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Synthesis, crystal structural study and catalyst active of benzyloxycarbonylmethyl triphenylphosphonium hexabromopalladate (II) in amination of aryl halides and Suzuki crosscoupling reaction

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Abstract

In this study, palladium (II) chloride reacted with the phosphonium salt $[PhCH_2COOCH_2P(Ph)_3]Br$ to give $[PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6]$ (1). The characterization of synthesized compound was performed by elemental analysis, FT-IR, ¹H, ³¹P, ¹³C NMR and also X-ray crystallography. It was found that this compound works as an efficient catalyst for the amination of aryl halides to afford primary amines, the results of which were satisfactory. Furthermore, it was found that the catalyst showed a high activity for Suzuki carbon–carbon cross-coupling of aryl halides and phenylboronic acid. Interestingly, the catalyst can be recovered from the reaction mixture and recycled four consecutive runs without any significant loss in activity.

Keywords Crystal structure · Phosphonium · Palladium (II) chloride · Amination · Suzuki cross-coupling

Introduction

Researchers often use triphenylphosphine and its derivatives to prepare organic phosphines. Triphenylphosphine and its derivatives easily react as nucleophiles with alkyl/ aryl halides and give rise to phosphonium salts which are attractive, since they have enhanced thermal stability [1, 2]. Different types of phosphonium salts as precursors have also been applied to prepare corresponding ylide complexes of transition metals such as Pd(II), Au(I) and Hg(II) [3–5]. Phosphonium compounds have a range of advantages including synthesis of a wide variety of organic derivatives and functionalizing types of branches. Moreover, they have been used as catalyst in a variety of organic reactions such as

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Arash Ghorbani-Choghamarani arashghch58@yahoo.com; a.ghorbani@mail.ilam.ac.ir polymerization, oxidation and cross-coupling reactions [6, 7]. Furthermore, these compounds have numerous applications like the ability of the triphenylphosphonium group to travel across cell membranes which leads to the use of phosphonium compounds such as anticancer agents [7], transport vectors for targeting mitochondria [8, 9], and tumors diagnostic agents [10, 11].

The present study tries to investigate the synthesis and the characterization of a crystal structure of a novel phosphonium salt containing triphenylphosphonium and hexabromodipalladate (II) moiety. This compound was first tested successfully as a heterogeneous catalyst for the amination reaction of various aryl halides by aqueous ammonia as a source of nitrogen under air atmosphere and solvent free conditions to produce aniline and other primary aryl amines. Aniline and its derivatives are useful intermediates in the production of pharmaceuticals, agrochemicals, pigments, dyes, etc. [13]. A desired approach in the preparation of aniline and its derivatives is to use ammonia directly due to its low cost and availability [14]. Using phosphonium salt which contains hexabromodipalladate (II) as a heterogeneous catalyst in amination reaction of aryl halides with ammonia has several advantages

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including direct utilization of ammonia, ammonia equivalents with initial protection and final de-protection, no need for argon or nitrogen atmosphere, high temperatures and pressures, lack of by-products such as secondary and tertiary amines [15, 17]. Moreover, we found the catalytic activity of this phosphonium compound for C–C bond formation by the Suzuki coupling reaction using phenyl boronic acid to obtain biphenyl derivatives. A bundle of activities of biphenyl derivatives includes: antifungal, anti-proliferative, antimicrobial, anti-diabetic, immunosuppressant, analgesic, etc [18]. Phosphonium salts are also used in biological studies as targeting and pharmacological agents due to their antimicrobial activity against gram negative and positive bacteria [19].

Experimental

Materials and physical measurements

All starting materials were purchased from Merck and Aldrich Chemical Companies and were used without any additional purification. Mentioned microbial strains were purchased from microbial collection of Iranian Research Organization for Science and Technology. Melting points were measured on a Stuart SMP₃ apparatus. Elemental analysis was carried out with a CHNS-O Costech ECS 4010 analyzer. IR spectra (in the range 4000–400 cm⁻¹) were recorded on a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. NMR spectra (¹H, ³¹P and ¹³C NMR) were recorded on a 400 MHz Bruker spectrometer in CDCl₃ or DMSO-d₆ as the solvent at room temperature. Thin-layer chromatography (TLC) was performed using Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence lamp.

