© 2010 The Chemical Society of Japan Bull. Chem. Soc. Jpn. Vol. 83, No. 11, 1367–1373 (2010)

1,3,2,4-Diazadiphosphetidines as Ligand and Base for Palladium-Catalyzed Suzuki–Miyaura, Sonogashira–Hagihara, and Homocoupling Reactions of Aryl Halides under Heterogeneous Conditions in Water

Nasser Iranpoor,*[1] **Habib Firouzabadi,***[1] **Abbas Tarassoli,**[2] **and Masood Fereidoonnezhad**[1]

[1]Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

[2]Department of Chemistry, College of Sciences, Shahid Chamran University, Ahwaz, Iran

Received November 18, 2009; E-mail: iranpoor@susc.ac.ir, firouzabadi@susc.ac.ir

1,3,2,4-Diazadiphosphetidines as easily prepared, cheap, and air-stable P(III) containing ligands are successfully used for the efficient C–C bond formation via Suzuki–Miyaura, Sonogashira–Hagihara, and homocoupling reactions of aryl iodides, bromides, and chlorides. The reactions occur heterogeneously in refluxing water and the nitrogen atoms in these ligands behave as base to exclude the need to add internally base. The ligand together with its Pd(0) complex is easily separated by filtration and reused for several runs.

The reactions involving Pd catalysts and reagents are particularly useful and versatile among many transition metals used for organic synthesis. Palladium catalysis has gained enormous relevance in various coupling reactions such as Heck, Suzuki–Miyaura, Sonogashira–Hagihara, and homocoupling reactions.[1]

The sp^2–sp^2 cross-coupling reaction between aryl halides and arylboronic acids and also the sp^2–sp intermolecular coupling reaction between aryl halides with terminal alkynes is usually performed using catalytic amounts of a palladium complex, often with phosphine ligands and in a polar solvent such as *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), *N*,*N*-dimethylacetamide (DMA), or *N*-methylformamide (NMF) at moderately high temperatures in the presence of organic or inorganic bases.[1,2] Much attention has been paid to improve these reactions by designing various new ligands, using new heterogeneous catalysts, and the use of less toxic solvents.[3–5]

The replacement of organic solvents by water in palladium-promoted reactions is an important goal for the development of environmentally and technologically safe processes,[6] as water is inexpensive, non-toxic, nonflammable, and environmentally sustainable, allows simple separation and reuse of the catalyst and increasing selectivity and efficiency.[7]

Phosphazanes are molecules that involve P and N atoms with connectivity to other skeleton atoms. An interesting class of phosphazanes, are the four-membered-ring 1,3,2,4-diazadiphosphetidines[8,9] containing phosphorus(III) and N–H bonds in a P_2N_2 ring system.

The oligomer ligand $\mathbf{L^1}$, $[(PhNH)P_2(NPh)_2]_2NPh$,[10,11] the trimer ligand $\mathbf{L^2}$, $[(PhNH)PNPh]_3$,[10,12] and the dimer ligand $\mathbf{L^3}$, $[(PhNH)PNPh]_2$, have been reported to be prepared easily from the reaction of PCl_3 with $PhNH_2$. Replacement of $PhNH_2$ with isopropylamine under optimized reaction conditions produces the ligand $\mathbf{L^4}$ which contains isopropyl moiety[13] (Scheme 1).

In a study for the complex formation of these ligands with molybdenum carbonyls, it has been shown that $\mathbf{L^1}$ and $\mathbf{L^2}$ behave as bidentate ligands and only two of their phosphorous atoms incorporate in the complex formation.[14]

The interesting point about these compounds is that they can act as a potential complexing agent through their P(III) atoms while acting as a base through their N sites whenever a base is required in the reaction. Replacement of the phenyl groups of $\mathbf{L^3}$ with isopropyl affords $\mathbf{L^4}$ in which the basicity of the nitrogen atoms in this compound could be increased.

In continuation of our recent works on coupling reactions and the use of phosphazanes,[3b–3f] we introduce the use of easily prepared $\mathbf{L^1}$–$\mathbf{L^4}$ in conjunction with Pd(II) salts for carbon–carbon bond formation through Suzuki–Miyaura, Sonogashira–Hagihara, and homocoupling reactions under heterogeneous conditions in refluxing neat water without adding any internal base.

