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Five-membered cyclopalladated complex containing bidentate phosphine ligands; Synthesis, characterization, and highly efficient Suzuki cross-coupling reactions

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A nonsymmetric phosphorus ylide and its palladium(II) complex have been synthesized as potential catalytically active compounds. The reaction of 1 equiv nonsymmetric phosphorus ylide, $Ph_2PCH_2PPh_2C(H)C(O)PhBr$ with $[Pd(dppe)Cl_2]$, followed by treatment with 2 equiv AgOTf led to $[(dppe)Pd(Ph_2PCH_2PPh_2C(H)C(O)PhBr)](OSO_2CF_3)_2$, which contains a five-membered P,P chelate ring on one side and a five-membered P,C chelate ring on the other side. The palladium complex was synthesized and investigated by fourier transform infrared spectroscopy (FT-IR), UV–visible, multinuclear (^1H, ^{31}P and ^{19}F) nuclear magnetic resonance (NMR), and electrospray ionisation-mass spectroscopic techniques. FT-IR and ^{31}P NMR studies revealed that the phosphorus ylide is coordinated to palladium via the terminal phosphorus (P_c) of the ylide and methene group (CH). Suzuki reactions for varying aryl halides using the cyclopalladated complex as an efficient catalyst were performed. Various aryl halides were coupled with arylboronic acids in DMF, under air, in the presence of 0.001 mol% of the homogeneous catalyst to afford the corresponding cross-coupled products in good to excellent yields.

Keywords: Cyclopalladated complex; Bidentate phosphine ligands; Arylboronic acids; Nonsymmetric phosphorus ylide; Suzuki cross-coupling reaction

1. Introduction

Palladium-catalyzed reactions, such as carbon–carbon bond formation, have attracted considerable interest [1,2]. Specifically, the Suzuki cross-coupling reaction of aryl halides with organoboron reagents is one of the most important and reliable methods for the construction of biaryls, which are present in a wide range of natural products, pharmaceuticals, agrochemicals, and functional polymer materials [3–10]. Like other types of palladium catalyzed coupling reactions, the Suzuki coupling is highly dependent on the nature of the ligand structure. Bulky, electron-rich phosphines are outstanding in the palladium-catalyzed Suzuki cross-coupling reaction, resulting from their superior donor capability and stabilization effects [11–14]. New palladacyclic complexes as active and air-stable catalytic candidates have been employed in Suzuki reactions [15,16]. Cyclopalladated complexes are important starting materials in organometallic chemistry [17,18], known for over 30 years [19–25], and have applications in many areas, including organic synthesis, [26–29]

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material science, [30] biologically active compounds [31], and as building blocks in macromolecular chemistry [32–34].

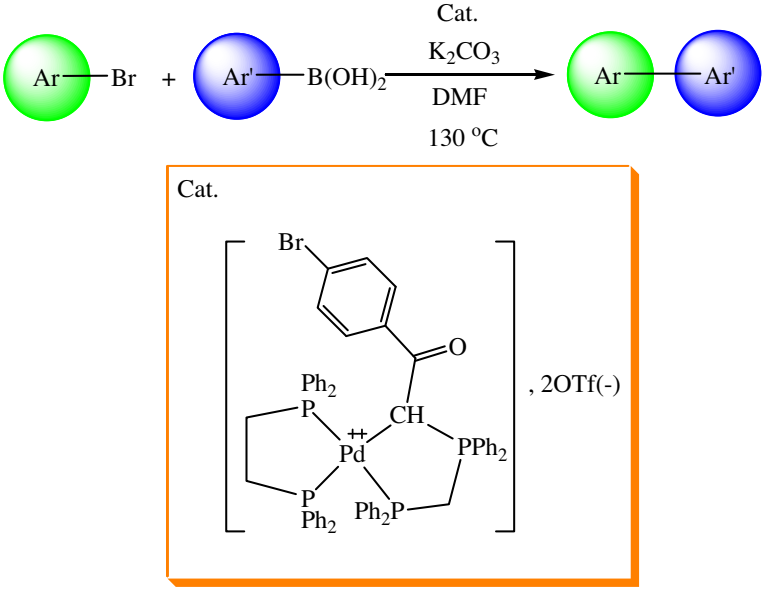
Our group has obtained cyclopalladated complex from the nonsymmetric phosphorus ylide, $Ph_2PCH_2PPh_2C(H)C(O)PhBr$ with $[Pd(dppe)(OTf)_2]$, and the complex is an excellent catalyst for Suzuki cross-coupling reactions. Coordination, organometallic chemistry, and catalytic chemistry of stabilized phosphorus ylides with palladium(II) have been investigated extensively and their ambidenticity was explained in terms of a delicate balance between electronic and steric factors [35–38]. In conjunction of our previous work on the synthesis and structural characterization of dichlorocyclopalladated complexes, [19] herein we report the application of a new cyclopalladated complex (scheme 1) in Suzuki cross-coupling reactions of various aryl halides under relatively mild experimental conditions.