X-ray crystallography

The single crystal X-ray diffraction data of suitable crystals was collected on a STOE IPDS-II diffractometer at 298 (2) K, using graphite monochromated Mo Ka radiation (0.71073 Å). The data collection was performed using the ω -scan technique and using the STOE X-AREA software package [20], whereas data diminution was carried out using the program X-RED [21]. The structure was determined by direct methods and subsequent difference Fourier maps and then refined on F^2 by full-matrix least-squares procedures using the programs SHELX and SHELXL respectively [22], and all refinements were performed using the XSTEP32 crystallographic software package [23]. All hydrogen atoms were added in geometrically idealized positions.

Synthesis of bis](benzyloxycarbonylmethyl)tri phenylphosphonium[hexabromopalladate (II), [PhCH₂COOCH₂P(Ph)₃]₂[Pd₂Br₆]

To a solution of benzylbromoacetate (0.573 g, 2.5 mmol) in benzene (5 mL), a solution of triphenylphosphine (PPh₃)

 $\label{eq:scheme1} \begin{array}{l} \mbox{Synthesis of } [PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6] \end{array}$





Fig. 1 Asymmetric unit of [PhCH₂COOCH₂P(Ph)₃]₂[Pd₂Br₆]

(0.655 g, 2.5 mmol) in benzene (5 mL) was added and the resulting mixture was stirred at room temperature for 3 h. The separated solid was filtered off and washed with diethyl ether to give [PhCH₂COOCH₂P(Ph)₃]Br as a white powder. Yield: 0.246 g (83%). M.p.: 128 °C. Anal. Calc. for $C_{27}H_{24}BrO_2P$ (491.36 g/mol): C, 66.00; H, 4.92. Found: C, 65.72; H, 5.16%. IR (KBr disk, ν cm⁻¹): 1705 (CO); 687–930 (C–H in Ph); 1588 (C=C in Ph); 1438 (P–CH₂).

The prepared (benzyloxycarbonylmethyl)triphenylphosphonium bromide (0.737 g, 3.0 mmol) was dissolved in 10 mL of methanol. Then, palladium(II) chloride (0.265 g, 1.5 mmol) in 10 mL of methanol was added to this solution and the mixture was stirred at room temperature for 6 h. The suspension that formed was filtered off, washed with diethyl ether and dried to give [PhCH₂COOCH₂P(Ph)₃]₂[Pd₂Br₆] as an orange powder. Yield: 0. 67 g, 59%. M.p.: 218 °C. Anal. Calc. for C₅₄H₅₀Br₆O₄P₂Pd₂ (1517.63 g/mol): C, 42.75; H, 3.32. Found: C, 43.02; H, 3.41%. IR (KBr disk, ν cm⁻¹): 1725 (CO); 687–930 (C–H in Ph); 1445–1588 (C=C in Ph); 1456 (P–CH₂). ¹H NMR (400 MHz, CDCl₃, $\delta_{\rm H}$ ppm): 4.98 (s, 2H, CH₂O); 5.32 (d, 2H, *J*=15.01 Hz, PCH₂); 7.10–7.47 (m, 20H, PPh₃, Ph). ¹³C NMR (100 MHz, CDCl₃, $\delta_{\rm C}$ ppm): 34.22 (d, *J*=36.03 Hz, PCH₂); 68.37 (s, CH₂O); 117.21,

118.38, 119.27, 121.36, 129.74, 130.18, 133.13, 134.66 (Ph); 171.04 (s, CO). ³¹P NMR (162 MHz, CDCl₃, δ_P ppm): 22.54 (s, PPh₃).