Results and Discussion

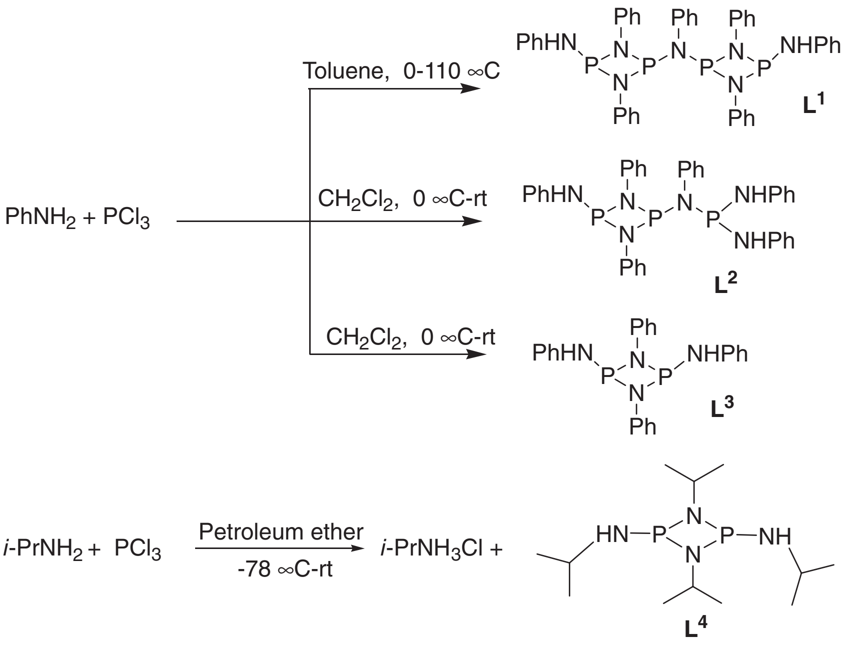
Ligands $\mathbf{L^1}$–$\mathbf{L^4}$ were prepared from the reaction of PCl_3 and $PhNH_2$ or isopropylamine according to the literature (Scheme 1).[10–13]

In the following, we discuss the applications of these compounds in conjunction with $PdCl_2$ as pre-catalyst for the Suzuki–Miyaura, Sonogashira–Hagihara, and homocoupling reactions under heterogeneous conditions in refluxing water.

Suzuki–Miyaura Coupling Reactions. The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids is a useful methodology for the synthesis of biaryl derivatives.[15] Over the past decades, significant achievements have been made for improvement of the reaction conditions to be applicable for the synthesis of a wide range of biologically and industrially significant material.[4a,16–18]

In order to compare the reactivity of these ligands $\mathbf{L^1}$–$\mathbf{L^4}$, we applied them in the presence of catalytic amounts of $PdCl_2$ for the Suzuki–Miyaura coupling reaction of bromobenzene and

Published on the web November 15, 2010; doi:10.1246/bcsj.20090299



Scheme 1. 1,3,2,4-Diazadiphosphetidine-based ligands $\mathbf{L^1}$–$\mathbf{L^4}$.

Table 1. Coupling of Bromobenzene (1 mmol) with Phenylboronic Acid (1.5 mmol) in the Presence of $\mathbf{L^1}$–$\mathbf{L^4}$ Using 2.5 mol % of $PdCl_2$ at 100 °C

Entry	Ligand	Solvent	Ligand /mmol[a)]	Time	Conversion[b)] /%
1	$\mathbf{L^1}$	H_2O	0.3	50 min	100
2	$\mathbf{L^2}$	H_2O	0.4	50 min	95
3	$\mathbf{L^3}$	H_2O	0.6	50 min	95
4	$\mathbf{L^4}$	H_2O	0.6	25 min	100
5	$\mathbf{L^1}$	Toluene	0.3	20 h	90
6	$\mathbf{L^1}$	DMF	0.3	3.5 h	100
7	$\mathbf{L^1}$	DMSO	0.3	5 h	100
8	$\mathbf{L^1}$	CH_3CN	0.3	20 h	25
9	$\mathbf{L^1}$	THF	0.3	20 h	30

a) In each reaction, the quantity of $\mathbf{L^1}$–$\mathbf{L^4}$ are chosen in which equal amounts of phosphorous(III) are present. The reaction of Entry 1 with 0.2 and 0.1 mmol of the ligand $\mathbf{L^1}$ was also completed within 1 h. b) Conversion yield is based on GC analysis using octane as internal standard.

Table 2. Effect of Base on Coupling of Bromobenzene (1 mmol) with Phenylboronic Acid (1.5 mmol) in the Presence of $\mathbf{L^1}$–$\mathbf{L^4}$ (0.3–0.6 mmol)[a)] Using 2.5 mol % of $PdCl_2$ at 100 °C

Entry	Base[c)]	Time/min				Conversion[b)] /%
		$\mathbf{L^1}$	$\mathbf{L^2}$	$\mathbf{L^3}$	$\mathbf{L^4}$	
1	None	50	50	50	25	100
2	NaOH	35	40	40	15	100
3	K_2CO_3	40	45	45	20	100
4	K_3PO_4	40	40	45	25	100
5	$CsCO_3$	35	35	40	20	100
6	Et_3N	30	35	40	15	100
7	DBU	40	40	45	15	100

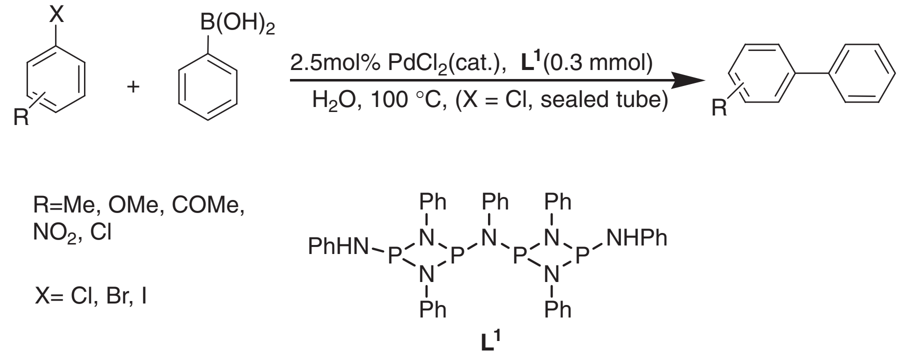
a) GC analysis. b) In each reaction, the quantity of $\mathbf{L^1}$–$\mathbf{L^4}$ are chosen in which equal amounts of phosphorous(III) are present ($\mathbf{L^1}$–$\mathbf{L^4}$: 0.3, 0.4, 0.6, and 0.6 equimolar respectively). c) Two molar equivalents of base were used.

phenylboronic acid in different organic solvents as well as in water at 100 °C. Preliminary studies showed that the coupling reaction can take place efficiently with no internally added base.