2. Results and discussion

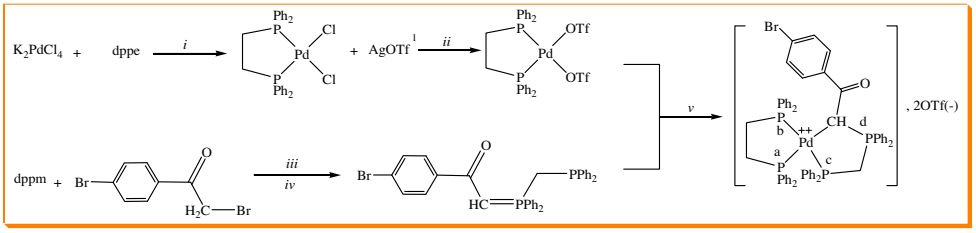
2.1. *Synthesis and characterization*

The nonsymmetric phosphorus ylide and its Pd(II) complex were synthesized (synthetic route, scheme 2) and its structure was elucidated using a variety of physico-chemical techniques.

The proclivity of OTf to be replaced by nucleophiles is shown by the poorly coordinated OTf in $[Pd(dppe)(OTf)_2]$ being exchanged with the phosphorus ylide. Fluorine nuclear magnetic resonance (NMR) (measured in $CDCl_3$) shows a weak peak for trifluoromethanesulfonate at 67.5 ppm in $[Pd(dppe)(OTf)_2]$. ^{19}F NMR spectroscopy at room temperature reveals a single resonance due to OTf at −77.9 ppm in the final complex, which indicates that trifluoromethanesulfonate is a counter ion [39–41].



Scheme 1. Suzuki cross-coupling reactions of various aryl halides with arylboronic acid in catalytic amount of Pd complex.



Scheme 2. Synthetic route for preparation of Pd(II) complex. Reagents and conditions: (*i*) In ethanol, in the presence of hydrochloric acid, using Celite and refluxing for 8 h. (*ii*) In dichloromethane, using aluminum foil to prevent oxidation and Celite for filtering precipitate, 2 h at 25 °C. (*iii*) In chloroform, using dry nitrogen, 2 h at 25 °C. (*iv*) In triethyl amine (0.5 mL) in toluene, 15 min at 25 °C. (*v*) In methanol, using dry nitrogen, 12 h at 25 °C. [1]Silver trifluoromethanesulfonate.

The IR spectrum of the phosphorus ylide and its complex showed a band at ~1500 cm^{-1} assigned to carbonyl. The ν(CO), which is sensitive to complexation, occurs at 1600 cm^{-1} in the parent ylide [42,43]. Coordination of the ylide through carbon causes an increase in the ν(CO), while, when O-coordination occurs, a lowering in the value of ν(CO) would be expected [44]. The band at 850−900 cm^{-1} characteristic of the P–CH of the phosphorus ylide and its complex are assigned to P–C vibration. Thus, the IR absorption bands for the complex at lower frequencies indicate that C-coordination has occurred [45].

In the ^{31}P $\{^1H\}$ NMR spectra of $Ph_2PCH_2PPh_2C(H)C(O)PhBr$, the signal due to PCH (P_d) and PCH_2 (P_c) appears as two doublets at 11.4 and −30 ppm, respectively. The ^{31}P chemical shift of $[Pd(dppe)Cl_2]$ due to P_a and P_b is a singlet at 66.7 ppm. The ^{31}P NMR spectrum of the complex shows an interesting pattern of signals which allows the assignment of the structure of this complex. The four P atoms in this complex are chemically and magnetically nonequivalent (scheme 2); therefore, the ^{31}P $\{^1H\}$ NMR spectrum exhibits four separate resonances. The upfield peak ($\delta p = 55$, m), ($\Delta\delta = -11.7$ ppm) is assigned to P_a of the bidentate dppe, directly attached to Pd trans to CH and thus, shielded. The $^3J P_bP_a$ coupling constant of 20 Hz lies within the typical values for similar systems [46–48]. The $^2J P_cP_a$ and $^3J P_dP_a$ coupling constants are 58.1 and 14 Hz, respectively [49]. The upfield peak ($\delta p = 55.1$, ddd), ($\Delta\delta = -11.6$ ppm) is assigned to P_b of dppe, directly attached to Pd trans to PCH_2 (P_c) and thus, shielded [this value is intermediate between the two peaks at 50.1 and 60.1 (see Supplementary material). The extremely strong coupling with P_b of dppe ($^2J P_bP_c = 355$ Hz) can only be rationalized in the context of a trans arrangement between P_b and P_c [47,48,50,51]. The $^3J P_bP_d$ coupling constant is 12 Hz. Two downfield peaks are assigned to two phosphorus of the chelate phosphorus ylide. The ylidic P_d of the phosphorus ylide is not directly coordinated to the metal center, thus coupling with P_c is weak ($^2J P_dP_c = 27$ Hz) as expected [49]. Coupling with P_b ($^3J P_dP_b = 12$) and P_a ($^3J P_dP_a = 14$ Hz) gives a downfield ddd ($\delta p = 37.6$, ddd), ($\Delta\delta = +26.2$ ppm). The chemical shifts for the two nonequivalent phorphorus of the ambidentate P,CH–ligand are assigned on the basis of published NMR data for related complexes [19]. Finally, the downfield peak ($\delta p = 19.1$, ddd), ($\Delta\delta \approx +49.1$ ppm) is assigned to PCH (P_c). The significant downfield shift of the signal from that of the free ylide is in agreement with the C-bonding of the ylide. The coordination via the phosphine moiety is also clearly evidenced from the strong downfield shifts of the signal due to PPh_2 when compared to that of the same signal in the free ylide [45,50].