General procedure for amination of aryl halides

In a typical procedure, a mixture of aryl halide (1 mmol), ammonium hydroxide (28%) (1 mL), K₂CO₃ (1.5 mmol), 0.007 g of [PhCH₂COOCH₂P(Ph)₃]₂[Pd₂Br₆] as catalyst was



Fig. 2 Distorted square-planar geometry around Pd(II) central ions

Table 1 Crystal data and structure refinement for $[PhCH_2COOCH_2P\ (Ph)_3]_2[Pd_2Br_6]$

Identification code	$[PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6]$
Empirical formula	C ₂₇ H ₂₄ O ₂ P, 0.5 (Br ₆ Pd ₂)
Formula weight	757.53
Temperature (K)	298 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
<i>a</i> (Å)	9.1369(18)
<i>b</i> (Å)	11.287 (2)
<i>c</i> (Å)	14.472 (3)
α (°)	87.22 (3)
β (°)	74.47 (3)
γ (°)	71.51 (3)
Volume (Å3)	1362.7 (6)
Ζ	2
Calculated density, Mg/m ³	1.846
<i>F</i> (000)	736
Theta range for data collec- tion, (°)	2.35 to 25.00
Limiting indices	$-10 \le h \le 10, -12 \le k \le 13, \\ -16 \le l \le 17$
Completeness to theta=25	99.5%
Absorption correction	Numerical
Absorption coefficient (mm ⁻¹)	5.161
Crystal size (mm ³)	$0.35 \times 0.18 \times 0.15$
Reflections collected/unique	10,064/4776 [<i>R</i> (int)=0.1061]
Max. and min. transmission	0.5116 and 0.2653
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4776/0/301
Goodness-of-fit on F^2	0.919
Final <i>R</i> indices $[I > 2 \delta(I)]$	$R_1 = 0.0623, WR_2 = 0.1400$
R indices (all data)	$R_1 = 0.1232, WR_2 = 0.1594$
Largest diff. peak and hole, $e \text{ Å}^{-3}$	1.305 and -0.791

added and the reaction mixture was stirred at 80 °C and the progress of the reaction was followed by TLC. When the reaction completed, the product was extracted with ethyl acetate. The combined ethyl acetate extracts were dried over anhydrous sodium sulfate, filtered and evaporated to give the pure product.

General procedure for Suzuki cross-coupling reaction

In a typical procedure, a mixture of aryl halide (1 mmol), phenylboronic acid (1 mmol), K₂CO₃ (1.5 mmol), 0.010 g

Table 2 Selected bond lengths (Å) and bond angles (°) for $[PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6]$

Bond lengths		Bond angles	
Pd(1)–Br(1)	2.3869 (15)	Br(1)-Pd(1)-Br(2)	91.09 (6)
Pd(1)–Br(2)	2.3887 (16)	Br(1)-Pd(1)-Br(3)	91.27 (5)
Pd(1)–Br(3)	2.4521 (14)	Br(2)-Pd(1)-Br(3)	176.02 (5)
P(1)–C(1)	1.795 (9)	C(1)–P(1)–C(19)	110.9 (4)
P(1)–C(13)	1.796 (9)	C(1)-P(1)-C(13)	111.3 (4)
P(1)–C(7)	1.780 (9)	C(7)–P(1)–C(1)	108.4 (4)
P(1)–C(19)	1.783 (9)	C(19)–P(1)–C(13)	109.5 (4)
O(1)–C(20)	1.166 (13)	C(7)–P(1)–C(19)	107.8 (4)
O(2)–C(20)	1.318 (12)	C(7)–P(1)–C(13)	108.9 (4)
O(2)–C(21)	1.480 (12)	C(20)–O(2)–C(21)	116.7 (9)
C(19)–C(20)	1.508 (13)	O(1)-C(20)-O(2)	125.1 (10)

of $[PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6]$ as catalyst and 2 mL polyethylene glycol (PEG) as solvent were heated at 80 °C and the progress of the reaction was followed by TLC. After completion of the reaction, the mixture was cooled down to room temperature. Water was added to the reaction mixture, filtered to remove the catalyst and extracted three times with diethyl ether. The combined ethyl acetate extracts were dried over anhydrous sodium sulfate, filtered and evaporated to give the pure product.

Selected spectral data

Aniline: ¹H NMR (400 MHz, CDCl3, ppm): δ =7.22–7.26 (m, 2H), 6.83–6.87 (tt, *J*=7.3, 1 Hz, 1H), 6.75–6.77 (m, 2H), 3.66 (s, 2H).

4-Nitroaniline: ¹H NMR (400 MHz, CDCl₃. ppm): $\delta = 8.092 - 8.115$ (d, J = 9.3 Hz, 2H); 6.649-6.671 (d, J = 8.8 Hz, 2H); 4.43 (br, 2H).