According to the results of Table 1, Pd(II) in the presence of all ligands $\mathbf{L^1}$–$\mathbf{L^4}$ efficiently catalyses the coupling reaction of bromobenzene and phenylboronic acid in water at 100 °C. In this comparative study, the stoichiometries of ligands (0.3–0.6 equimolar) are chosen in each reaction on the basis of their number of P(III) atoms so that equal amounts of P(III) are present. Under these conditions not much difference in their reactivity was obtained. Then, we studied the effect of different bases on the coupling reaction of bromobenzene with phenylboronic acid in the presence of $\mathbf{L^1}$–$\mathbf{L^4}$ using 2.5 mol % of $PdCl_2$ at 100 °C.

As it is demonstrated in Table 2, the presence of internally added base has no pronounced effect on the performance of the reaction. However, due to the greater number of P(III) atoms per molecule in $\mathbf{L^1}$ which offers higher atom economy and also its insolubility in water which provides heterogenous conditions, $\mathbf{L^1}$ was selected as the ligand of choice for this reaction. The ligand $\mathbf{L^1}$ was found to be stable when it was placed in refluxing water for several hours. Lowering the amounts of $\mathbf{L^1}$ to 0.2 and 0.1 mmol did not show considerable effect on the progress of the reaction. However, due to the insolubility of solid substrates in water which usually causes the problem of sublimation at high temperature, higher amounts of the ligand reduce the problem of sublimation.

Under the optimized reaction conditions, 0.3 mmol of ligand $\mathbf{L^1}$, $PdCl_2$ (2.5 mol %) in the absence of any internally added base, the desired products were obtained in excellent yields for a wide array of aryl iodides, bromides, and chlorides with

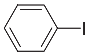
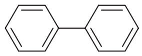
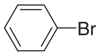
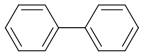
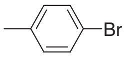
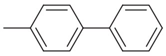
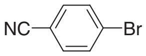
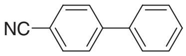
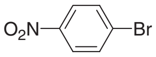
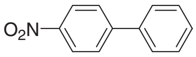
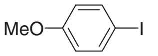
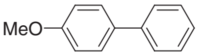
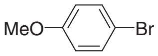
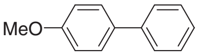
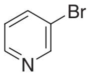
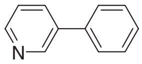
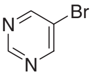
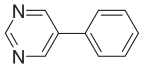
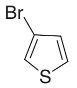
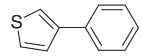
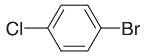
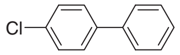
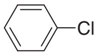
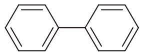
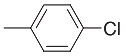
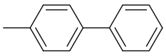
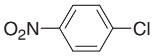
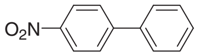
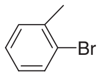
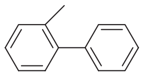


$\mathbf{L^1}$

Scheme 2. Suzuki–Miyaura reactions of aryl halides with phenylboronic acid using $\mathbf{L^1}$ in refluxing water without adding any internally base.

phenylboronic acid at 100 °C (Scheme 2 and Table 3). The reactions of aryl chlorides were performed in a sealed tube under the same reaction conditions.

Table 3. Suzuki–Miyaura Reaction of Aryl Halides with Phenylboronic Acid in the Presence of $\mathbf{L^1}$ in Refluxing Water

Entry	Ar–X	Product	Time /h	Isolated yield/%
1			0.67	92
2			0.83	90
3			1.42	86
4			3.5	89
5			3.5	88
6			1.33	80
7			1.5	80
8			1.5	83
9			2.5	81
10			1	82
11			3	80
12			10[a]	70
13			10[a]	83
14			15[a]	70
15			5	71

a) The reaction was placed in a sealed tube at 100 °C.

The coupled products were simply isolated by diethyl ether extraction.

As it is shown in Table 3, Entries 8–10, the Suzuki–Miyaura cross-coupling reaction is also applicable to heteroaryl halides. For example use of 3-bromopyridine, 3-bromothiophene, and phenylboronic acid as substrates gave satisfactory results and the desired products were isolated in 80% yield.

We have also shown the utility of the method for using aryl chlorides as the substrates for Suzuki–Miyaura reaction. For this purpose, chlorobenzene, 4-chlorotoluene, and 1-chloro-4-nitrobenzene were subjected to the reaction at 100 °C in the presence of 2.5 mol % of $PdCl_2$ and 0.3 mmol ligand in neat water under sealed tube conditions. The reactions proceeded well under these reaction conditions and the desired products were isolated in 70–80% yield (Scheme 2 and Table 3, Entries 12–14).

