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Article

Suzuki-Miyaura cross-coupling reaction catalyzed by a highly stable Pd(P-Phos)Cl_2 complex at room temperature under air

Yicen Ge, Yujing Cheng, Haiyan Fu #, Xueli Zheng, Ruixiang Li, Hua Chen *, Xianjun Li

Key Laboratory of Green Chemistry and Technology Ministry of Education; College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China

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ABSTRACT

A new Pd(P-Phos)Cl_2 complex was synthesized and characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and X-ray single crystal structure determination. The complex proved to be a highly stable and efficient catalyst for substrates with a wide range of functional groups in Suzuki-Miyaura cross-coupling reactions under air at room temperature. Low catalyst loadings were employed and turnover number of up to 49000 was obtained.

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1. Introduction

Palladium-catalyzed cross-coupling reactions have emerged as powerful tools for C–C bonds formation [1–3]. Among them, the Suzuki cross-coupling between aryl or vinyl halides with organoboron compounds [4,5] has many advantages over other cross-coupling reactions in terms of functional group tolerance, mild reaction conditions, and easy handling of by-products [6]. For these reasons, it has received much attention by researchers preparing biaryl compounds, and numerous reports have used it in synthetic organic chemistry and material science over the past two decades [7,8].

Recently, extensive efforts have been devoted to the development of highly active palladium catalysts to realize the coupling of challenging electrophiles, such as electron-rich aryl chlorides and sterically demanding substrates. Various kinds of ligands have been used to meet these ends, and the palladium complexes employing bulky and electron-rich monodentate phosphines have increased the activity of the reactions. Beginning in 1998, Fu's group [9,10] reported that catalysts formed in situ from either P(*t*Bu)$_3$ (**L1**) or PCy$_3$ (**L2**) (see Fig. 1) with [Pd_2(dba)$_3$] (dba = dibenzylideneacetone) furnished the target biaryls in good yields, even when catalyzing the reaction of non-activated 4-chlorotoluene. A breakthrough was made by Martin and coworkers [11] almost at the same time, as a family of dialkyl(*o*-biphenyl)phosphine ligands was developed that could conduct a variety of transformations, especially in Pd-catalyzed carbon-carbon bond forming processes. Later they found these catalytic systems employing SPhos (**L3**) and XPhos (**L4**) as supporting ligands to be remarkably efficient for the Suzuki cross-coupling of hindered unactivated aryl chlorides at elevated temperature [12,13]. Considering these strong σ-donor phosphine ligands to be toxic, *N*-heterocyclic carbenes such as IBiox [14] and IPr [15] were also employed as alternatives in the reactions of inactivated substrates with good yields under mild conditions. On the other hand, in a drive towards

* Corresponding author. Tel/Fax: +86-28-85412904; E-mail: scuhchen@163.com
# Corresponding author. Tel/Fax: +86-28-85412904; E-mail: scufhy@scu.edu.cn
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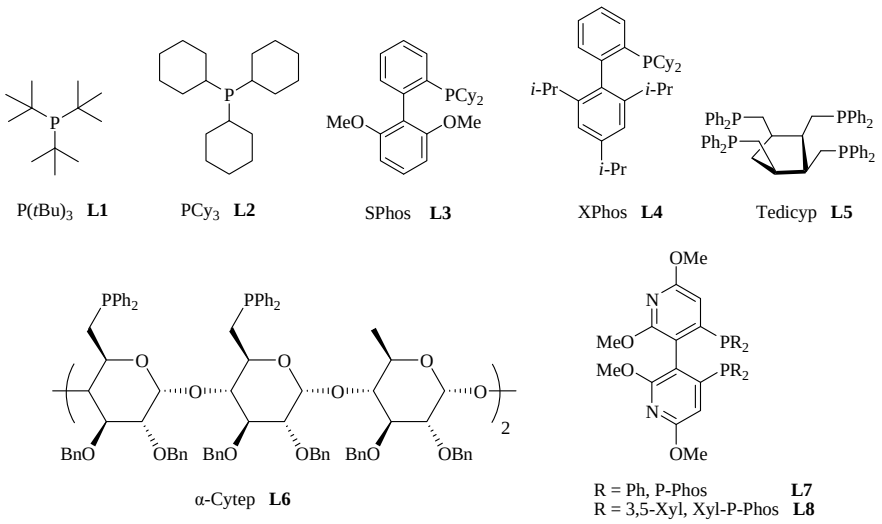


