3:7) was separated, dried in vacuo, and the **TSTpSPP** was subjected to purification using neutral Al_2O_3 -packed-CC with the eluent, MeOH:acetone (3:7).

3.1.3. Synthesis of *N*-pincer Pd(II)-porphyrin Complexes

PdTPP, PdTpAP, PdTmCPP, and PdTmCPP [10]: 5 mmol of porphyrin (**TPP/TpAP/TmHPP/TmCPP**), 7.5 mmol of PdCl_2 in 20 mL DMF were refluxed for 2 h, cooled to rt, and filtered. The filtrate was diluted with 40 mL EtOAc, washed using 2×20 mL of water and 2×15 mL of brine. EtOAc was evaporated in vacuo and the resultant residue of the Pd-porphyrin complexes subjected to purification using CC with eluent, MeOH: CH_2Cl_2 (5:95).

PdTSTpSPP [10]: **TSTpSPP** (2.56 g, 2.5 mmol), PdCl_2 (0.53 g, 3 mmol) in 12 mL DMF was refluxed for 2 h and cooled to rt and subjected to evaporation to obtain a dried reaction mass. The crude solid was employed for the purification of **PdTSTpSPP** using CC with the eluent acetone:MeOH (8:2).

3.1.4. PABs Homocoupling Procedure

To **PdTSTpSPP** (0.05 mol%) and PATFB (**1**) (1.10 mmol), 4 mL of deionized water was added and the mixture stirred at rt in open-air for the appropriate time (Table 2). To ensure the completion of the reaction by TLC, to the reaction mixture was added 5 mL water and it was extracted using EtOAc (2×5 mL). The EtOAc combined solution was dried in vacuo and subjected to silica-gel packed-CC to obtain the pure symmetrical biaryls (**6**). The products (**6**) structures were determined by their ^1H and ^{13}C NMR and mass data. The characterization data of **6** (Section 3.2) was found to be similar to that of that reported [27,30,66,67] and the copies of ^1H and ^{13}C NMR spectra has been provided as Supplementary Materials with the manuscript.

3.2. Characterization Data of Symmetrical Biaryls

6a [27,30]: ^1H NMR (400 MHz, chloroform- d_6): δ (ppm) = 7.46 (d, J = 7.4 Hz, 4H, Ar-H), 6.94 (d, J = 7.4 Hz, 4H, Ar-H), 3.83 (s, 6H, -OMe); ^{13}C NMR (100 MHz, chloroform- d_6) δ (ppm) = 158.8, 133.6, 127.8, 114.2, 55.4; LCMS (m/z): 215 (M + H); Formula: $\text{C}_{14}\text{H}_{14}\text{O}_2$.

6e [27]: ^1H NMR (400 MHz, chloroform- d_6): δ (ppm) = 7.49 (d, J = 7.3 Hz, 4H, Ar-H), 7.30 (d, J = 7.3 Hz, 4H, Ar-H), 2.51 (s, 6H, -SMe); ^{13}C NMR (100 MHz, chloroform- d_6) δ (ppm) = 137.6, 137.4, 127.2, 127.1, 16.0; LCMS (m/z): 247 (M + H); Formula: $\text{C}_{14}\text{H}_{14}\text{S}_2$.

6f [27]: ^1H NMR (400 MHz, chloroform- d_6): δ (ppm) = 7.54–7.49 (m, 4H, Ar-H), 7.46–7.42 (m, 4H, Ar-H), 1.35 (s, 18H, ^tBu); ^{13}C NMR (100 MHz, chloroform- d_6) δ (ppm) = 150.0, 138.3, 126.7, 125.7, 34.6, 31.5; LCMS (m/z): 267 (M + H); Formula: $\text{C}_{20}\text{H}_{26}$.

6h [27,67]: ^1H NMR (400 MHz, chloroform- d_6): δ (ppm) = 7.49–7.46 (m, 4H, Ar-H), 7.42–7.38 (m, 4H, Ar-H); ^{13}C NMR (100 MHz, chloroform- d_6) δ (ppm) = 138.5, 133.8, 129.3, 128.3; LCMS (m/z): 224 (M + H); Formula: $\text{C}_{12}\text{H}_8\text{Cl}_2$.

6m [27]: ^1H NMR (400 MHz, chloroform- d_6): δ (ppm) = 7.38 (d, J = 7.8 Hz, 4H, Ar-H), 7.31 (t, J = 7.1 Hz, 2H, Ar-H), 7.14 (d, J = 7.3 Hz, 2H, Ar-H); ^{13}C NMR (100 MHz,

chloroform- d_6) δ (ppm) = 141.4, 138.3, 128.7, 128.0, 127.9, 124.2, 21.4; LCMS (m/z): 183 (M + H); Formula: C₁₄H₁₄.

6q [27,66]: ¹H NMR (400 MHz, chloroform- d_6): δ (ppm) = 9.83 (s, 2H, -CHO), 8.05 (d, J = 7.4 Hz, 2H, Ar-H), 7.66 (t, J = 7.1 Hz, 2H, Ar-H), 7.59 (t, J = 7.2 Hz, 2H, Ar-H), 7.36 (d, J = 7.4 Hz, 2H, Ar-H); ¹³C NMR (100 MHz, chloroform- d_6) δ (ppm) = 191.2, 141.3, 134.7, 133.5, 131.8, 128.9, 128.7; LCMS (m/z): 211 (M + H); Formula: C₁₄H₁₀O₂.

6u [27,66]: ¹H NMR (400 MHz, chloroform- d_6): δ (ppm) = 9.90 (s, 2H, -CHO), 7.71 (d, J = 3.8 Hz, 2H, HetAr-H), 7.41 (t, J = 3.8 Hz, 2H, HetAr-H); ¹³C NMR (100 MHz, chloroform- d_6) δ (ppm) = 182.6, 144.8, 144.0, 136.9, 126.4; LCMS (m/z): 223 (M + H); Formula: C₁₀H₆O₂S₂.

4. Conclusions

To summarize, we developed a new, nature-inspired procedure for the aerobic self-coupling of PATFBs in water using the nitrogen-bridged polycyclic *N*-pincer Pd(II)-porphyrin complex, **PdTSTpSPP**, as a safe catalyst at rt in open-air. This protocol showed advantages with the use of water as solvent, high TON and TOF values, low catalyst loading, large substrate feasibility, and avoidance of oxidant, base, phosphine ligands, and toxic solvents. To the best of our knowledge this is the first report on the use of metalloporphyrins for self-couplings of arylboron compounds.

Supplementary Materials: The copies of ¹H and ¹³C-NMR spectra of symmetrical biaryls are available online.

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