4- Chloroaniline: ¹H NMR (400 MHz, CDCl₃. ppm): δ =7.12–7.15 (d, *J*=8.7 Hz, 2H); 6.64–6.67 (m, 2H); 3.59 (br, 2H).

4-methoxy-1,1'-biphenyl: ¹H NMR (400 MHz, $CDCl_{3}$, ppm): δ = 7.56–7.60 (m, 4H); 7.44–7.49 (m, 2H); 7.32–7.37 (m, 1H); 7.03–7.7.05 (m, 2H); 3.89 (s, 3H).

4-Nitro-1, 1'-biphenyl: ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.32–8.35 (d, *J* = 8.7 Hz, 2H), 7.75–7.78 (dt, *J* = 7.8 Hz, 2H), 7.65–7.67 (m, 2H), 7.50–7.55 (m, 2H), 7.57–7.50 (m, 1H).

4-Cyano-1,1'-biphenyl: ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.76–7.79 (m, 2H); 7.70–7.73 (m, 2H); 7.61–7.64 (m, 2H); 7.50–7.54 (m, 2H); 7.44–7.48 (m, 1H).



Fig. 3 The Br1...H interactions between Pd(II) complexes and phosphonium cations

Results and discussion

Catalyst preparation

Compound bis (benzyloxycarbonylmethyl)triphenylphosphonium hexabromopalladate (II) (1) was synthesized as follows: the treatment of benzylbromoacetate with triphenylphosphine in benzene as a solvent yielded the corresponding phosphonium salt as an exclusive product, because the monophosphonium salts are insoluble in benzene and their diphosphonium derivatives are dissolved in benzene afterwards, the reaction of the phosphonium bromide with palladium(II) chloride in a molar ratio of 2:1 in methanol at room temperature led to the formation of compound **1** as an orange solid (Scheme 1). The ³¹P NMR spectra of the compound displayed a significant singlet signal range 22.54 ppm implying some local electron density reduction in the P–C bonds in comparison with that in the literature for PPh₃.



Fig. 4 The Br1···H and Br1··· π interactions between Pd(II) complexes and phosphonium cations



Fig. 5 The Br2…H interactions between Pd(II) complexes and phosphonium cations



Fig. 6 The H···H bonding and C–H··· π interaction between adjacent phosphonium units



Fig. 7 The packing diagram of title compound along c axis

X-ray crystallographic study of compound 1

Suitable crystals of [PhCH₂COOCH₂P(Ph)₃]₂[Pd₂Br₆] (1) were gained by slow evaporation from chloroform/ methanol solutions over several days and its structure was determined by X-ray diffraction. The crystallization of compound was done in the triclinic space group P-1 with two molecules in the unit cell. Figure 1 shows asymmetric unit of the compound. The crystal structure of this compound consists of binuclear anionic complexes of Pd(II), namely Pd₂Br₆²⁻, and triphenylphosphonium cations for charge neutrality. In the bromopalladate(II) unites, the geometry around metal ion centres are slightly distorted square-planar. The central metal ions are out of plan and the Br2-Pd-Br1 and Br2-Pd-Br2 angels are smaller than 180 degree (see Fig. 2). The Pd-Br bonds distances are within a range typical for other structures containing bromopalladate(II). The Br3 atoms act as bridge ligands and thus the Pd-Br3 bond length is longer than terminate Pd-Br length. Significant crystallographic data are summarized in Table 1 and selected bond distances and angles are summarized in Table 2.

The ion-ion attraction between anionic complexes and triphenylphosphonium cations is the most important intermolecular force in this crystal structure. Moreover, intermolecular noncovalent interactions between various units help in stabilization of the crystal structure in three dimensions. The Br…H [24] (Br1…H5, Br1…H19A and Br2…H19B interactions with distances 2.92, 2.86 and 2.96 Å, respectively) and Br… π interactions [25] between Br1 and Cg1 (Cg1: C1–C6) with distance 3.527 Å that is smaller than Van der Waals radii of carbon and bromine (3.55 Å), are formed between neighbour Pd(II) complexes and phosphonium cations (see Figs. 3, 4, 5). In addition, C–H… π interaction between C–H26 group and Cg2 (Cg2: C13–C18) with distance 2.974 Å and also H–H bonding with H…H distance equal to 2.361 Å that is less than sum of Van der Waals radii of H atoms (2.4 Å), are created between adjacent phosphonium units (see Fig. 6).



