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Synthesis and X-ray structural characterization of a bidendate phosphine (dppe) palladium(II) complex and its application in Stille and Suzuki cross-coupling reactions

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The synthesis, characterization, crystal structure and catalyst activity of the bidentate phosphine complex [1,2-bis(diphenylphosphino)ethane]palladium(II) bromide, [PdBr$_2$(dppe)], are presented. Treatment of 1,2-bis(diphenylphosphino)ethane with palladium(II) bromide under mild conditions resulted in the compound in high yield and purity. The characterization of the synthesized compound was performed using spectroscopic methods, such as Fourier transform infrared and NMR, CHN analysis and X-ray crystallography. The structure of the compound was slightly distorted square planar. This compound was found to work as an efficient catalyst for both Stille and Suzuki cross-coupling reactions of various aryl halides with triphenyltin chloride and/or phenylboronic acid. Also, the catalyst could be recovered and reused several times without significant loss of its catalytic activity. Copyright © 2016 John Wiley & Sons, Ltd.

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Keywords: crystal structure; phosphonium; palladium; Stille reaction; Suzuki cross-coupling

Introduction

Phosphine compounds are a group of species with very specific and interesting physical and donor–acceptor properties, among which stands out their high stability, which is conferred on the metal complexes that they form. Because of thermal stability and robustness, phosphine combinations have attracted the continuous attention of the chemistry community for multiple applications, this being specifically true in the case of homogeneous catalysis.[1–4] The expansion of new phosphine ligands has a great effect in continuing to attract much interest,[5–8] particularly in transition metal-catalysed organic reactions.[9,10]

The success of phosphine ligands in catalysis is a function of both electronic and steric properties, and it is advantageous to be able to vary both autonomously. This allows good tuning of the coordinated species, thus enabling the diverse steps of a catalytic cycle to be optimized.[11] 1,2-Bis(diphenylphosphino)ethane (dppe) and triphenylphosphine are typical mono- and bidentate phosphine ligands, respectively, which are used most frequently in a wide variety of homogeneous catalysts.[12] A good deal of knowledge about the performance of dppe and triphenylphosphine as ligands has been accumulated for much transition metal catalysis. Lately, Schiff bases have been recognized as good alternatives to phosphines in Suzuki reactions.[13]

Palladium-catalysed coupling reactions such as Stille and Suzuki cross-coupling reactions have become an extremely strong method for the formation of C&bond;C bonds in organic synthesis,[14–16] biologically active compounds,[17] materials science,[18] pharmaceuticals and bioactive compounds.[19] Clear advantages over other palladium-catalysed cross-coupling reactions include: (i) tolerance towards various functional groups; (ii) mild reaction conditions; and (iii) low toxicity of starting materials and by-products.[20] Suzuki cross-coupling reactions with heterogeneous nano-palladium catalysts have been studied by several researchers.[21] Triphenyltin chloride (TPTCl) is a very good reagent in organic synthesis such as thioetherification[22] and C&bond;C coupling reactions.[23] Although TPTCl has been applied as a useful reagent for the synthesis of sulfides through C&bond;S coupling reactions,[24] it was shown to be toxic to the rotifer *Brachionus koreanus* across different levels of biological organization,[25] and should be handled with care. To prevent environmental toxicity, one can detoxify the final waste including TPTCl by common method and direct photolysis.[26]

In this paper, we report the synthesis, characterization and crystal structure determination of the complex [1,2-bis(diphenylphosphino)ethane]palladium(II) bromide, [PdBr$_2$(dppe)], as a novel and efficient catalyst for C&bond;C bond formation in

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coupling reactions in the presence of TPTCl (Stille reaction) and phenylboronic acid (Suzuki reaction) under mild reaction conditions.

Experimental

Materials and Physical Measurements

The required chemicals were obtained from Merck and Aldrich and were used without further purification. Melting points were measured with a Stuart SMP$_3$ apparatus. Infrared (IR) spectra in the range 400–4000 cm^{-1} were recorded with a Shimadzu 435-U-04 spectrophotometer and samples were prepared as KBr pellets. NMR spectra (^{1}H, ^{13}C and ^{31}P) were recorded with a 400 MHz Bruker spectrometer in CDCl$_3$ as the solvent at room temperature. Elemental analysis was carried out with a CHNS-O Costech ECS 4010 analyser. TLC was performed using Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized using a UV fluorescence lamp.