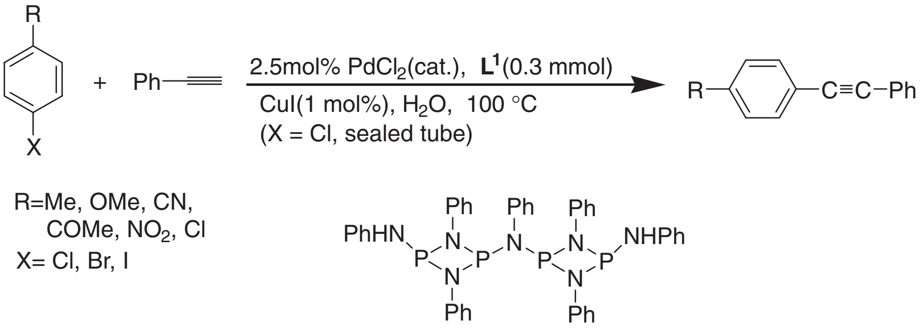
We have also studied the recycling of the catalyst for the reaction of iodobenzene with phenylboronic acid at 100 °C using $PdCl_2$ and $\mathbf{L^1}$. Recycling of the catalyst was successfully achieved ten times. Each run afforded biphenyl in 93–88% yield.

Sonogashira–Hagihara Cross-Coupling Reactions. sp^2–sp Coupling reaction between aryl or alkenyl halides and terminal alkynes catalyzed with Pd(II), with or without copper(I) cocatalyst, is an important methodology for preparation of arylalkynes and conjugated enynes.[1d,19]

In order to find more applications for this phosphazane $\mathbf{L^1}$, we applied this ligand with catalytic amounts of $PdCl_2$ for Sonogashira reaction of aryl iodides, bromides, and chlorides with phenylacetylene under optimized conditions without adding any internally base in refluxing water (Scheme 3).

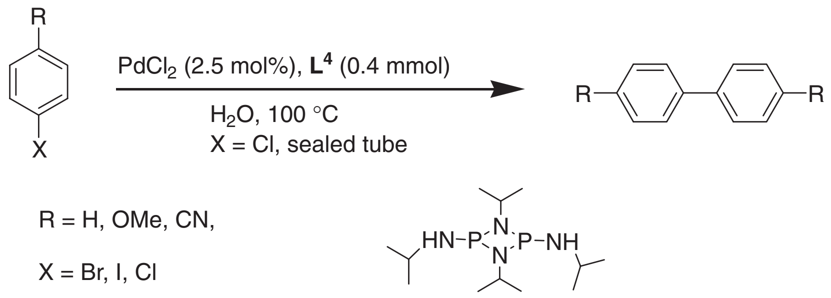
For the optimization of the reaction conditions, we chose the cross coupling of bromobenzene with phenylacetylene as the model reaction in the presence and also in the absence of internally added base. Here again, the presence of internal base had little effect on the progress of the reaction, so base-free reaction was selected as the preferred condition. The optimized reaction temperature was again chosen at 100 °C for aryl iodides and bromides and the same temperature in sealed tube for aryl chlorides in water as the most suitable media.

Under our optimized reaction conditions, 0.3 mmol phosphazane, 2.5 mol % of $PdCl_2$, 1 mol % CuI, and no internally



L^1

Scheme 3. Sonogashira–Hagihara reactions of aryl halides with phenylacetylene using **L**^{1} in refluxing water.



L^4

Scheme 4. Homocoupling reactions of aryl halides using **L**^{4} in neat water.

added base, the desired products were obtained in excellent yields for a wide array of aryl iodides and bromides with phenylacetylene at 100 °C (Scheme 4 and Table 4).

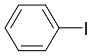
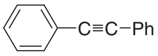
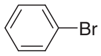
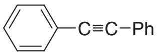
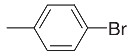
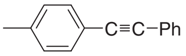
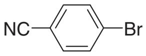
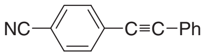
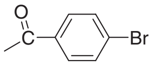
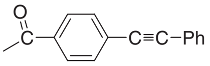
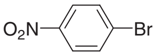
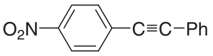
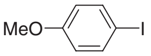
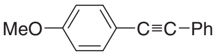
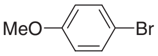
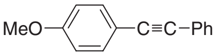
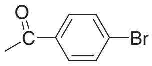
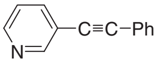
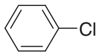
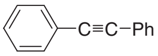
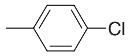
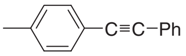
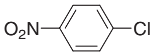
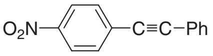
The reaction of chlorobenzene with phenylacetylene was occurred under sealed tube conditions at 100 °C and diphenylacetylene was obtained in 80% yield (Table 4, Entry 10).

Homocoupling Reaction. Homocoupling reactions have been widely used by chemists for the synthesis of biaryls via formation of carbon–carbon bonds and occupy a special place.[20]

We also applied 1,3,2,4-diazadiphosphetidine **L**^{1} as the ligand with catalytic amounts of $PdCl_2$ for the homocoupling of aryl halides. We first tried the homocoupling of iodobenzene in the presence of **L**^{1} in water at 100 °C. After, 2 h, it was observed that only trace amount of biphenyl is produced. The low yield of the reaction, suggested the need for a stronger base in the reaction mixture. We therefore repeated the reaction in the presence of bases such as NaOH, K_2CO_3, Cs_2CO_3, K_3PO_4, and also triethylamine. When iodobenzene was treated as a model compound with 0.3 mmol of **L**^{1}, 0.025 mmol of $PdCl_2$, and 2.0 mmol of Et_3N, the homocoupling product was obtained in highest yield (Table 5, Entry 1).