Fig. 1. Structure of several ligands employed in Suzuki reactions.

sustainable chemistry, Suzuki systems capable of ultra-low catalyst loadings were also being pursued. Some researchers [16–20] reported that the complex formed from Tedicyp (**L5**) and $[PdCl(C_3H_5)]_2$ was an extremely efficient catalyst for the Suzuki cross-coupling of aryl bromides, and the catalyst loading could be decreased to 1×10^{-7} mol% with high yields for a broad scope of substrates. More recently, a cyclodextrin-based tetraphosphine ligand α-Cytep (**L6**) was investigated by Zaborova et al. [21], which displayed high turnover numbers of up to 3.4×10^{11} at 120 °C. However, all of these effective but air-sensitive phosphine ligands have to be used under the protection of an inert gas and thus are inconvenient for handling and further application. Additionally, elevated temperatures and long reaction time are often required to obtain high TONs. In such a situation, the development of high efficient and robust catalysts for the Suzuki reaction under mild conditions (at room temperature and in air) is still highly desirable.

P-Phos (**L7**), 4,4'-bis(diphenylphosphino)-2,2',6,6'-tetramethoxy-3,3'-bipyridine, was a family of atropisomeric dipyridylphosphine ligands first introduced by Pai et al. in 2000 [22]. Since then, intensive studies have been focused on the utility of these chiral ligands, which have proved to be highly versatile and effective in tradition-metal-catalyzed asymmetric reactions including hydrogenation, hydrosilylation, and nucleophilic arylation [23]. In contrast, the application of P-Phos to cross-coupling reactions has been seldom reported possibly because of its poor σ-donor ability. Although it may cause slow oxidative addition of aryl halides to the palladium center, the electron-deficiency and sterically congested dipyridyl blocks renders the Pd complex of P-Phos to be resistant to oxidation [23,24]. Obviously, these features greatly favor catalyst stability. In 2009, our group first reported the use of P-Phos in the palladium-catalyzed Suzuki coupling of 3-pyridylboronic acids with aryl halides [24], which were otherwise challenging owing to the easy deboronation of the 3-pyridylboronic acids during the reaction [13, 25–27]. The cross-coupling reaction proceeded smoothly when catalyzed by 1 mol% $PdCl_2$ in the presence of 2 mol% P-Phos at 100 °C under a nitrogen atmosphere, which demonstrated the efficiency of P-Phos in catalyzing Suzuki reactions. Moreover, Chen et al. [28] also described a palladium-catalyzed Buchwald-Harttwig coupling reaction also employing *rac*-P-Phos as a ligand in the same year. Motivated by these results, we set out to further explore the application of P-Phos in C–C bonds formation. Herein we first report the Suzuki-Miyaura cross-coupling reaction efficiently catalyzed by Pd(P-Phos)Cl_2 under mild conditions. The amount of palladium catalyst is low (0.1–0.001 mol%), and the TONs can be improved up to 49000 under aerobic, ambient conditions.

2. Experimental

2.1. General

All solvents were obtained from commercial sources and used without further purification. The P-Phos (**L7**) was prepared according to published procedures [22]. All other chemicals were used as purchased. Gas chromatographic analyses were performed on an Agilent 6890N GC System equipped with a KB-1 Capillary GC column. The GC yields of the cross-coupling reactions were determined from normalized peak areas using an internal standard. ^1H, ^{13}C, and ^{31}P NMR spectra of P-Phos, Pd(P-Phos)Cl_2, and the coupling products were recorded on a Bruker AVANCE AV-Ⅱ 400MHz spectrometer. The chemical shifts of the ^1H and ^{13}C NMR are reported relative to tetramethylsilane (TMS) as an internal standard. The chemical shifts of ^{31}P NMR are reported relative to 85% H_3PO_4 as an external standard.

2.2. Preparation of complex *1*

Rac-4,4'-bis(diphenylphosphino)-2,2',6,6'-tetramethoxy-3,3'-bipyridine (*rac*-P-Phos **L9**) was synthesized according to Pai's procedure [22] and characterized by ^1H NMR and ^{31}P NMR, which were consistent with the reported values [24].