X-ray Crystallography

Single-crystal X-ray diffraction data of suitable crystals were collected with a STOE IPDS-II diffractometer at 120(2) K, using graphite monochromated Mo Kα radiation (0. 0.71073 Å). The data collection was performed using the ω-scan technique and using the STOE X-AREA software package,[27] whereas data reduction was carried out using the program X-RED.[28] The structure was solved 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,[29] and all refinements were performed using the X-STEP32 crystallographic software package.[30] All hydrogen atoms were added in geometrically idealized positions.

Synthesis of [PdBr$_2$(dppe)]

Refluxing diphenylphosphinoethane (597 mg, 1.5 mmol) and palladium(II) bromide (399 mg, 1.5 mmol) at room temperature in a molar ratio of 1:1 in toluene for 6 h gave a yellowish precipitate, which was extracted from the obtained suspension. Suitable yellowish crystals for X-ray diffraction analysis were obtained by slow addition of methanol to a chloroform solution containing the compound.

Yield 132 mg, 85%; m.p. 194 °C. Anal. Calcd for $C_{26}H_{24}P_2PdBr_2$ (665.87 g mol^{-1}) (%): C, 46.98; H, 3.64. Found (%): C, 46.81; H, 3.58. IR (KBr disc, ν, cm^{-1}): 3143–3100 (C&bond;H in Ph), 1585–1608 (C&dbond;C in Ph), 1400.1 (P&bond;CH$_2$). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ, ppm): 3.82 (br, 4H, CH$_2$P), 7.08–7.9 (m, 20H, Ph). ^{13}C NMR (100 MHz, DMSO-*d*$_6$, δ_C, ppm): 70.22, (br, DMSO-*d*$_6$), 35.17 (d, *J* = 16.03, CH$_2$P), 128.8, 130.01, 130.5, 132.1, (d, *J* = 17.63, Ph). ^{31}P {^{1}H} NMR (162 MHz, DMSO-*d*$_6$, δ_P, ppm): 30.53 (s, PPh$_2$).

General Procedure for Stille and Suzuki Cross-Coupling Reactions

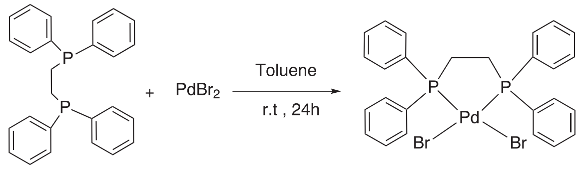
Aryl halide (0.5 mmol) and K$_2$CO$_3$ (1.5 mmol) were added to PEG-400. To this mixture, 3 mg of [PdBr$_2$(dppe)] was added and heated at 90 °C in an oil bath. Finally, 0.5 mmol of phenylating reagent (TPTCl or phenylboronic acid) was added and the reaction mixture was vigorously stirred. The progress of the reaction was monitored by TLC. After completion of the reaction, the corresponding biphenyl product was separated by filtration and the reaction mixture was extracted with water and diethyl ether. The organic layer was dried over magnesium sulfate and then evaporated under reduced pressure. The products may be purified by column chromatography on silica gel using ethyl acetate–*n*-hexane (3:7) if necessary.

Results and Discussion

To the best of our knowledge, there is no report of the complex [PdBr$_2$(dppe)]. This monochelated complex was easily synthesized by reaction of 1,2-bis(diphenylphosphino)ethane with palladium (II) bromide in 1:1 molar ratio in toluene at room temperature for 24 h, leading to the formation of a yellow solid as shown in Scheme 1. The observed singlet peak at 30.53 ppm in the ^{31}P NMR spectrum confirmed the purity of the product.

X-ray Crystallographic Study of [PdBr$_2$(dppe)]

Suitable crystals of [PdBr$_2$(dppe)] were obtained by slow evaporation over several days from chloroform solution. Its structure was determined using single-crystal X-ray diffraction. The molecular structure of the neutral palladium(II) complex is shown in Fig. 1. The complex crystallizes in the monoclinic space group P21/c with four molecules in the unit cell. The asymmetric unit consists of one palladium(II) cation, two bromine anions and one dppe ligand, with all atoms in general positions.