Scheme 2 $[PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6]$ catalyzed the amination of aryl halides

Table 3Optimization of variousparameters for the aminationof iodobenzene with aqueousammonia

Entry	Cat (mg)	Solvent	Base	Temp (°C)	Time (h)	Yield (%) ^a
1	5	EtOH	K ₂ CO ₃	60	6	57
2	5	NH ₃ ·H ₂ O	K ₂ CO ₃	60	6	84
3	5	H ₂ O	K ₂ CO ₃	60	6	64
4	5	PEG	K ₂ CO ₃	60	6	71
5	5	DMF	K ₂ CO ₃	60	6	75
6	5	NH ₃ ·H ₂ O	KHCO3	60	6	80
7	5	NH ₃ ·H ₂ O	Et ₃ N	60	6	76
8	5	NH ₃ ·H ₂ O	КОН	60	6	82
9	5	NH ₃ ·H ₂ O	K ₂ CO ₃	r.t	6	_
10	5	NH ₃ ·H ₂ O	K ₂ CO ₃	80	6	87
11	5	NH ₃ ·H ₂ O	K ₂ CO ₃	100	6	90
12	_	NH ₃ ·H ₂ O	K ₂ CO ₃	80	24	-
13	7	NH ₃ ·H ₂ O	K ₂ CO ₃	80	6	94
14	10	NH ₃ ·H ₂ O	K ₂ CO ₃	80	6	95

^aYields refer to those of pure isolated products

Table 4 Preparation of anilinederivatives from aryl halides inthe presence of catalytica

Entry	Aryl halide	product	Time (h)	Yield (%) ^a	M.P. (°C)
1		NH ₂	6	94	Yellow oil [15]
2	Br	NH ₂	12	90	Yellow oil [15]
3	Me	Me NH2	10	91	42–45 [13]
4	Me	Me NH2	13	88	42–45 [26]
5	MeO	MeO NH2	8	89	57–59 [13]
6	MeO	MeO NH2	9	87	57–59 [15]
7	OHC	OHC NH2	7	85	69–71 [26]
8	O ₂ N Br	O ₂ N NH ₂	5	93	147–149 [13]
9	NC	NC NH2	4	87	84–86 [13]
10	Br H ₂ N	H ₂ N NH ₂	6	86	135–137 [15]

Reaction conditions: aryl halide (1 mmol), NH₄OH (1 mmol), K₂CO₃ (1.5 mmol), 7 mg catalyst at 80 °C ^aIsolated yield



Scheme 3 Carbon–carbon coupling reaction using phenyl boronic acid in the presence of $[PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6]$

For better vision, packing diagram of crystal structure in direction of c axis is shown in Fig. 7.

Catalytic studies

To extend applications of the catalytic activity of $[PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6]$, this catalyst was investigated in the direct amination of aryl halides using aqueous ammonia (Scheme 2).

For this purpose, aqueous ammonia was used as the amine group supplier. First, the reaction of iodobenzene with aqueous ammonia was performed in various organic solvents the results of which are shown in Table 3. On the basis of the achieved results, the reaction in the presence of $NH_3 \cdot H_2O$ as solvent proceeded much better than other solvents with a good yield in short reaction time (Table 3, entry 2). Then, amount of catalyst optimization was conducted and the optimal amount was found to be 0.007 g (Table 3, entry 13). After that the effect of temperature on the rate of the reaction was examined. It was observed that at room temperature, the reaction did not proceed (Table 3, entry 9). At 80 °C, the reaction proceeded and gave the corresponding product a good yield (Table 3, entry 10). Increasing the temperature to 100 °C had little effect on the rate of reaction (Table 3, entry 11). Therefore, we kept reaction temperature at 80 °C as the optimal temperature. Finally, base optimization was carried out in this study (Table 3, entries 2 and 6–8). As shown in Table 3, K_2CO_3 was selected as the optimum base among used bases.