A mixture of 35.5 mg $PdCl_2$ (0.2 mmol) and 129.0 mg P-Phos (0.2 mmol) in 5 ml of methanol and 20 ml of dichloromethane

was stirred at room temperature under N_2 overnight until the $PdCl_2$ was fully dissolved and the reaction mixture became homogeneous. After the solvent was evaporated, a yellow solid was obtained in 97% yield (m.p. >250 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (br, 4H, PhH); 7.63–7.68 (m, 4H, PhH); 7.43–7.47 (m, 4H, PhH); 7.31–7.41 (m, 8H, PhH); 5.93 (d, J = 11.6 Hz, 2H, PyH); 3.67 (s, 6H, OCH_3); 3.63 (s, 6H, OCH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 160.72; 159.62; 143.22 (d, J = 45.3 Hz); 134.43; 133.91; 130.53 (d, J = 60.4 Hz); 127.26; 126.77; 121.40 (d, J = 55.3 Hz); 104.34; 52.49; 52.48. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 25.47 (s).

2.3. Crystal structure determination of complex **1**

A single crystal of **1** was obtained by recrystallization from $CDCl_3$ at 5 °C for 30 d. Intensity data of **1** were measured on a SuperNova-Eos X-ray diffractometer using graphite monochromated Mo K_α radiation (0.071070 nm) at 20 °C. Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensity was corrected for Lorentz and polarization effects and empirical absorption. The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Structure solution and refinement were performed with the SHELXL-97 package.

CCDC 933108 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from the Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif.

2.4. General procedure for the Suzuki-Miyaura cross-coupling reaction of aryl bromides with aryl boronic acids

A mixture of the aryl bromide (0.5 mmol), aryl boronic acid (0.75 mmol), KOH (1.0 mmol), complex **1** (0.1–0.01 mol%, dissolved in CH_2Cl_2), and EtOH (3 ml) was stirred vigorously at 25 °C under air. The reaction mixture was stirred for 6–24 h and then diluted with water and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate three times. The combined organic phase was dried with $MgSO_4$. After filtration, the remaining solvent was removed on a rotary evaporator. The product was isolated by silica gel column chromatography (*n*-hexane:ethyl acetate = 99:1) and dried overnight in vacuum. The ^{1}H NMR spectra of the purified products were identical to those previously reported in Refs. [29–34].

3. Results and discussion

3.1. The properties and molecular structure of complex **1**

^{31}P NMR experiments for P-Phos, P-Phos dioxide, and complex **1** were conducted to examine the catalyst stability. Their spectra are shown in Fig. 2. The ^{31}P peak of P-Phos shifts from −13.25 to 25.47 on complexation to Pd. The solution of complex **1** in CH_2Cl_2 was kept in aerobic conditions for over 100 d and the complex remained the same with no P-Phos or P-Phos dioxide being detected. This clearly demonstrates the high stability of Pd(P-Phos)Cl_2.

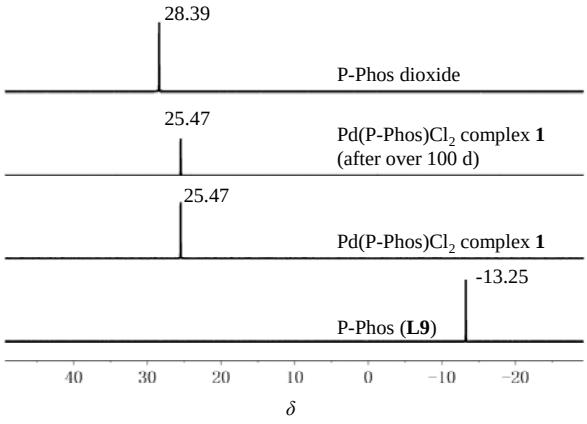


Fig. 2. ^{31}P NMR spectra of P-Phos, P-Phos dioxide, and complex **1**.

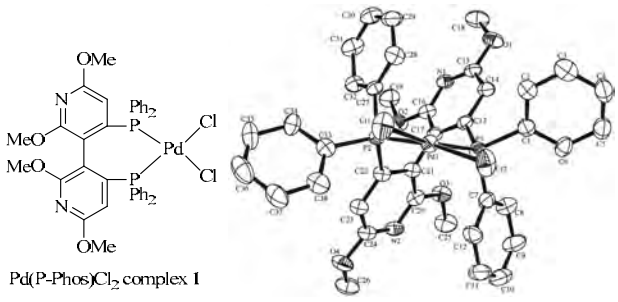


Fig. 3. The molecular structure and ORTEP representation of complex **1**. The hydrogen atoms have been omitted for clarity.