Scheme 1. Synthesis of [PdBr$_2$(dppe)].

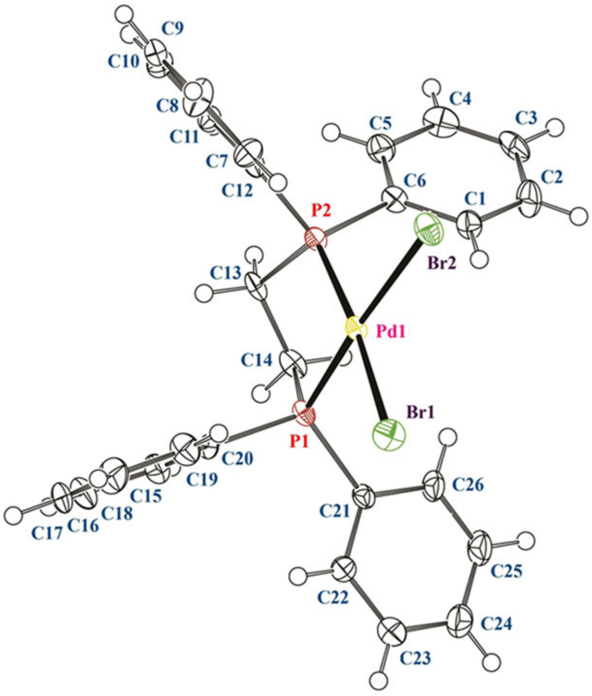


Figure 1. X-ray structure of [PdBr$_2$(dppe)].

Table 1. Crystal data and structure refinement for [$PdBr_2$(dppe)]

	[$PdBr_2$(dppe)]
Empirical formula	$C_{26}H_{24}Br_2P_2Pd$
Formula weight	664.59
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	
a (Å)	11.092(2)
b (Å)	13.293(3)
c (Å)	16.747(3)
α (°)	90.00
β (°)	99.55(3)
γ (°)	90.00(3)
Volume ($Å^3$)	2435.1(9)
Z	4
Calculated density (Mg m^{-3})	1.813
F(000)	1304
Theta range for data collection (°)	2.47 to 29.15
Limiting indices	$-10 \leq h \leq 15$, $-16 \leq k \leq 18$, $22 \leq l \leq 22$
Completeness to θ = 29.15°	99.5%
Absorption correction	Numerical
Absorption coefficient (mm^{-1})	4.188
Crystal size (mm^3)	0.35 × 0.25 × 0.10
Reflections collected/unique	16 389/6539 [*R*(int) = 0.1222]
Max. and min. Transmission	0.6795 and 0.3219
Refinement method	Full-matrix least-squares on F^2
Data/restraints/ parameters	6539/0/280
Goodness-of-fit on F^2	1.013
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.698, WR_2 = 0.1299
R indices (all data)	R_1 = 0.1236, WR_2 = 0.1470
Largest diff. Peak and hole (e $Å^{-3}$)	1.046 and −0.972

Relevant parameters concerning refinement and data collection are given in Table 1 and selected bond distances and angles are given in Table 2. Furthermore, crystallographic data for the structure in this paper can be found in the supporting information. The Pd(II) centre is chelated by two bromo ligands and two phosphine groups of the dppe ligand in a distorted square planar geometry with PdP_2Br_2 surroundings (Fig. 2). Considering the difference between the angles Br(2)–Pd(1)–P(1) of 90.67(5)° and Br(1)–Pd(1)–P(2) of 89.80(6)° shows that the Pd atom is slightly out of the plane of the molecule. The smaller than ideal P–Pd–P angle leads to an opening of the Br–Pd–Br angle to 94.52(3)°. Comparison of Pd&bond;Br (2.4859 Å) and Pd&bond;P (2.2385 Å) average distances and Br(1)–Pd(1)–Br(2) (94.52(3)°) and P(2)–Pd(1)–P(1) (85.43(7)°) angles in [Pd(dppe)Br_2] shows a significant difference between these two bond lengths and angles.