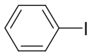
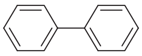
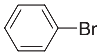
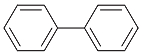
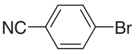
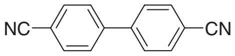
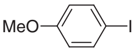
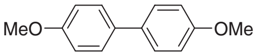
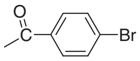
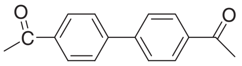
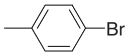
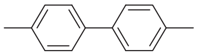
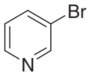
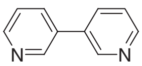
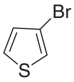
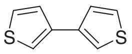
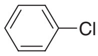
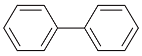
In order to exclude the internal base, it was decided to study this reaction in the presence of ligand **L**^{4}. We hoped the presence of isopropylamino moiety in this ligand instead of N–Ph group in **L**^{1}, could act as a stronger base and the reaction proceeds without the need to add Et_3N. As hoped, when we did the reaction of iodobenzene in the presence of **L**^{4} which is considerably soluble in water at 100 °C, the reaction was completed within 1.5 h without the need to use triethylamine

Table 4. Sonogashira Reaction of Aryl Halides with Phenylacetylene in the Presence of **L**^{1} in Refluxing Water

Entry	Ar–X	Product	Time /h	Isolated yield/%
1			1	95
2			1.5	91
3			2	90
4			5	93
5			6	80
6			10	84
7			2	86
8			2.5	85
9			8	81
10			10[a)]	80
11			15[a)]	80
12			15[a)]	83

a) The reaction was placed in a sealed tube at 100 °C.

Table 5. Homocoupling of Aryl Halides Using $\mathbf{L^1}$ in the Presence of Triethylamine and $\mathbf{L^4}$ without Internal Base in Refluxing Water

Entry	Ar–X	Product	Time/h		Isolated yield/%	
			$\mathbf{L^4}$	$\mathbf{L^1}$	$\mathbf{L^4}$	$\mathbf{L^1}$
1			1.5	0.5	94	93
2			2.5	0.75	89	90
3			15	10	76	83
4			3	1.5	93	91
5			18	12	67	70
6			4.5	3.5	76	76
7			10	7	65	66
8			5.5	2	80	91
9[a]			10	8	80	82

a) The reaction was placed in a sealed tube at 100 °C.

as internal base. We therefore used ligand $\mathbf{L^1}$ together with triethylamine and also ligand $\mathbf{L^4}$ without adding any internal base for the homocoupling of aryl bromides and iodides (Scheme 4). The obtained results are shown in Table 5.

For example, iodobenzene was completely converted to biphenyl in the presence of $\mathbf{L^1}$ and triethylamine as the base after 30 min (Table 5, Entry 1), while it reacted within 1.5 h in the presence of $\mathbf{L^4}$ and no internally added base to give the homocoupling product (Table 5, Entry 1).

As it is in Table 5, this catalytic system is applicable for the electron-neutral, and electron-deficient bromides as well as heteroaryl bromides.

In order to show the efficiency of this system, the results of coupling reaction of bromobenzene with our system are compared with the results from the same reaction in water in the absence of any ligand and also in the presence of Ph_3P as a conventional ligand. The obtained results are shown in Table 6.

In addition to the higher reactivity of $\mathbf{L^1}$, the presence of this ligand greatly reduces the problem of sublimation of solid samples when water is used as the solvent.

As it was reported before,[3f] the spectrophotometric studies has revealed that the complex formation between the $\mathbf{L^1}$ and Pd(II) occurs with the formation of a ML_2 complex. The presence of Pd(0) complex through the reaction of $\mathbf{L^1}$ and Pd(II) precatalyst was studied by X-ray powder diffraction. The powder X-ray diffraction (XRD) patterns for the catalyst showed the expected pattern of Pd(0) (Figure 1). The diffraction peaks of (111), (200), (220), and (311) crystallographic planes of the Pd(0) particles were observed according to the literature.[21] The same results were also obtained for the XRD patterns of the catalysts after its use in the coupling reaction of iodobenzene and phenylboronic acid.