Because of the high stability, a single crystal of complex **1** was obtained from $CDCl_3$ in air by slow evaporation of the solvent, allowing for structural elucidation by X-ray single crystal analysis. The molecular structure is illustrated in Fig. 3. Crystal data are presented in Table 1. Selected bond lengths and angles are given in Table 2. The bond lengths and angles are all within the expected range, with a slightly distorted square-planar geometry (the dihedral angle between the plane of Cl(1)–Pd(1)–Cl(2) and the plane of P(1)–Pd(1)–P(2) is 12.32°) [35,36]. The Pd–Cl(1) and Pd–Cl(2) bond distances (0.2327(2) nm and 0.2340(2) nm, respectively) are similar.

3.2. The Suzuki-Miyaura cross-coupling reaction

In the previous report [29], 4-bromoanisole has been employed to evaluate the efficiency of a newly designed catalyst system because of the relatively low activity of arylbromides. Hence the Suzuki coupling of 4-bromoanisole with 1.5 equivalents of phenylboronic acid in the presence of 2 equivalents of base was chosen as a model reaction to test the catalytic activity of Pd(P-Phos)Cl_2. Various reaction parameters such as catalyst loading, solvent, and base were also investigated. Some selected results are summarized in Table 3. Initially, the reaction was carried out in methanol using 1.0 mol% Pd(P-Phos)Cl_2 as catalyst with the variation of base under nitrogen at 25 °C. As can be seen, potassium hydroxide proved to be the most effective base examined (Table 3, entries 1–4), giving an almost qualitative yield (> 99%). However, reducing the catalyst load-

Table 1
Crystallographic data and structure refinement for complex **1**.

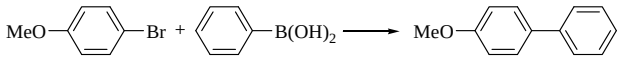
Compound	**1**
Empirical formula	$C_{38}H_{34}Cl_2N_2O_4P_2Pd$
Formula mass	821.91
Temperature (°C)	20
Crystal system	monoclinic
Space group	$P2_1/c$
a (nm)	1.13176(6)
b (nm)	1.50401(8)
c (nm)	3.07739(19)
α (°)	90.00
β (°)	105.653(5)
γ (°)	90.00
Cell volume (nm^3)	5.0440(5)
Z/calculated density (g/cm^3)	4/1.082
Absorption coefficient (mm^{-1})	0.568
F (000)	1672.0
Crystal size (mm × mm × mm)	0.30 × 0.20 × 0.20
2θ range for data collection (°)	5.76–52.74
Limiting index	$-14 \le h \le 14$, $-18 \le k \le 18$, $-38 \le l \le 38$
Reflection collected	49826
Independent reflection	10297 (R_{int} = 0.1073)
Data/restraint/parameter	10297/0/446
Goodness-of-fit on F^2	1.047
Final R index [$I > 2\sigma(I)$]	R_1 = 0.1014, wR_2 = 0.2778
Final R index (all data)	R_1 = 0.1201, wR_2 = 0.2946
Largest difference peak and hole (e/nm)	14.4 and −8.5

Table 2
Selected bond lengths (nm) and angles (°) for complex **1**.

Pd(1)–Cl(1)	0.2327(2)	Pd(1)–Cl(2)	0.2340(2)
Pd(1)–P(1)	0.22621(17)	Pd(1)–P(2)	0.22678(16)
P(1)–C(1)	0.1824(7)	P(1)–C(7)	0.1790(8)
P(1)–C(13)	0.1820(7)	P(2)–C(22)	0.1830(6)
P(2)–C(27)	0.1808(6)	P(2)–C(33)	0.1796(7)
Cl(1)–Pd(1)–Cl(2)	89.10(9)	P(1)–Pd(1)–Cl(1)	170.13(8)
P(1)–Pd(1)–Cl(2)	87.18(8)	P(1)–Pd(1)–P(2)	94.47(6)
P(2)–Pd(1)–Cl(1)	90.63(7)	P(2)–Pd(1)–Cl(2)	170.94(8)

