

Palladium-catalyzed cross-coupling of trimethoxysilylbenzene with aryl bromides and chlorides using phosphite ligands

Jinhun Ju,^a Hyungoog Nam,^a Hyun Min Jung^b and Sunwoo Lee^{a,*}

^aDepartment of Chemistry, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500-757, Republic of Korea

^bAdvanced Materials Division, Korea Research Institute of Chemical Technology, 100 Jang-dong, Yuseong-gu, Daejeon 305-600, Republic of Korea

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Abstract—Phosphites were employed as ligands in palladium-catalyzed Hiyama coupling reactions. The optimized reaction conditions were equimolar amounts (5 mol % each) of Pd(acac)₂ and phosphite **1** in *p*-xylene at 80 °C with TBAF as an additive. This catalyst system exhibited high activities in the reactions with trimethoxysilylbenzene and aryl bromides that have electron-donating or electron-withdrawing groups. In the case of aryl chlorides, substrates possessing electron-withdrawing groups gave the coupled products in high yields.

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Palladium-catalyzed carbon–carbon bond formation reactions are useful tools to construct molecules such as materials and drugs in modern chemistry.¹ In particular, for the formation of sp² carbon and sp² carbon bonds, several types of cross-coupling reactions have been developed based on the transmetallations of a variety of hard or soft organometallic nucleophiles such as the Kumada,² Negishi,³ Stille,⁴ Suzuki,⁵ Hiyama,⁶ Sonogashira,⁷ and other related couplings.^{8,9} Among them, the Suzuki and the Stille reactions are the most studied and utilized. However, they have several disadvantages for practical organic synthesis. Stille coupling requires a large excess of a toxic tin reagent and the removal of the tin byproduct. By using boronic acids, the Suzuki reaction allows the problems which stem from the reagent toxicity to be solved, but boronic acids are difficult to synthesize and purify.¹⁰ Therefore, Hiyama coupling reactions using organosilicon reagents have been developed and utilized in organic synthesis. The organosilicon reagents used as reactants in Hiyama reactions are available at low cost or are very easily prepared, nontoxic, and are very stable to other functionalities and to the reaction conditions.

In palladium-catalyzed coupling reactions, in order to accomplish cross-coupling with a high efficiency, most studies have focused on the development of suitable ligands, for example, sterically bulky alkyl phosphines^{4c,5c,d,8f–h,9d,f,g,i} or carbene-type ligands.^{5e,9d,e} Recently, there have been several reports on the extension of these methods to aryl chlorides, which are the most challenging substrates.^{1b,4c,5c–e,8f,h,9d,g} However, alkyl phosphine ligands have a drawback from the viewpoint of their practical application. They are sensitive to oxygen and moisture, and so they require an inert environment.^{4c,5d} In addition, most of these ligands are not commercially available, and of those that are, many are quite expensive. Although carbene-type ligands are more stable than alkyl phosphines, they must be synthesized through multi-steps.^{5c}

In contrast to the well-developed phosphine ligands, phosphite ligands have received relatively little attention, despite the fact that phosphites have an advantage in terms of their stability towards air and moisture. There have been a few examples of the use of phosphites as ligands in Hiyama cross-coupling reactions.^{6h,p} On the other hand, phosphites have been more widely used as anti-oxidants in polymer chemistry than as ligands in transition metal-catalyzed chemistry.¹¹ They are commercially available, very inexpensive and very stable. Therefore, our attention was drawn to those of them, which have sterically hindered groups (Fig. 1), so that

Keywords: Palladium; Phosphite; Organosilicon; Hiyama coupling; Aryl bromides; Aryl chlorides.

* Corresponding author. Tel.: +82 62 530 3385; fax: +82 62 530 3389; e-mail: sunwoo@chonnam.ac.kr

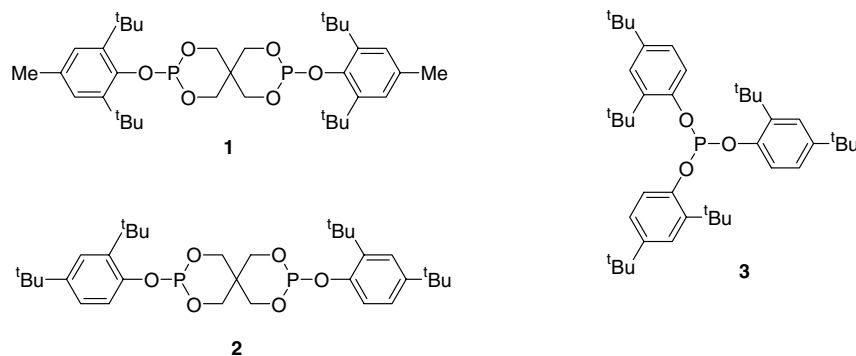


Figure 1. Phosphite ligands.

they can be employed as ligands. Herein, we report on the subject of Hiyama cross-coupling reactions using phosphite ligands.