Table 6. Suzuki–Miyaura, Sonogashira–Hagihara, and Homocoupling Reactions of of Bromobenzene Using 2.5 mol % of $PdCl_2$ at 100 °C in Water under Different Conditions

Entry	Ligand[a]	Reaction	Base[b]	Time /h	Conversion[c] /%
1	$\mathbf{L^1}$	Suzuki	—	0.83	90
2	Ligand-free	Suzuki	—	5	15
3	Ph_3P	Suzuki	—	5	24
4	Ph_3P	Suzuki	NaOH	5	48
5	Ph_3P	Suzuki	K_2CO_3	5	57
6	Ph_3P	Suzuki	Et_3N	5	61
7	$\mathbf{L^1}$	Sonogashira	—	1	95
8	Ligand-free	Sonogashira	NaOH	1	15
9	Ph_3P[d]	Sonogashira	NaOH	1	40
10	Ph_3P[d]	Sonogashira	Et_3N	1	55
11	$\mathbf{L^1}$	Homocoupling	Et_3N	0.75	90
12	$\mathbf{L^4}$	Homocoupling	—	2.5	89
13	Ligand-free	Homocoupling	NaOH	5	10
14	Ph_3P	Homocoupling	NaOH	5	18
15	Ph_3P	Homocoupling	Et_3N	5	25

a) One molar equivalent of ligand was used. b) Two molar equivalents of base were used. c) GC analysis. d) This reaction has been shown to perform at 120 °C in sealed tube in the presence of different bases in 21–93% yield.[19c]

Conclusion

In this study we have introduced the applicability of 1,3,2,4-diazadiphosphetidines carrying different number of P(III) atoms and also different amino groups as easily prepared, cheap, and air-stable ligands for C–C bond formation via

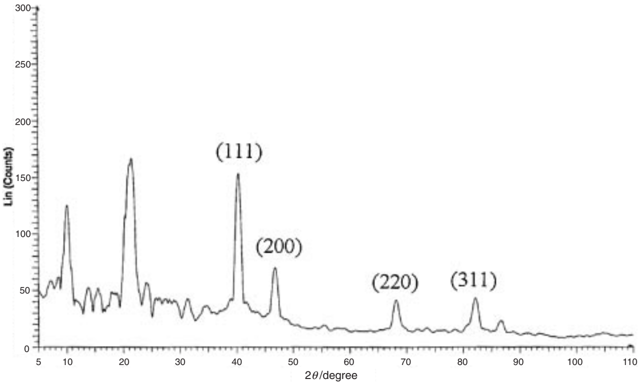


Figure 1. XRD pattern of the catalyst.

hetero- and homocoupling reactions in refluxing water. The reactions can occur under heterogenous condition in water without adding any internally base. The ease of separation of the products and reusability of the catalyst can also be considered as strong practical advantages of this method.

Experimental

FT-IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX-250 (^{1}H NMR 250 MHz, ^{13}C NMR 62.9 MHz) spectrometer in $CDCl_3$ or DMSO-d_6 solvents using TMS as an internal standard. X-ray diffractions were obtained using XRD, D8, Avance, Bruker, axs.

Determination of the purity of the products and the reaction monitoring were carried out on silica gel 254 analytical sheets or by GLC on a Shimadzu model GC-10A instrument. All compounds had been reported previously, and their identities were confirmed by comparison of their physical and spectroscopic data with those of known compounds.

General Experimental Procedure for the Suzuki Reactions. $PdCl_2$ (0.025 mmol, 4.4 mg) was added to a flask containing 1,3,2,4-diazadiphosphetidine **L^1** (0.3 mmol, 0.23 g) and water (3 mL). Then aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol, 0.18 g) were added to the mixture and refluxed. In the case of aryl chlorides the reaction mixtures were placed in a sealed tube at 100 °C. GC and TLC monitory of the reaction mixture showed the completion of the reaction after 0.67–15 h (Table 3). After completion of reaction, the mixture was cooled to room temperature and was extracted with diethyl ether (3 × 5 mL). The combined ethereal solution was dried with anhydrous $MgSO_4$ and evaporated. Chromatography of the crude product on a short column of silica gel using *n*-hexane/ethyl acetate with the ratio varies in the range of 5/1 to 2/1 as eluent gave biaryl in 70–90% yield (Table 3). The catalyst can be recycled as follows: The reaction mixture was cooled and filtered. The filtrate which contains both the ligand, the Pd catalyst and the product was washed first with diethyl ether (3 mL) to remove any of the product and then twice with 1% aqueous solution of NaOH (3 mL) followed by water (2 × 3 mL). The residue was dried in vacuum and used for the coupling of iodobenzene and phenylboronic acid. This was repeated ten times and biphenyl was obtained in the range of 93–88% yields.

General Experimental Procedure for the Sonogashira Reactions. To a mixture containing 1,3,2,4-diazadiphosphetidine **L^1** (0.3 mmol, 0.23 g) in water (3 mL), $PdCl_2$ (0.025 mmol, 4.4 mg) was added. Then aryl halide (1.0 mmol), phenylacetylene (1.5 mmol, 0.16 mL), and cupper(I) iodide (1 mol %) were added to the mixture and refluxed. In the case of aryl chlorides the reaction mixtures were placed in a sealed tube at 100 °C. The reaction completion (0.5–15 h) was monitored by GC and TLC (Table 5). After completion of reaction, the mixture was cooled to room temperature and filtered. The filtrate was washed with diethyl ether (2 × 5 mL) and the aqueous solution was extracted with diethyl ether (3 × 5 mL). After drying the combined ethereal solution with anhydrous $MgSO_4$ the solvent was evaporated. Chromatography of the crude product on a short column of silica gel using *n*-hexane/ethyl acetate with the ratio varies in the range of 5/1 to 2/1 a as eluent gave the pure product in 80–95% (Table 4).