Regarding the ^{1}H NMR spectrum of this complex, the phenyl protons of dppe and phosphorus ylide are observed in the aromatic region of the spectrum, between 6.9–7.7 ppm [19]. According to published data, the ^{1}H NMR spectrum of the Pd(II) complexes was consistent with coordination of the phosphorus ylide to the metal through the CH and P_c. In the ^{1}H NMR spectrum, the signal due to the methynic proton of the complex is broad [19]. Similar behavior was observed earlier for ylide complexes derived from $PtCl_2$ [52]. Furthermore, the complex showed a multiplet at 4.82 ppm due to the methynic proton. The expected lower shielding of the ^{1}H nuclei for PC(H) upon complexation in the case of C-coordination was observed in the corresponding spectra [53]. The complex showed multiple peaks at 2.66–2.76 ppm due to CH_2 of dppe. The CH_2 protons in the complex of the phosphorus ylide appear as a multiplet (m) $\delta = 4.63$ ppm.

Positive ion electrospray-mass spectrum (ESI+-MS) of the palladium catalyst was recorded as very dilute THF solution. The molecular ion was observed in the electrospray ionisation (ESI) mass spectrum. The mass spectrum of the Pd complex was characterized by the appearance of the fragment at *m/z* 1085.1 owing to the removal of two OTf groups and one proton, thus the $\{[Complex]^+ - H\}$ was formed. The peak at *m/z* 1235.06 is related to the molecular ion which is formed by elimination of one OTf group to give $[Complex]^+$. Also, the peak at *m/z* 543.05 is related to the ion produced by the elimination of two OTf groups and one radical hydrogen to give $[Complex]^{\bullet 2+}$ (Supplementary material). The above-mentioned data are in agreement with the calculated data (see Section 3).

The cyclopalladated complex has been found to be diamagnetic, indicating + 2 oxidation state for palladium. Electronic spectra of the Pd complex were recorded in the solid state and displayed three bands at 200–500 nm. The electronic spectrum of the phosphorus ylide as a ligand showed spectral bands due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. On complexation, these bands shift (see Supplementary material).

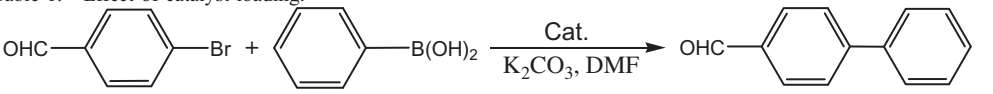
2.2. *Suzuki cross-coupling reactions*

Cyclopalladated complexes containing phosphorus ylides, which combines both good donor strength and π-accepting capacity, always have high catalytic activity in Suzuki cross-coupling reactions [38]. Therefore, we attempted to use our pd(II) complex as a catalyst in the Suzuki reaction. The ability to use small amounts of catalyst and still achieve high yields is a great concern in cross-coupling reactions due to the high cost of metals and ligands.

Low catalyst loading tests were performed to determine the catalytic efficiency of the catalyst in the presence of DMF and K_2CO_3. In order to optimize the reaction conditions for the coupling reactions, different amounts of catalyst (mol%) were taken and the results are summarized in table 1. Excellent yields were obtained from normal catalyst loads down to a level of 0.1 and 0.01 mol%. A moderate yield (65%) was obtained even at catalyst loading as low as 0.0005 mol%. Various catalyst concentrations were also tested and 0.001 mol% (table 1, entry 4) gave the best result. These are indications of an effective catalytic system that merits more exploration.

To study the effects of different solvents in our catalytic system, we have chosen the reaction between 4-bromobenzaldehyde with phenylboronic acid in the presence of various solvents and K_2CO_3. In all instances, the solvent was used as obtained commercially without further purification and the reactions were performed in air. After completion of the reaction, the biphenyl was isolated from the reaction mixture. The results of the above

Table 1. Effect of catalyst loading.[a]



Entry	Catalyst (mol%)	Time (h)	Yield[b] (%)
1	None	10	–
2	0.1	0.5	100
3	0.01	0.5	100
4	0.001	0.5	99
5	0.005	0.5	99
6	0.0005	5	65

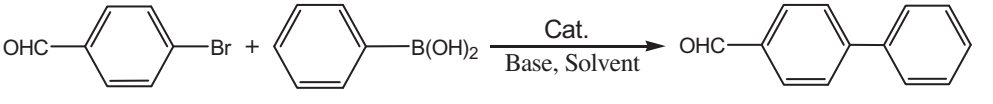
[a]Reaction conditions: 4-bromobenzaldehyde (0.75 mmol), phenyl boronic acid (1 mmol), K_2CO_3 (1.5 mmol), DMF (2 mL).
[b]Yield to the coupled product determined by GC based on aryl bromide.

reactions are summarized in table 2. A nonpolar solvent like toluene gave a moderate yield (67%, entry 3), whereas polar solvents such as DMF or methanol were more efficient for the yield of biaryl compounds to 99 and 73%, respectively (entries 2 and 4). A polar aprotic solvent (entry 1) gave a comparatively good yield. The lowest conversion (26%) was obtained with THF as solvent. This could be due to the reflux temperature of the solvent. In water, the reaction does not progress under reflux.