ing to 0.1 mol% significantly decreased the yield to 56% (Table 3, entry 5). Switching the solvent from methanol to ethanol returned the yields to 99% (Table 3, entry 6), which might be attributed to the better solubility of the catalyst in ethanol. However, an attempt to use alcohols with longer alkyl chains failed to give a satisfactory yield, in contrast to our previous report on the Suzuki reaction of 3-pyridylboronic acid [24]. Here *n*-propanol and *n*-butanol only gave yields of 21% and 11%, respectively (Table 3, entries 7 and 8). The loss of activity is possibly related to their weaker reductivity in the presence of strong bases when compared with ethanol. Further investigations showed that neither less polar solvents (e.g. 1,2-dimethoxylethane and toluene) nor more polar ones (e.g. water) were suitable for this reaction (Table 3, entries 9–11). To clarify the function of P-Phos, a control experiment was conducted using 0.1 mol% of $PdCl_2$ as catalyst in ethanol with KOH at room temperature. Only a 44% yield was obtained, which clearly demonstrated that the coordination of P-Phos improves the activity of the catalytic system (Table 3, entry 12). As complex **1** appeared to be air-stable, we tried the reaction in aerobic conditions at 25 °C with 0.01 mol% Pd(P-Phos)Cl_2. To

Table 3
Optimizing the reaction conditions for Suzuki-Miyaura cross-coupling of 4-bromoanisole with phenylboronic acid using Pd(P-Phos)Cl_2 complex **1** as catalyst.



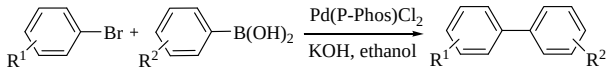
Entry	Catalyst loading (mol%)	Solvent	Base	Yield [a] (%)
1	1.0	MeOH	KOH	>99
2	1.0	MeOH	K_3PO_4	82
3	1.0	MeOH	Na_2CO_3	93
4	1.0	MeOH	CsF	77
5	0.1	MeOH	KOH	56
6	0.1	EtOH	KOH	99
7	0.1	*n*-PrOH	KOH	21
8	0.1	*n*-BuOH	KOH	11
9	0.1	DME	KOH	16
10	0.1	toluene	KOH	43
11	0.1	H_2O	KOH	40
12 [b]	0.1	EtOH	KOH	44
13	0.01	EtOH	KOH	93
14 [c]	0.01	EtOH	KOH	91

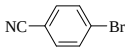
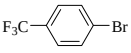
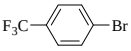
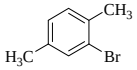
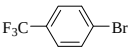
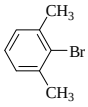
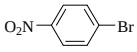
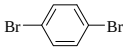
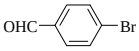
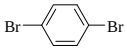
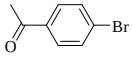
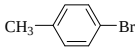
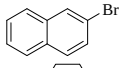
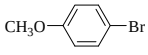
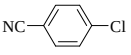
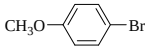
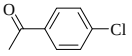
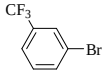
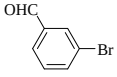
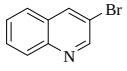
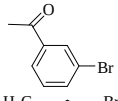
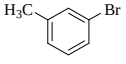
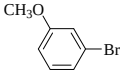
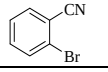
Reaction conditions: 4-bromoanisole 0.5 mmol, phenylboronic acid 0.75 mmol, base 1 mmol, solvent 3 ml, N_2 ([c] air) atmosphere, 24 h, 25 °C.
[a] GC yield.
[b] $PdCl_2$ was used as catalyst instead of Pd(P-Phos)Cl_2.

our delight, almost no loss in yield was observed compared with the system under N_2 (Table 3, entries 13 and 14). To explore this easy-handling protocol, the standard conditions were established for all following experiments, with Pd(P-Phos)Cl_2 as the catalyst and KOH as the base, in ethanol at 25 °C under air. To the best of our knowledge, this was the first report of this use of Pd(P-Phos)Cl_2.