General Experimental Procedure for the Homocoupling Reaction with L^1. $PdCl_2$ (0.025 mmol, 4.4 mg) was added to a flask containing 1,3,2,4-diazadiphosphetidine **L^1** (0.3 mmol, 0.23 g) and water (3 mL). Then aryl halide (1.0 mmol) and Et_3N (2.0 mmol, 0.20 g) were added to the mixture and refluxed. In the case of aryl chlorides the reaction mixtures was placed in a sealed tube. After completion of reaction which was indicated by GC and TLC, the mixture was cooled to room temperature and filtered and the filtrate was washed with diethyl ether (5 mL). The aqueous solution was extracted with diethyl ether (3 × 5 mL). The combined ethereal solution was dried with anhydrous $MgSO_4$ and evaporated. Chromatography of the crude product on a short column of silica gel using *n*-hexane/ethyl acetate as eluent with the ratio varied in the range of 5/1 to 2/1 gave the desired product in 65–93% yield (Table 4).

General Experimental Procedure for the Homocoupling Reaction with L^4. To a flask containing **L^4** ligand (0.3 mmol, 0.135 g) in water (3 mL), $PdCl_2$ (0.025 mmol, 4.4 mg) was added. Then aryl halide (1.0 mmol), was added and refluxed. In the case of aryl chlorides the reaction was performed in a sealed tube and placed in an oil bath at 100 °C. GC and TLC of the reaction mixture showed the completion of the reaction after 0.5–18 h. After completion of reaction, the mixture was cooled to room temperature and extracted with diethyl ether (3 × 5 mL). The combined ethereal solution was dried ($MgSO_4$). Evaporation of the solvent followed by chromatography on a short column of silica gel using *n*-hexane/ethyl acetate with the ratio varies in the range of 5/1 to 2/1 as eluent gave the product in 65–95% yield (Table 5).

Preparation of Catalyst for XRD Analysis. The sample for XRD was prepared by refluxing a mixture of **L^1** (0.3 mmol) and $PdCl_2$ (0.08 mmol) in water (3 mL) for 50 min. After cooling to 0 °C, the gray precipitate was filtered. The filtrate was washed by cold THF (2 × 2 mL) to remove the excess of ligand and dried in vacuum.

The authors are grateful for the partial financial support from the Shiraz University Research Council and Mr. Arash Ghaderi for repeating some of the experiments.

Supporting Information

^{1}H- and ^{13}C NMR data of the products are available. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

References

1 a) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009. b) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133. c) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457. d) R. Chinchilla, C. Nájera, *Chem. Rev.* **2007**, *107*, 874.

2 a) V. Farina, *Adv. Synth. Catal.* **2004**, *346*, 1553. b) F.-X. Felpin, T. Ayad, S. Mitra, *Eur. J. Org. Chem.* **2006**, 2679.

3 a) P. T. Anastas, M. M. Kirchhoff, *Acc. Chem. Res.* **2002**, *35*, 686. b) N. Iranpoor, H. Firouzabadi, R. Azadi, *Eur. J. Org. Chem.* **2007**, 2197. c) N. Iranpoor, H. Firouzabadi, R. Azadi, *J. Organomet. Chem.* **2008**, *693*, 2469. d) A. Safavi, N. Maleki, N. Iranpoor, H. Firouzabadi, A. R. Banazadeh, R. Azadi, F. Sedaghati, *Chem. Commun.* **2008**, 6155. e) H. Firouzabadi, N. Iranpoor, M. Gholinejad, *Tetrahedron* **2009**, *65*, 7079. f) N. Iranpoor, H. Firouzabadi, A. Tarassoli, M. Fereidoonnezhad, *Tetrahedron* **2010**, *66*, 2415. g) A. D. Zotto, F. I. Prat, W. Baratta, E. Zangrando, P. Rigo, *Inorg. Chim. Acta* **2009**, *362*, 97.

4 a) F. Bellina, A. Carpita, R. Rossi, *Synthesis* **2004**, 2419, and references cited therein. b) P. Zheng, W. Zhang, *J. Catal.* **2007**, *250*, 324. c) G. Durgun, Ö. Aksın, L. Artok, *J. Mol. Catal. A: Chem.* **2007**, *278*, 189. d) H. Türkmen, T. Pape, F. E. Hahn, B. Çetinkaya, *Eur. J. Inorg. Chem.* **2009**, 285. e) Y.-J. Shang, J.-W. Wu, C.-L. Fan, J.-S. Hu, B.-Y. Lu, *J. Organomet. Chem.* **2008**, *693*, 2963.

5 a) A. F. Littke, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 6989. b) M. R. Netherton, G. C. Fu, *Org. Lett.* **2001**, *3*, 4295. c) J. Liu, Y. Zhao, Y. Zhou, L. Li, T. Y. Zhang, H. Zhang, *Org. Biomol. Chem.* **2003**, *1*, 3227. d) T. Chen, J. Gao, M. Shi, *Tetrahedron* **2006**, *62*, 6289.

6 a) C.-J. Li, T.-H. Chan, *Organic Reactions in Aqueous Media*, Wiley, New York, **1997**. b) *Organic Synthesis in Water*, ed. by P. A. Grieco, Blackie Academic & Professional, London, **1998**. c) B. Cornils, W. A. Herrmann, *Aqueous-Phase Organometallic Catalysis: Concepts and Applications*, Wiley-VCH, Weiheim **1998**. d) P. Tundo, P. Anastas, D. StC. Black, J. Breen, T. Collins, S. Memoli, J. Miamoto, M. Polyakoff, W. Tumas, *Pure Appl. Chem.* **2000**, *72*, 1207.