The effect of different mineral bases on this reaction was investigated by using the coupling of 4-bromobenzaldehyde with phenylboronic acid as a test case. First, the reaction was conducted without any base and no reaction was observed. In the presence of NaOAc and NaF yields of 76 and 59%, respectively, were observed inorganic bases (table 2, entries 8–11) which were much better than organic ones (table 2, entry 7); K_2CO_3 was the best choice of base, and the yield of product could be increased to 99% (table 2, entry 2).

Under the optimized reaction conditions at hand, we have taken a series of aryl halide and arylboronic acids and the yield of the coupled products are given in table 3. A general

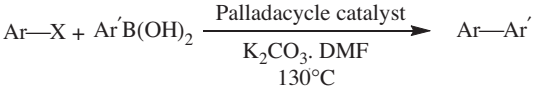
Table **2.** Optimization of base and solvent for Suzuki cross-coupling reaction.[a]



Entry	Base	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	K_2CO_3	Dioxane	130	0.5	85
2	K_2CO_3	DMF	130	0.5	99
3	K_2CO_3	Toluene	130	3	67
4	K_2CO_3	Methanol	65	12	73
5	K_2CO_3	THF	60	24	26
6	K_2CO_3	H_2O	100	24	–
7	Et_3N	DMF	130	24	Trace
8	Na_2CO_3	DMF	130	1	90
9	Cs_2CO_3	DMF	130	1	89
10	NaOAc	DMF	130	12	76
11	NaF	DMF	130	12	59

[a]Reaction conditions: 4-bromobenzaldehyde (0.75 mmol), phenyl boronic acid (1 mmol), base (1.5 mmol), solvent (2 mL), catalyst (0.001 mol%), 130 °C.
[b]GC yield.

Table 3. Suzuki cross-coupling reaction of aryl halides with aryl boronic acids catalyzed by Pd complex.[a]



Entry	Ar-X	Ar-B(OH)2	Product (Ar-Ar′)	Time (h)	Yield[b] (%)
1	*p*-O_2N-Ph-Br	$PhB(OH)_2$	*p*-O_2N-Ph-Ph	0.5	98
2	*p*-O_2N-Ph-Br	*p*-Et-$PhB(OH)_2$	*p*-O_2N-Ph-Ph-Et	0.5	96
3	*p*-OHC-Ph-Br	$PhB(OH)_2$	*p*-OHC-Ph-Ph	0.5	99
4	*p*-OHC-Ph-Br	*p*-Et-$PhB(OH)_2$	*P*-OHC-Ph-Ph-Et	0.5	98
5	*p*-Me-Ph-Br	$PhB(OH)_2$	*p*-Me-Ph-Ph	1.5	88
6	*p*-Me-Ph-Br	*p*-Et-$PhB(OH)_2$	*p*-Me-Ph-Ph-Et	1.5	87
7	$C_{10}H_7$-Br	$PhB(OH)_2$	$C_{10}H_7$-Ph	2	83
8	$C_{10}H_7$-Br	*p*-Et-$PhB(OH)_2$	$C_{10}H_7$-Ph-Et	2	80
9	Ph-Br	$PhB(OH)_2$	Ph-Ph	1.5	90
10	Ph-Br	*p*-Et-$PhB(OH)_2$	*p*-Et-Ph-ph	1.5	86
11	*p*-Br-Ph-CO_2H	$PhB(OH)_2$	*p*-HO_2C-Ph-Ph	0.5	95
12	*P*-Br-Ph-CO_2H	*p*-Et-$PhB(OH)_2$	*p*-HO_2C-Ph-Ph-Et	0.5	93
13	C_4H_3SBr	$PhB(OH)_2$	C_4H_3S-Ph	2	83
14	C_4H_3SBr	*p*-Et-$PhB(OH)_2$	C_4H_3S-Ph-Et	2	81
15	*p*-CH_3OC-Ph-Br	$PhB(OH)_2$	*p*-CH_3OC-Ph- Ph	0.5	91
16	*P*-CH_3OC-Ph-Br	*p*-Et-$PhB(OH)_2$	*p*-CH_3OC-Ph- Ph-Et	0.5	84
17	Ph-Cl	$PhB(OH)_2$	Ph-Ph	3	88
18	Ph-Cl	*p*-Et-$PhB(OH)_2$	*p*-Et-Ph-Ph	3	83
19	*p*-CH3OC-Ph-Cl	$PhB(OH)_2$	*p*-CH_3OC-Ph- Ph	2	82
20	*P*-CH_3OC-Ph-Cl	*p*-Et-$PhB(OH)_2$	*p*-CH_3OC-Ph- Ph-Et	2	80
21	*p*-Me-Ph-Cl	$PhB(OH)_2$	*p*-Me-Ph-Ph	3	76
22	*p*-Me-Ph-Cl	*p*-Et-$PhB(OH)_2$	*p*-Me-Ph-Ph-Et	3	69
23	Ph-I	$PhB(OH)_2$	Ph-Ph	0.5	97
24	Ph-I	*p*-Et-$PhB(OH)_2$	*p*-Et-Ph-Ph	0.5	93
25	*p*-Me-Ph-I	$PhB(OH)_2$	*p*-Me-Ph-Ph	0.5	90
26	*p*-Me-Ph-I	*p*-Et-$PhB(OH)_2$	*p*-Me-Ph-Ph-Et	0.5	88
27[c]	*p*-OHC-Ph-Br	$PhB(OH)_2$	*p*-OHC-Ph-Ph	0.5	75
28[c]	*p*-Me-Ph-Cl	$PhB(OH)_2$	*p*-Me-Ph-Ph	3	61