Table 2. Selected bond lengths and bond angles for [$PdBr_2$(dppe)]

Bond lengths (Å)		Bond angles (°)	
Pd(1)–Br(1)	2.4790(11)	P(2)–Pd(1)–P(1)	85.43(7)
Pd(1)–Br(2)	2.4928(13)	P(2)–Pd(1)–Br(1)	89.80(6)
Pd(1)–P(1)	2.2428(18)	P(1)–Pd(1)–Br(1)	174.17(5)
Pd(1)–P(2)	2.2342(19)	P(2)–Pd(1)–Br(2)	171.05(5)
P(1)–C(6)	1.816(7)	P(1)–Pd(1)–Br(2)	90.67(5)
P(1)–C(12)	1.822(8)	Br(1)–Pd(1)–Br(2)	94.52(3)
P(1)–C(13)	1.819(5)	C(6)–P(1)–Pd(1)	111.8(2)
P(2)–C(14)	1.842(7)	C(12)–P(1)–Pd(1)	117.1(2)
P(2)–C(20)	1.817(5)	C(13)–P(1)–Pd(1)	108.5(2)
P(2)–C(21)	1.819(7)	C(21)–P(2)–Pd(1	113.9(1)
C(1)–C(6)	1.386(9)	C(20)–P(2)–Pd(1)	115.3(2)
C(1)–C(2)	1.390(10)	C(14)–P(2)–Pd(1)	106.8(2)

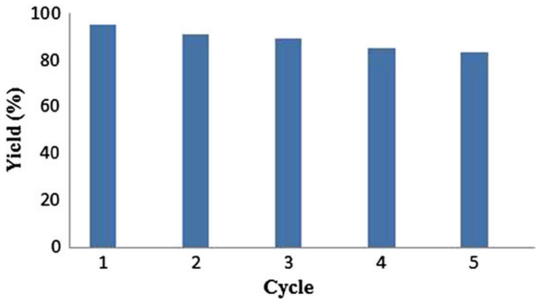


Figure 2. Reuse of the catalyst in Suzuki cross-coupling reaction.

Catalytic Study

The catalytic activity of the palladium catalyst [$PdBr_2$(dppe)] was examined in C&bond;C bond formation reactions. Initially the Stille reaction was studied. To this end, the cross-coupling reaction of aryl halides with TPTCl was considered. In order to find ideal reaction conditions we studied the effect of various parameters on the outcome of the reaction such as the amount of catalyst and the nature of base and solvent in the reaction of iodobenzene with Ph_3SnCl as a model reaction. The reaction conditions were optimized, and the results are summarized in Table 3.

The model reaction was carried out in the presence of various solvents and bases and different amounts of reactants and catalyst. As evident from Table 3, the product yield increases with increasing amount of catalyst (Table 3, entries 1–3). Also, the yield decreases when the amount of catalyst increases from 3 to 4 mg (Table 3, entries 3 and 4). Consequently, 3 mg of [$PdBr_2$(dppe)] (Table 3, entry 3)

Table 3. Optimization of reaction parameters for Stille cross-coupling reaction of iodobenzene withPh_3SnCl

Entry	Cat. (mg)	Solvent	Base	Temp. (°C)	Time (min)	Yield (%)[a]
1	1	PEG	K_2CO_3	90	65	83
2	2	PEG	K_2CO_3	90	50	89
3	3	PEG	K_2CO_3	90	30	96
4	4	PEG	K_2CO_3	90	35	94
5	3	PEG	K_2CO_3	r.t.	—	—
6	3	PEG	K_2CO_3	50	125	80
7	3	PEG	K_2CO_3	70	95	84
8	3	PEG	K_2CO_3	110	35	87
9	3	EtOH	K_2CO_3	90	85	90
10	3	DMSO	K_2CO_3	90	120	86
11	3	DMF	K_2CO_3	90	180	76
12	3	PEG	NaOAc	90	60	90
13	3	PEG	$KHCO_3$	90	75	88
14	3	PEG	Et_3N	90	80	86

[a] Isolated yield.