7 a) R. A. Sheldon, *Green Chem.* **2005**, *7*, 267. b) S. Mecking, A. Held, F. M. Bauers, *Angew. Chem., Int. Ed.* **2002**, *41*, 544. c) F. Joó, *Acc. Chem. Res.* **2002**, *35*, 738. d) K. Manabe, S. Kobayashi, *Chem.—Eur. J.* **2002**, *8*, 4094.

8 The 1,3,2,4-diazadiphosphetidine nomenclature system advocated by Chemical Abstracts is used throughout this paper. An alternate system, based on the stem name cyclodiphosph(III)-azane is frequently used in the European literature.

9 a) R. A. Shaw, *Phosphorus, Sulfur Silicon Relat. Elem.* **1978**, *4*, 101. b) A. F. Grapov, N. N. Mel'nikov, L. V. Razvodovskaya, *Russ. Chem. Rev.* **1970**, *39*, 20.

10 a) M. L. Thompson, R. C. Haltiwanger, A. D. Norman, *J. Chem. Soc., Chem. Commun.* **1979**, 647. b) H. J. Chen, R. C. Haltiwanger, T. G. Hill, M. L. Thompson, D. E. Coons, A. D. Norman, *Inorg. Chem.* **1985**, *24*, 4725. c) A. Tarassoli, M. L. Thompson, R. C. Haltiwanger, T. G. Hill, A. D. Norman, *Inorg. Chem.* **1988**, *27*, 3382.

11 M. L. Thompson, A. Tarassoli, R. C. Haltiwanger, A. D. Norman, *Inorg. Chem.* **1987**, *26*, 684.

12 M. L. Thompson, A. Tarassoli, R. C. Haltiwanger, A. D. Norman, *J. Am. Chem. Soc.* **1981**, *103*, 6770.

13 T. G. Hill, R. C. Haltiwanger, M. L. Thompson, S. A. Katz, A. D. Norman, *Inorg. Chem.* **1994**, *33*, 1770.

14 A. Tarassoli, H. J. Chen, M. L. Thompson, V. S. Allured, R. C. Haltiwanger, A. D. Norman, *Inorg. Chem.* **1986**, *25*, 4152.

15 a) S. P. Stanforth, *Tetrahedron* **1998**, *54*, 263. b) S. R. Chemler, D. Trauner, S. J. Danishefsky, *Angew. Chem., Int. Ed.* **2001**, *40*, 4544. c) A. F. Littke, G. C. Fu, *Angew. Chem., Int. Ed.* **2002**, *41*, 4176. d) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem., Int. Ed.* **2005**, *44*, 4442. e) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609. f) S. Nara, J. Martinez, C.-G. Wermuth, I. Parrot, *Synlett* **2006**, 3185.

16 a) J. Hassan, M. Sévignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359. b) A. Suzuki, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. by F. Diederich, P. J. Stang, Wiley-VCH, Weinheim, **1998**, Chap. 2, pp. 49–98. c) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147. d) N. Miyaura, *Top. Curr. Chem.* **2002**, *219*, 11. e) S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* **2002**, *58*, 9633.

17 a) Y. Urawa, H. Naka, M. Miyasawa, S. Souda, K. Ogura, *J. Organomet. Chem.* **2002**, *653*, 269. b) N. Yasuda, *J. Organomet. Chem.* **2002**, *653*, 279.

18 a) M. B. Goldfinger, K. B. Crawford, T. M. Swager, *J. Am. Chem. Soc.* **1997**, *119*, 4578. b) M. Miura, *Angew. Chem., Int. Ed.* **2004**, *43*, 2201.

19 a) L. Brandsma, *Synthesis of Acetylenes, Allenes and Cumulenes: Methods and Techniques*, Elsevier, Oxford, **2004**, p. 293. b) R. R. Tykwinski, *Angew. Chem., Int. Ed.* **2003**, *42*, 1566. c) E. Negishi, L. Anastasia, *Chem. Rev.* **2003**, *103*, 1979. d) J. T. Guan, T. Q. Weng, G.-A. Yu, S. H. Liu, *Tetrahedron Lett.* **2007**, *48*, 7129.

20 a) J. D. Holbrey, M. B. Turner, W. M. Reichert, R. D. Rogers, *Green Chem.* **2003**, *5*, 731. b) D. D. Hennings, T. Iwama, V. H. Rawal, *Org. Lett.* **1999**, *1*, 1205. c) S. Venkatraman, C.-J. Li, *Org. Lett.* **1999**, *1*, 1133. d) M. G. Banwell, B. D. Kelly, O. J. Kokas, D. W. Lupton, *Org. Lett.* **2003**, *5*, 2497. e) L. Wang, Y. Zhang, L. Liu, Y. Wang, *J. Org. Chem.* **2006**, *71*, 1284. f) M. K. Robinson, V. S. Kochurina, J. M. Hanna, Jr., *Tetrahedron Lett.* **2007**, *48*, 7687.

21 S. Martínez, M. Moreno-Mañas, A. Vallribera, U. Schubert, A. Roig, E. Molins, *New J. Chem.* **2006**, *30*, 1093.