[a]Reaction conditions: aryl halide (0.75 mmol), boronic acid (1 mmol), K_2CO_3 (1.5 mmol), DMF (2 mL), catalyst (0.001 mol%), 130 °C.
[b]GC yields based on aryl halide.
[c]With precursor complex $[Pd(dppe)(OTf)_2]$ as catalyst (0.001 mol%). See Ref. [70].

catalytic cycle for the cross-coupling reaction of organoboron reagents with aryl halides involves oxidative-addition of the aryl halide, transmetalation, and reductive elimination [3,4]. In a typical Suzuki cross-coupling reaction, the Pd^{II} species is reduced to Pd^0 prior to the oxidative addition step (see scheme 3).

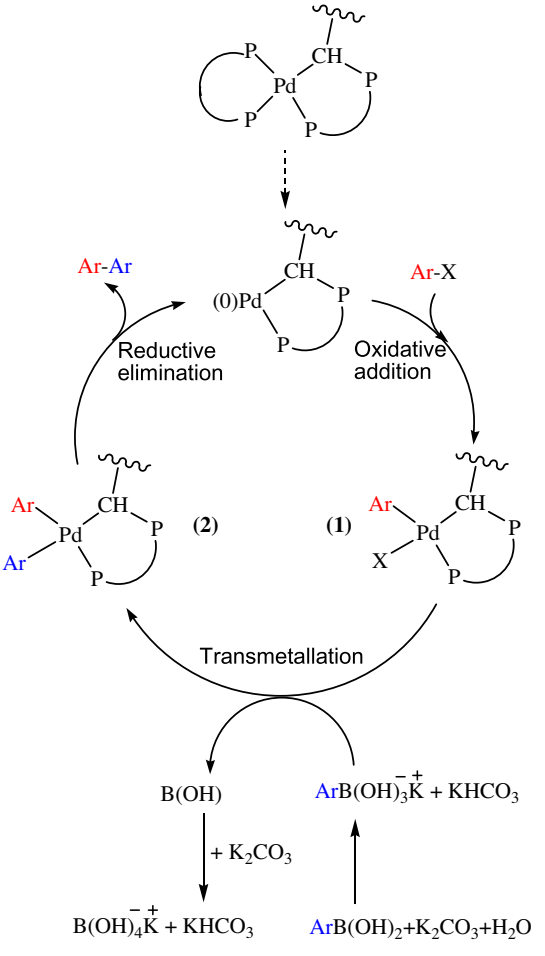
Aryl bromides with various functional groups efficiently reacted with boronic acids (table 3, entries 1–14) using K_2CO_3 and 2 mL DMF at reflux temperature in the presence of the palladium(II) catalyst to give Suzuki products in good to excellent yields. In palladium-catalyzed carbon–carbon bond formation reactions, it is commonly believed that better yields are achieved for aryl halides with electron-withdrawing rather than electron-donating substituents [54]. Electron-deficient aryl bromides were transformed efficiently to the coupling products in $\geqslant 80\%$ yield in short reaction times (table 3, entries 1–4, 11–12, 15–16, and 19–20). The reaction of *p*-bromo-nitrobenzene with boronic acid derivatives showed excellent yields (entries 1–2, 98-96%). In electron-rich or deactivated *p*-bromotoluene, the yields are good in all the cases (entries 5–6, 88–87%). The electron-poor 4-bromobenzaldehyde also afforded excellent yields (entries 3–4,

99–98%). The electronically neutral bromobenzene (entries 9–10) produced a good amount of the desired product when coupled with arylboronic acid. As expected, very satisfactory results were obtained with the electron-deficient substrate of phenylboronic acid (entries 1, 3, 11, 15, 19) and showed excellent yields. 2-Bromothiophene was an efficient substrate (table 3, entries 13–14). Aryl chlorides were active for the Suzuki reaction with good yields even for a prolonged time at 130 °C (entries 17–18). Electron-deficient substrates such as 4-chloroacetophenone coupled with arylboronic acid yield the coupling products (table 3, entries 19, 20). In electron-rich p-chlorotoluene, the yields are moderate in all the cases (entries 21–22, 76–69%). Aryl iodides with arylboronic acids for the Suzuki reaction gave good yields of the corresponding products under optimized conditions (table 3, entries 23–26). The main drawback of the Pd-mediated Suzuki cross-coupling reaction is that only aryl iodides and aryl bromides can be used efficiently. Increasing the reaction rate of aryl chlorides allows us to overcome this problem [55]. The stronger C–Cl bond is responsible for slower reaction rate of aryl halides, because the oxidative addition step was rate determining in the cross-coupling catalytic cycle. In all reactions of aryl halides, the color of the reaction mixture changed very fast (~30 s) from light brown to black. Thus, it can be inferred that the reaction mechanism starts with a pre-dissociation and/or reduction step [56]. In this state, the Pd(II) source is converted into the more active and coordinatively unsaturated Pd(0) catalyst. This state is followed by oxidative addition of the aryl halide which is often the rate-determining step in C–C coupling catalytic cycles [57]. The catalytic cycle is completed by transmetallation, aryl group transfer from boron to palladium, and a final reduction–elimination to release the biaryl product. A proposed mechanistic description of the Suzuki reaction is presented in scheme 3. Initially, Pd(II) converts to Pd(0) [58], followed by oxidative addition of aryl halide to Pd(0) to form the aryl palladium(II) intermediate **1**. Then, phenylboronic acid which is activated by K_2CO_3 reacts with intermediate **1**. After the transmetallation reaction, intermediate **2** is obtained. Finally, reductive elimination of **2** produces the desired coupling products.