Optimal conditions for the reaction were defined as follows: 1 mL of aqueous ammonia, 1 mmol of iodobenzene, 1.5 mmol of K_2CO_3 as base and 0.007 g of catalyst at 80 °C of catalyst in solvent free conditions. When the reaction conditions are optimized, the coupling reaction proceeds easily with aryl bromides and iodides with aqueous ammonia. The results are summarized in Table 4. In all cases, the yields of products were in a good to an excellent range.

The other studied reaction in this work was Suzuki crosscoupling reaction. we were interested in finding a simple and efficient method for the carbon–carbon coupling reaction in the presence of complex $[PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6]$ (Scheme 3).

То examine the catalytic activity $[PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6]$ in the Suzuki reaction, the reaction between iodobenzene with phenyl boronic acid in presence of catalyst was chosen as model reaction. Influences of different parameters including base, solvent, temperature, and catalyst concentration were examined to obtain the best possible combination (Table 5). Unsurprisingly, no product was observed in the absence of the catalyst (Table 5, entry 1). At first, the model reaction was carried out in several solvents such as polyethylene glycol 400 (PEG-400), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and ethanol (EtOH), and it was found that PEG gave the best yield, and in other solvents lower yields were observed (Table 5, entries 3 and 5-7). The reaction was significantly affected by the nature of base and the additive used. Therefore, a variety of bases were tested (Table 5, entries 3 and 8–10). As shown in Table 5, K₂CO₃ was selected as the optimum base among the used bases. Therefore, the best results were achieved in water at 80 °C in the presence of 5 mg of [PhCH₂COOCH₂P(Ph)₃]₂[Pd₂Br₆] using 1.5 mmol of K_2CO_3 (Table 5, entry 3).

Entry	Cat (mg)	Solvent	Base	Temp (°C)	Time (min)	Yield (%) ^a
1	-	PEG	K ₂ CO ₃	80	120	_
2	3	PEG	K ₂ CO ₃	80	120	92
3	5	PEG	K ₂ CO ₃	80	35	95
4	7	PEG	K ₂ CO ₃	80	30	95
5	5	DMF	K ₂ CO ₃	80	35	79
6	5	DMSO	K ₂ CO ₃	80	35	73
7	5	EtOH	K ₂ CO ₃	80	35	66
8	5	PEG	Et ₃ N	80	35	54
9	5	PEG	КОН	80	35	81
10	5	PEG	KHCO3	80	35	85
11	5	PEG	K ₂ CO ₃	r.t.	35	Trace
12	5	PEG	K ₂ CO ₃	60	35	69

Table 5The optimization ofreaction parameters for theSuzuki reaction of iodobenzenewith phenyl boronic acid

^aIsolated yields

Entry	Aryl halide	Product	Time (min)	Yield (%) ^a	Mp (°C)
1	I I	Ph	35	95	66–68 [27]
2	H ₃ C	H ₃ C Ph	30	91	45–47 [27]
3	H ₃ CO	H ₃ CO Ph	35	89	85–88 [28]
4	Br	Ph	40	90	66–68 [27]
5	H ₃ C Br	H ₃ C	35	88	45–47 [27]
6	Br H ₃ CO	H ₃ CO Ph	45	86	83–85 [28]
7	O ₂ N Br	O ₂ N Ph	30	93	111–113 [27]
8	NC	NC	35	90	82–84 [28]
9	Cl	Cl	40	87	76–78 [28]
10	Cl	Ph	55	89	66–68 [27]
11	O ₂ N	O ₂ N Ph	50	86	111–112 [27]
12	NC	NC	65	90	83–84 [28]

Reaction conditions: aryl halide (1 mmol), phenyl boronic acid (1 mmol), K_2CO_3 (1.5 mmol), PEG (1 mL) and 5 mg catalyst at 80 °C ^bIsolated yield

After the optimization of the reaction conditions, the various aryl halides with and phenylboronic acid comprising several functional groups have been reacted in optimum conditions. The results are summarized in Table 6. As illustrated in Table 6, biphenyl reactions were gained in short reaction times with good to excellent yields. However, aryl bromides and aryl iodides show lower reaction times compared to those corresponding aryl chlorides.