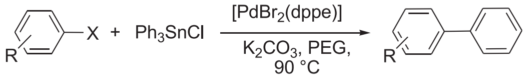
was chosen as optimal amount of catalyst in all coupling reactions. The coupling yield increases as temperature increases from 50 to 90 °C (Table 3, entries 3, 6 and 7). However, the yield decreases when the temperature increases to 110 °C (Table 3, entry 8). Also, the model reaction was carried out in various solvents: polyethylene glycol 400 (PEG-400), ethanol (EtOH), dimethylsulfoxide (DMSO) and dimethylformamide (DMF) (Table 3, entries 3, 9–11). The results show that PEG-400 is the most desirable solvent. Finally, we examined the effects of bases on the outcome of the Stille cross-coupling reaction in PEG-400. Organic and inorganic bases, K_2CO_3, NaOAc, $KHCO_3$ and Et_3N, were investigated (Table 3, entries 3, 12–14). K_2CO_3 is the best base for the reaction in terms of product yield.

The optimized conditions are: Ph_3SnCl (0.5 mmol), iodobenzene (0.5 mmol), catalyst (3 mg), K_2CO_3 (1.50 mmol) and PEG-400 as solvent at 90 °C (Table 3, entry 3).

After optimizing the reaction conditions, the C&bond;C coupling reactions of various substituted aryl halides with Ph_3SnCl were carried out (Table 4). As evident from Table 4, aryl iodides, bromides and chlorides with electron-donating and electron-withdrawing groups react efficiently with Ph_3SnCl. Coupling reactions of Ph_3SnCl with aryl iodides and bromides produce the corresponding products in excellent yields and suitable times. The coupling reactions of aryl chlorides with Ph_3SnCl need longer reaction time than those of aryl iodides and bromides, which gives us the desired product in moderate yield.

The palladium catalyst $[PdBr_2(dppe)]$ can also be applied in the Suzuki reaction which is one of the most powerful methods for the production of asymmetric biaryls. As evident from Table 5, various aryl halides containing both electron-donating and electron-withdrawing groups react with phenylboronic acid to give the

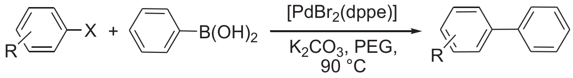
Table 4. Reaction of structurally different aryl halides with Ph_3SnCl in presence of catalyst[a]



Entry	Aryl halide	Product	Time (min)	Yield (%)[b]	M.p. (°C)
1	Iodobenzene	Biphenyl	30	96	69[30]
2	4-Iodotoluene	4-Phenyltoluene	45	92	45–46[30]
3	4-Iodoanisole	4-Methoxybiphenyl	80	86	86–88[30]
4	Bromobenzene	Biphenyl	45	93	69[30]
5	4-Bromotoluene	4-Phenyltoluene	50	90	45–46[30]
6	4-Bromoanisole	4-Methoxybiphenyl	90	84	86–88[30]
7	4-Bromonitrobenzene	4-Nitrobiphenyl	95	87	111–113[30]
8	4-Bromobenzonitrile	4-Cyanobiphenyl	105	84	85–87[31]
9	4-Bromochlorobenzene	4-Chlorobiphenyl	45	88	76–77[30]
10	Chlorobenzene	Biphenyl	65	85	69[31]
11	4-Chloronitrobenzene	4-Nitrobiphenyl	125	81	111–113[31]
12	4-Chlorobenzonitrile	4-Cyanobiphenyl	135	78	85–87[31]

[a] Reaction conditions: aryl halide (1 mmol), Ph_3SnCl (0.5 mmol), K_2CO_3 (1.5 mmol), PEG (1 ml), catalyst (0.003 g).
[b] Isolated yield.

Table 5. Coupling of aryl halides with phenylboronic acid in presence of catalytic amount of $[PdBr_2(dppe)]$[a]



Entry	Aryl halide	Product	Time (min)	Yield (%)[b]	M.p. (°C)
1	Iodobenzene	Biphenyl	25	97	69[30]
2	4-Iodotoluene	4-Phenyltoluene	40	92	45–46[30]
3	4-Iodoanisole	4-Methoxybiphenyl	75	85	86–88[30]
4	Bromobenzene	Biphenyl	40	92	69[30]
5	4-Bromotoluene	4-Phenyltoluene	45	89	45–46[30]
6	4-Bromoanisole	4-Methoxybiphenyl	80	83	86–88[30]
7	4-Bromonitrobenzene	4-Nitrobiphenyl	90	82	111–113[30]
8	4-Bromobenzonitrile	4-Cyanobiphenyl	95	83	85–87[23]
9	4-Bromochlorobenzene	4-Chlorobiphenyl	55	87	76–77[30]
10	Chlorobenzene	Biphenyl	55	90	69[23]
11	4-Chloronitrobenzene	4-Nitrobiphenyl	115	80	111–113[23]
12	4-Chlorobenzonitrile	4-Cyanobiphenyl	120	76	85–87[23]

[a] Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1 mmol), K_2CO_3 (1.5 mmol), PEG (1 ml) and catalyst (0.003 g).
[b] Isolated yield.