[Pd(dppe)$(OTf)_2$] can also be used as an active resource for producing Pd(0). We used this complex as main catalyst under identical conditions. As can be seen in table 3, the activity of [Pd(dppe)$(OTf)_2$] with an 'easy' set of substrates (entry 27) and a 'difficult' set of substrates (entry 28) was tested. When we use this complex as a catalyst in the Suzuki reaction under the mentioned optimized conditions, moderate catalytic activity was observed for the catalyst in both substrates.

Although several catalytic systems have been reported to support Suzuki C–C coupling reactions, a homogeneous catalyst of this type is novel for its P donor dppe and P and CH of the phosphorus ylide. The homogeneous nature of the catalysis was checked by the classical mercury test [59]. Addition of a drop of mercury to the reaction mixture did not affect the conversion of the reaction, which suggests that the catalysis is homogeneous in nature, since heterogeneous catalysts would form an amalgam, thereby poisoning it.

The high efficiency of this catalyst at very low catalyst loading and short reaction time make it valuable. Monomeric complexes are easier to reduce to the active Pd(0) species compared with the dimeric Pd catalyst [60,63]. The comparison of data presented in table 4 shows the efficiency of this new catalyst towards the coupling reactions. Therefore, we compared various homogeneous catalysts in the Suzuki reaction under the same conditions (aryl halide, base and solvent) with the cyclopalladated complex used in this work. Low catalyst loading, high reactivity with bromobenzene in short reaction time, and stability toward air make it an ideal complex for Suzuki cross-coupling reactions.



Scheme 3. Proposed mechanism for Suzuki cross coupling.

This method proved successful in most cases to give the product in > 99% purity. ^{1}H and ^{13}C NMR data of the products indicated no Suzuki coupling by-products and NMR spectra of the Suzuki products are given in Supplementary material.

3. Experimental

3.1. *Materials and techniques*

Aryl halides and arylboronic acids were purchased from Sigma-Aldrich. Technical grade DMF was used for all catalytic reactions. GC analysis was performed on a Shimadzu 14B gas chromatograph equipped with a flame ionization detector. Melting points were measured on a SMPI apparatus and are reported without correction. Elemental analyses for C, H, and N were performed using a Perkin–Elmer 2400 series analyzer. Fourier transform IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer from 400–4000 cm^{-1} and samples were prepared as KBr pellets. UV–vis spectra were recorded on a JASCO,

V-670 Spectrophotometer, Japan, from 190–2700 nm. Mass spectra were recorded from a JEOL JMS 700 B/ES spectrometer. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded either on a 400 MHz Bruker or on a 90 MHz Jeol spectrometer using $CDCl_3$ as a solvent at 25 °C. Chemical shifts (δ) are reported relative to internal TMS (^{1}H and ^{13}C), internal $CFCl_3$ (^{19}F), and external 85% phosphoric acid (^{31}P). [Pd(dppe)Cl_2] [69], [Pd(dppe)$(OTf)_2$] [70], and $Ph_2PCH_2PPh_2C(H)C(O)PhBr$ [19] were prepared by published procedures (see Supplementary material).

3.2. *General procedure for preparation of the palladium catalyst*

To [Pd(dppe)$(OTf)_2$] (0.4 g, 0.5 mmol) in methanol solution (10 mL), a solution of ($Ph_2PCH_2PPh_2C(H)C(O)PhBr$) (0.29 g, 0.5 mmol) (10 mL, CH_3OH) was added dropwise. The resulting solution was stirred for 12 h at room temperature and then concentrated to 2 mL and treated with diethylether (2 × 10 mL) to give a final product. The product as a white solid was collected and dried under *vacuum* (yield: 0.58 g, 84%). M.p. 225–227 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 6.91–7.77 (m, 44H, C_6H_5), 2.66 (m, 2H, CH_2(dppe)), 2.76 (m, 2H, CH_2(dppe)), 4.82 (br, 1H, CH(methine)), 4.63 (m, 2H, CH_2(ylide)). ^{31}P NMR ($CDCl_3$): δ (ppm) 55 (m, P_a), 55.1 (ddd, P_b, $^{2}J(P_bP_c) = 355.1$ Hz, $^{3}J(P_bP_a) = 20$ Hz, $^{3}J(P_bP_d) = 12$ Hz), 19.15 (ddd, P_c, $^{2}J(P_cP_b) = 355$ Hz, $^{2}J(P_cP_a) = 58.1$ Hz, $^{2}J(P_cP_d) = 27$ Hz), 37.65 (ddd, P_d, $^{2}J(P_dP_b) = 58$ Hz, $^{2}J(P_dP_c) = 20.1$ Hz, $^{3}J(P_dP_a) = 14$ Hz). ^{19}F NMR ($CDCl_3$): δ (ppm) −77.9 (s, CF_3). Selected IR data (KBr, cm^{-1}): $\nu = 997$ (m, P–CH_2), 820 (m, P–CH), 1616 (s, C=O). UV–vis (λ_{max}, nm): 241 (intra-ligand transition, phenyl group), 257 (intra-ligand transition, C=O), 300 (LMCT, s→d), 325 (MLCT). ESI-MS: $m/z = 1235.06$ ((Calcd 1235.06), [(dppe)Pd($Ph_2PCH_2PPh_2C(H)C(O)PhBr$)]$^{+}$), 1085.10 ((Calcd 1085.10), [(dppe)Pd($Ph_2PCH_2PPh_2C(H)C(O)PhBr$)]$^{+}$ minus a proton), 543.05 ((Calcd 543.05), [(dppe)Pd($Ph_2PCH_2PPh_2C(H)C(O)PhBr$)]$^{\bullet 2+}$ minus a radical hydrogen). Anal. Calcd for $C_{61}H_{51}BrF_6O_7P_4PdS_2$: C, 52.92; H, 3.71. Found: C, 52.81; H, 3.65%.