Using the optimized conditions, we then examined the scope and limitations of this catalytic system. Various substrates were tested and the results are summarized in Table 4. First, phenyl bromide and *para*-substituted aryl bromides were studied as the Suzuki coupling partner with phenylboric acid (Table 4, entries 1–6). For these electron-neutral or deficient aryl bromides, a catalyst loading as low as 0.01 mol% was employed because of the facile oxidative addition of such substrates. After 24 h, isolated yields of at least 93% were achieved for all of these active substrates. Even the electron-rich 4-bromotoluene and 4-bromoanisole could be converted to the corresponding products, in 91% and 84% yields, respectively (Table 4, entries 7 and 8). When the catalyst loading was increased to 0.1 mol% in the reaction of 4-bromoanisole (Table 4, entry 8), the yield improved to 93% over much shorter time (6 h). With the catalyst loading of 0.1–0.01 mol%, both *meta*- and *ortho*-substituted aryl bromides reacted smoothly at 25 °C (Table 4, entries 9–17). Higher catalyst loading and reduced reaction time were used for active but air- or light-sensitive substrates (Table 4, entries 10 and 11). Various aryl bromides, regardless of the electronic donating groups at *meta*- or *ortho*- positions, provided the corresponding biaryl products in 91%–99% yields over 6 h. Several dimethyl substituted phenyl bromides were also investigated. An obvious steric hindrance effect was observed for the most demanding substrates, like 2-bromo-1,3-dimethylbenzene (Table 4, entry 19), which only

Table 4
Suzuki-Miyaura cross-coupling reactions of aryl bromides with arylboronic acids catalyzed by Pd(P-Phos)Cl_2.



Entry	Aryl bromide	Catalyst loading (mol%)	Time (h)	Yield [a] (%)	Entry	Aryl bromide	Catalyst loading (mol%)	Time (h)	Yield [a] (%)
1		0.01	24	94	15		0.1	6	93
2		0.01	12	>99	16		0.01	24	87
3		0.01	24	93	17		0.1	6	98
		0.001	240	49	18		0.1	6	94
		0.0001	240	3 [b]	19		0.1	24	51
4		0.01	12	>99	20		0.01	24	66(32) [c]
5		0.1	6	>99			0.01	24	64 [d]
6		0.01	24	98	21		0.1	6	92
7		0.01	24	91	22		0.1	6	95
8		0. 1	6	93	23		1	24	6 [b]
		0.01	24	84	24		1	24	9 [b]
9		0.01	24	93	25		0.1	24	71
10		0.1	6	>99	26		0.1	24	92
11		0.1	6	91	27 [e]		0.1	0.5	99
12		0. 1	6	97	28 [f]		0.1	48	8 [b]
13		0.01	24	92	29 [g]		0.1	6	48
14		0.1	6	99					

Reaction conditions: aryl bromide 0.5 mmol, phenylboronic acid ([e] 4-methoxylphenylboronic acid, [f] 3-nitrophenylboronic acid, [g] 1-naphthalenylboronic acid) 0.75 mmol ([d] 1.5 mmol (3.0 equiv.)), KOH 1 mmol, EtOH 3 ml, air, 25 °C.
[a] Isolated yield. [b] GC yield. [c] Products of mono-arylation were examined with the yield given in parenthesis.

gave a poor yield of 51%. This might be caused by the difficult intermolecular approach causing both the oxidative addition and transmetalation steps to be sluggish [4]. On the contrary, 2-bromo-1,4-dimethylbenzene (Table 4, entry 18) remained active and afforded product in 94% yield in just 6 h. These results indicated that only with the presence of two groups at both positions *ortho* to the bromine atom the steric factor have an obvious effect. In the case of 1,4-dibromobenzene as substrate, the diarylation product was obtained in a moderate yield (66%), which was not improved even with additional boronic acids present (Table 4, entry 20). The aromatic bromides of 1- or 2-bromonaphthalenes were also reacted with phenylboronic acid, giving the target compounds in yields of 92% and 95%, respectively (Table 4, entries 21 and 22).