Table 6. Comparison of results for [$PdBr_2$(dppe)] with those for other catalysts for the coupling of iodobenzene with phenylboronic acid

Entry	Catalyst	Conditions	Time (min)	Yield (%)[a]	Ref.
ss	[$PdBr_2$(dppe)]	PEG, K_2CO_3, 90 °C	25	97	This work
2	$PdCl_2$	DMF, Cs_2CO_3, 130 °C	120	95	[32]
3	Pd NPs	H_2O, KOH, 100 °C	720	95	[33]
4	Pd-MPTAT-1	NaOH, DMF–H_2O (1:5), 85 °C	480	95	[34]
5	NHC-Pd(II) complex	THF, Cs_2CO_3, 80 °C	720	88	[35]
6	*N*,*N*′-bis(2-pyridinecarboxamide)-1,2-benzene palladium complex	H_2O, K_2CO_3, 100 °C	180	97	[36]
7	CA/Pd(0)	H_2O, K_2CO_3, 100 °C	120	94	[37]
8	Pd/Au NPs	EtOH–H_2O, K_2CO_3, 80 °C	1440	88	[38]
9	PANI–Pd	K_2CO_3, 1,4-dioxane–H_2O (1:1), 95 °C	240	91	[39]
10	PVP–Pd NPs	K_2PO_4, EtOH–H_2O, 90 °C	120	94	[40]

[a] Isolated yield.

corresponding biaryls. The Suzuki reaction was performed under the optimized reaction conditions determined for Stille cross-coupling reactions. Moreover, the coupling of aryl iodides and aryl bromides with phenylboronic acid proceeds at 90 °C and the corresponding products are obtained in high yields, similar to Stille reactions. We also examined the reaction with several substituted aryl chlorides and phenylboronic acid under the optimized reaction conditions. A diverse range of aryl chlorides react with phenylboronic acid to give the desired products in moderate to good yields.

Reusability of Catalyst

One of the advantages of catalysts which make them commercially significant is their reusability. We have found that the catalyst could be rapidly recovered and demonstrated excellent recyclability. To investigate this issue, the recyclability of the catalyst was examined for the reaction of iodobenzene with phenylboronic acid under the optimal conditions. After the completion of the reaction, the reaction mixture was cooled to room temperature. Then, to separate the catalyst, the mixture was filtered off. Finally, the catalyst was dried at 100 °C and was directly used for the next run. As shown in Fig. 1, the catalyst can be recycled for up to five consecutive runs without any significant loss of its catalytic activity.

Comparison of Catalyst

The results were compared in order to examine the efficiency of the coupling of iodobenzene and phenylboronic acid (Table 6) with some reported C&bond;C coupling reactions in the presence of other catalysts. Table 6 shows that the catalyst under investigation leads to shorter reaction time and higher reaction yield than the previously reported catalysts. In particular, the reaction catalysed by [$PdBr_2$(dppe)] can be performed efficiently without using toxic organic solvent, and this new catalyst is also an appropriate catalyst with higher stability and easier separation than the previously reported catalysts.

Conclusions

In summary, the method presented represents an attractive and easy procedure for the synthesis of [$PdBr_2$(dppe)] by direct reaction of 1,2-bis(diphenylphosphino)ethane with palladium(II) bromide, the structure of which was characterized using X-ray crystallography. The complex [$PdBr_2$(dppe)] was employed as an efficient catalyst for both Stille and Suzuki cross-coupling reactions. The present system shows attractive advantages such as the use of effective and inexpensive catalyst, convenient one-pot operation, short reaction time, good to excellent yields of products and the use of PEG as a green reaction medium that is considered to be a relatively environmentally benign solvent. High activity was observed for the catalyst and its reusability was tested in five consecutive cycles.

Acknowledgement

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