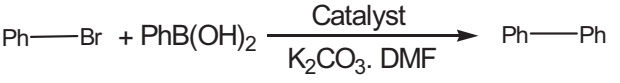
3.3. *General experimental procedure for Suzuki cross-coupling reactions*

A mixture of an aryl halide (0.75 mmol), phenyl boronic acid (1 mmol), Pd complex (0.001 mol%), K_2CO_3 (1.5 mmol), and DMF (2 mL) was heated to 130 °C for a specified time. The reactions were monitored by thin-layer chromatography. The reaction mixture was then cooled to room temperature. The combined organic extracts were washed with brine and dried over $CaCl_2$ and Na_2SO_4. The solvent was evaporated and a crude product was obtained, analyzed by ^{1}H and ^{31}C NMR. A small aliquot of the reaction mixture was diluted in MeOH for direct GC analysis. Yields were calculated against consumption of the aryl halides.

3.4. *Characterization of the products of Suzuki cross-coupling reactions*

3.4.1. 4-Nitro-4′-ethyl-biphenyl (entry 2, table 3). M.p. 82–83 °C. ^{1}H NMR (89.6 MHz, $CDCl_3$): $\delta = 7.28$–8.34 (m, phenyl, 8H), 2.70 (q, CH_2, $^{3}J = 7.5$ Hz, 2H), 1.30 (t, CH_3, $^{3}J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 147.5$ (s, phenyl), 146.8 (s, phenyl), 138.7 (s, phenyl), 129.1 (s, phenyl), 128.8 (s, phenyl), 127.7 (s, phenyl), 127.3 (s, phenyl), 124.0 (s, phenyl), 32.4 (s, CH_2), 14.6 (s, CH_3).

Table 4. Comparison with other catalytic system.



Entry	[Pd] catalyst	mol%	Conditions	Yield (%)	Refs.
1	$[Pd(S\hat{}O)_2]$	0.01	100 °C, 1 h	73	[61]
2	$[Pd(N\hat{}O)_2]$	0.001	100 °C, 6 h	88	[62]
3	$[PdCl_2(Imidazole)_2]$	0.001	120 °C, 12 h	97	[63]
4	$[Pd(C\hat{}N)(\mu\text{-}Br)]_2$	0.001	130 °C, 3 h	92	[64]
5	$[Pd(SC_6F_4\text{–}4\text{-}H)_2(TMEDA)]$	0.1	110 °C, 12 h	43	[65]
6	$[Pd(C\hat{}N\hat{}N)Cl]$	1	80 °C, 5 h	96	[66]
7	$[PdCl_2(HL)_2]$	0.1	100 °C, 1 h	100	[67]
8	$[Pd(C\hat{}C)(PPh_3)Cl]$	0.001	75 °C, 1 h	46	[68]
9	$[Pd(P\hat{}p)(C\hat{}p)]$	0.001	130 °C, 1.5 h	90	This work

3.4.2. 4-Carboxaldehyde-4′-ethyl-biphenyl (entry 4, table 3). M.p. 81–82 °C. IR (KBr, cm^{-1}): $\nu = 3024$, 2965, 2936, 1682 (C=O), 1605, 881, 835, 808. ^1H NMR (89.6 MHz, $CDCl_3$, ppm): $\delta = 10.04$ (s, CHO, 1H), 7.24–7.59 (m, phenyl, 8H), 2.68 (q, CH_2, $^3J = 7.9$ Hz, 2H), 1.30 (t, CH_3, $^3J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 191.8$ (s, C=O), 147.0 (s, phenyl), 144.7 (s, phenyl), 136.8 (s, phenyl), 134.8 (s, phenyl), 130.1 (s, phenyl), 128.4 (s, phenyl), 127.3 (s, phenyl), 127.1 (s, phenyl).

3.4.3. 4-Methyl-4′-ethyl-biphenyl (entries 6 and 26, table 3). M.p. 59–61 °C. ^1H NMR (89.6 MHz, $CDCl_3$, ppm): $\delta = 7.21$–7.82 (m, phenyl, 8H), 2.71 (q, CH_2, $^3J = 7.9$ Hz, 2H), 2.45 (s, CH_3, 3H), 1.30 (t, CH_3 (ethyl), $^3J = 8.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 143.0$ (s, phenyl), 138.4 (s, phenyl), 138.2 (s, phenyl), 136.6 (s, phenyl), 129.4 (s, phenyl), 128.2 (s, phenyl), 126.85 (s, phenyl), 126.80 (s, phenyl), 28.4 (s, CH_2), 21.0 (s, CH_3), 15.6 (s, CH_3 (ethyl)).