Subsequently, the electron-deficient aryl chlorides 4-chlorobenzonitile and 4-chloro-acetophenone were tried in this process. Unfortunately, GC yields less than 10% were detected and considerable amounts of biphenyl as the ho-

mo-coupling product of phenylboronic acid were observed (Table 4, entries 23 and 24). As the aryl-heteroaryl bonds are common in drugs and fungicides [37,38], we used some common *N*-heteroaryl bromides, such as 3-bromopyridine and 3-bromoquinoline, as the coupling partner. The desired aryl-heteroaryl products were isolated in 71% and 92% yields, respectively (Table 4, entries 25 and 26). Finally, the scope of the arylboronic acids was also investigated. As shown, electron-deficient and sterically hindered boronic acids led to a significant decrease in yields even with prolonged reaction time (Table 4, entries 28 and 29), while the electron-rich 4-methoxyphenylboronic acid could be quantitatively converted to the target coupling product in only 0.5 h (Table 4, entries 27).

To further explore the stability of the catalyst Pd(P-Phos)Cl_2, catalyst loading as low as 0.001 mol% was used to couple 1-bromo-4-(trifluoromethyl)benzene with phenylboronic acid. We were delighted to obtain the desired coupling product in 49% yield after 240 h. This gives a TON value of 49000, indicating that the complex Pd(P-Phos)Cl_2 is a very stable and long-lived catalyst when exposed to both air and moisture [16–21].

4. Conclusions

We have reported an easy-to-handle system for the Suzuki-Miyaura coupling reaction using a new Pd(P-Phos)Cl_2 complex as catalyst. The air and moisture stability of Pd(P-Phos)Cl_2 enabled the reaction to be carried out at room temperature in air. A wide range of substrates could be coupled with arylboronic acids to afford the desired products in moderate to good yields. A TON of 49000 revealed that this complex is a very stable and robust catalyst even when exposed to air and moisture. This study will be helpful for the development of new stable and effective catalytic systems for Pd-catalyzed cross-coupling reactions.

Acknowledgments

We are grateful to the Analytical and Testing Center of Sichuan University for providing support with the characterization of compounds.

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Graphical Abstract

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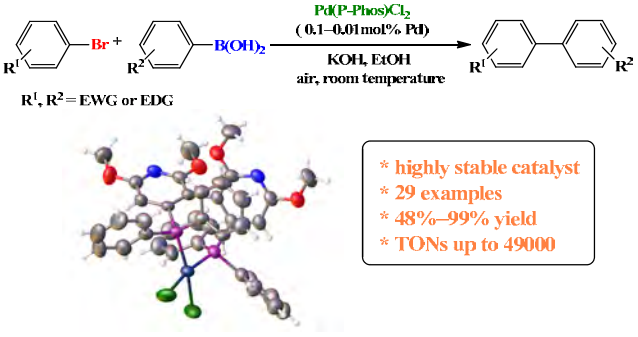
Suzuki-Miyaura cross-coupling reaction catalyzed by a highly stable Pd(P-Phos)Cl_2 complex at room remperature under air

Yicen Ge, Yujing Cheng, Haiyan Fu *, Xueli Zheng, Ruixiang Li, Hua Chen *, Xianjun Li
Sichuan University



A new Pd(P-Phos)Cl_2 complex has been synthesized and characterized. The complex catalyzed the Suzuki-Miyaura cross-coupling reactions of various aryl halide and arylboronic acids in medium to excellent yields under air at room temperature.

Commun, 2013, 49: 312
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室温有氧条件下高稳定性Pd(P-Phos)Cl_2配合物催化Suzuki-Miyaura交叉偶联反应

葛轶岑, 程雨晶, 付海燕*, 郑学丽, 李瑞祥, 陈 华#, 李贤均
四川大学化学学院教育部绿色化学重点实验室, 四川成都610064

摘要: 制备了新型Pd(P-Phos)Cl_2配合物, 并通过^{1}H, ^{13}C和^{31}P核磁共振及X射线单晶衍射对其结构进行了确认及表征. 结果表明, 该配合物是室温有氧条件下Suzuki-Miyaura交叉偶联反应的高稳定高效催化剂, 并具有广泛的底物适用性. 催化剂用量较低, 且转化数(TON)最高可达49000.

关键词: 钯配合物; 联吡啶双膦配体P-Phos; Suzuki-Miyaura交叉偶联反应; 室温; 空气

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*通讯联系人. 电话/传真: (028)85412904; 电子信箱: scuhchen@163.com
#通讯联系人. 电话/传真: (028)85412904; 电子信箱: scufhy@scu.edu.cn
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