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Table 6 Reaction of structurallydifferent aryl halides withphenyl boronic acid in the

presence of catalyst

Reusability of the catalyst

Reusability is an advantage of catalysts that makes them significant from a commercial point of view. Therefore, the recovery and recyclability of $[PhCH_2COOCH_2P(Ph)_3]_2[Pd_2Br_6]$ was studied in the coupling reaction of iodobenzene with aqueous ammonia and phenylboronic acid under the optimal conditions. The reaction mixture was cooled to room temperature after the completion of the reaction. Then, the mixture was



Fig.8 Reuse of the catalyst in Aniline and Suzuki cross-coupling reactions

filtered off to separate the catalyst. In the end, the catalyst was dried at 120 °C and directly used for the next run. After four consecutive runs, a negligible reduction in the activity of the catalyst indicated that the catalyst was not only very active, but also very stable (Fig. 8).

Comparison of the catalyst

To examine the efficiency of these procedures, we compared the results of the coupling of iodobenzene with phenylboronic acid (Table 7) with some reported C–C coupling reactions in the presence of other catalysts. As illustrated in Table 7, the achieved results indicate the superiority of the present catalyst in terms of yield or reaction time to the other catalysts reported in previous literatures. Mainly the reaction catalyzed by [PhCH₂COOCH₂P(Ph)₃]₂[Pd₂Br₆] can be performed efficiently without using toxic organic solvents and this catalyst also is a suitable catalyst in terms of stability, price and easy separation.

Conclusion

The present study describes the synthesis and the characteristics of new compound derived from reaction of palladium chloride and (benzyloxycarbonylmethyl)triphenylphosphoniumh salt. The physicochemical and spectroscopic data indicate that crystal structure of the title compound contains two crystallographically independent phosphonium cations and binuclear anionic complexes of Pd(II), namely Pd₂Br₆²⁻. A new phosphonium salt containing hexabromodipalladate(II) moiety was used as an efficient catalyst for the amination of aryl halides by aqueous ammonia in the absence of any organic solvent. This method enables direct synthesis of a number of primary amines with very good to excellent yields. Furthermore, it was demonstrated that this compound can act as an efficient catalyst for Suzuki cross-coupling reaction using commercially available and cheap reagent (phenyl boronic acid). The catalyst turned out to be highly active, and its reusability was tested in up to four consecutive cycles in both reactions.

Table 7	Comparison result	ts of [PhCH ₂ COOC	$CH_2P(Ph)_3]_2[Pd_2Br_6]$] with other catalysts	for the coupling of iodol	enzene with phenylb	oronic acid

Entry	Catalyst	Condition	Time (min)	Yield (%) ^a	Refs.
1	[PhCH ₂ COOCH ₂ P(Ph) ₃] ₂ [Pd ₂ Br ₆]	PEG, K ₂ CO ₃ , 80 °C	35	95	This work
2	$\{Pd[P(Ph)(CH_2Ph)(Ph-4-CH_3)]((\mu-Br)Br)\}$	PEG, K ₂ CO ₃ , 100 °C	25	96	[29]
3	PCP-pincer palladium complex	DMF, K ₂ CO ₃ , 80 °C	1 h	96	[30]
4	[Ph ₂ PCH ₂ PPh ₂ CH=C(O)(C ₁₀ H ₇)] PdCl ₂	H ₂ O, Cs ₂ CO ₃ , 80 °C	20	93	[31]
5	CA/Pd(0)	H ₂ O, K ₂ CO ₃ , 100 °C	120	94	[32]
6	Polymer anchored pd(II)	DMF, K ₂ CO ₃ , 80 °C	5 h	100	[33]
7	<i>N,N'</i> -bis(2-pyridinecarboxamide)-1,2-benzene palladium complex	H ₂ O, K ₂ CO ₃ , 100 °C	180	97	[34]
8	PVP–PdNPs	K ₂ PO ₄ , EtOH/H ₂ O, 90 °C	120	94	[35]
9	N ² ,N ⁶ -dibenzylpyridine- 2,6-dicarboxamidopalladium(II)triph- enylphosphine	H ₂ O/EtOH, K ₂ CO ₃ , 82 °C	6 h	97	[36]
10	PANI-Pd	K ₂ CO ₃ , 1,4-dioxane: H ₂ O (1:1), 95 °C	4 h	91	[37]

^aIsolated yield

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