3.4.4. 1-(4-Ethylphenyl)naphthalene (entry 8, table 3). ^1H NMR (89.6 MHz, $CDCl_3$, ppm): $\delta = 7.11$–8.50 (m, phenyl, 11H), 2.83 (q, CH_2, $^3J = 7.6$ Hz, 2H), 1.45 (t, CH_3, $^3J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 143.1$ (s, phenyl), 140.2 (s, phenyl), 137.9 (s, phenyl), 133.7 (s, phenyl), 131.6 (s, phenyl), 129.9 (s, phenyl), 128.2 (s, phenyl), 127.7 (s, phenyl), 127.3 (s, phenyl), 126.8 (s, phenyl), 126.0 (s, phenyl), 125.8 (s, phenyl), 125.6 (s, phenyl), 125.3 (s, phenyl), 28.6 (s, CH_2), 15.5 (s, CH_3).

3.4.5. 4′-Ethyl-biphenyl-4-carboxylic acid (entry 12, table 3). IR (KBr, cm^{-1}): $\nu = 3025$, 3014, 2984, 1722 (C=O), 1604, 792, 765, 739. ^1H NMR (89.6 MHz, $CDCl_3$, ppm): $\delta = 11.1$ (s, COOH, 1H), 6.92–7.81 (m, phenyl, 8H), 2.68 (q, CH_2, $^3J = 6.5$ Hz, 2H), 1.30 (t, CH_3, $^3J = 7.8$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 169.3$ (s, C=O), 141.6 (s, phenyl), 138.4 (s, phenyl), 135.8 (s, phenyl), 134.8 (s, phenyl), 130.1 (s, phenyl), 128.4 (s, phenyl), 127.8 (s, phenyl), 127.7 (s, phenyl), 30.6 (s, CH_2), 14.9 (s, CH_3).

3.4.6. 2-(4-Ethylphenyl)thiophene (entry 14, table 3). M.p. 48–49 °C. ^1H NMR (89.6 MHz, $CDCl_3$, ppm): $\delta = 6.91$–7.80 (m, phenyl, H), 2.62 (q, CH_2, $^3J = 8.1$ Hz, 2H), 1.16 (t, CH_3, $^3J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 131.8$ (s, phenyl),

128.3 (s, phenyl), 128.2 (s, phenyl), 127.8 (s, phenyl), 126.8 (s, phenyl), 125.9 (s, phenyl), 124.2 (s, phenyl), 122.5 (s, phenyl), 28.5 (s, CH_2), 15.5 (s, CH_3).

3.4.7. 4-Acetyl-4′-ethyl-biphenyl (entries 16 and 20, table 3). IR (KBr, cm^{-1}): $v = 3060$, 3019, 2976, 1655 (C=O), 1611, 815, 789, 751. ^1H NMR (89.6 MHz, $CDCl_3$, ppm): $\delta = 7.25$–8.01 (m, phenyl, 8H), 2.59 (q, CH_2, $^3J = 7.3$ Hz, 2H), 2.51 (s, CH_3, 3H), 1.24 (t, CH_3, $^3J = 8.0$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): $\delta = 190.8$ (s, C=O), 140.9 (s, phenyl), 138.4 (s, phenyl), 135.7 (s, phenyl), 133.7 (s, phenyl), 129.3 (s, phenyl), 128.3 (s, phenyl), 127.8 (s, phenyl), 127.7 (s, phenyl), 33.4 (s, CH_2), 30.3 (s, CH_3), 15.9 (s, CH_3).

The following compounds gave data consistent with those published: table 3: *4-Nitro-biphenyl* (entry 3) [71,72], *4-phenylbenzaldehyde* (entry 3) [73], *4-methyl-biphenyl* (entries 5, 25) [74], *1-phenylnaphthalene* (entry 7) [71], *biphenyl* (entries 9, 17, 23) [38], *4-ethyl-biphenyl* (entries 10, 18, 24) [75], *4-biphenylcarboxylic acid* (entry 11) [76], *2-phenylthiophene* (entry 13) [74], and *4-acetylbiphenyl* (entries 15, 19) [60].

4. Conclusion

The present study describes the very efficient synthesis and characterization of a mononuclear cyclopalladated complex. On the basis of the physicochemical and spectroscopic data, we have proposed that ligands employed herein exhibit a chelate coordination behavior to the metal center affording a five-membered chelate ring. The coordination ability of the phosphorus ylide and dppe has been proven in complexation with Pd(II). In this work, we used a palladium(II) complex as an efficient catalyst for the Suzuki reaction of various aryl halides. This complex is a highly active and efficient catalyst for promoting the Suzuki cross-coupling reaction of various aryl halides to produce the corresponding products in good to excellent yields. With the catalyst loading of 0.001 mol%, the electron-rich substrate 4-bromo*benzaldehyde* couples with phenylboronic acid in high yield. The ease of preparation of the complex (homogeneous catalyst), its high solubility in organic solvents, very low catalyst loading, and stability toward air make it an ideal complex for the above transformations.

Supplementary material

For complete information please refer to supplementary data file.

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