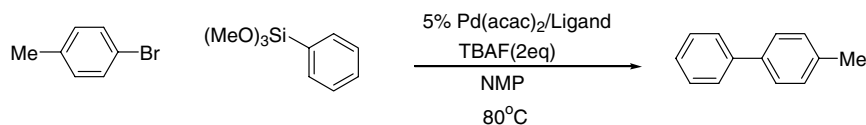
In order to investigate the activity of the ligands in Hiyama reactions, we first carried out the coupling reactions of 4-bromotoluene and trimethoxysilylbenzene in the presence of a palladium catalyst with a variety of phosphite and phosphine ligands. Considering the availability of the many kinds of silane compounds, we chose aryltrialkoxysilane.^{6d–n} The phosphite ligands were purchased from Adeka and used without further purification.¹² Table 1 summarizes our results from the screening of the ligands. Among the phosphite ligands examined, phosphite **1** was found to be the best, giving the desired product in a 68% yield (entry 1). However, phosphite **3**, which has shown good activities in several palladium-catalyzed coupling reactions, gave a lower yield than phosphite **1** (entry 3).¹³ Arylphosphine ligands including chelating type ones gave yields of less than 60% yield, and the yield of the coupled product was found to decrease with increasing steric hindrance of the ligand. DeShong and co-workers reported similar results.^{6d}

These results encouraged us to further optimize the reaction conditions in the presence of phosphite **1** by using different solvents and palladium sources as well as changing the ratio of ligand to palladium. As can be

seen from Table 2, the use of *p*-xylene as a solvent in the place of NMP led to a dramatically increased yield of the coupled product (entry 5). Other kinds of solvent, such as DMF, 1,4-dioxane and toluene, were not suitable for the coupling reactions. The reactions using phosphites **2** and **3** in *p*-xylene instead of NMP resulted in yields of 82% and 75%, respectively (entries 6 and 7). Among the palladium sources tested, Pd(acac)₂ was the best. When Pd(OAc)₂ or [PdCl(allyl)]₂ were used, the coupled product was obtained in a very low yield (entries 8 and 9). Pd₂(dba)₃ and Pd(CH₃CN)₂Cl₂ showed moderate yields (entries 10 and 11). These results implied that the oxidation state of the palladium source was not the key factor in the reactions. The most suitable palladium/ligand molar ratio was 1:1, even though phosphite **1** has two phosphorus atoms (entries 12 and 13). When the amount of catalyst used was less than 1 mol %, very low yields of the cross-coupled adducts were obtained (entries 16 and 17). In addition, the use of TBACl, TBABr or CsF to replace TBAF as an additive resulted in no coupled product being obtained (entries 20–22). However, the use of an aqueous solution of NaOH afforded the coupled product with a 76% yield (entry 23). Masuda and co-workers reportedly used the system of NaOH and phosphite, P(O*i*Pr)₃, in Hiyama coupling reactions.^{6h}

We compared the reaction rates of phosphite ligands **1**, **2** and **3** in the Hiyama cross-coupling reactions.

Table 1. Screening of ligands for the reaction of 4-bromotoluene and trimethoxysilylbenzene^a



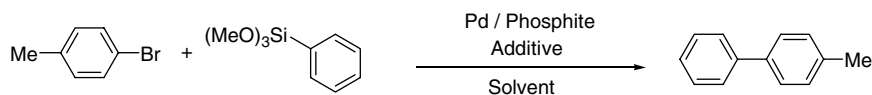
Entry	Ligand	Yield ^b (%)	Entry	Ligand	Yield ^b (%)
1	1	68	5	dppe ^d	48
2	2	57	6	PPh ₃	60
3	3	59	7	P(<i>o</i> -tol) ₃	55
4	dppe ^c	55	8	P(Mes) ₃	43

^a Reaction conditions: 1.0 mmol aryl halide, 1.2 mmol PhSi(OMe)₃, 3.0 ml solvent.

^b The yield was determined by GC by comparison to an internal standard (naphthalene).

^c 1,1'-Bis(diphenylphosphino)ferrocene.

^d 1,2-Bis(diphenylphosphino)ethane.

Table 2. Optimization of conditions for Hiyama coupling of 4-bromotoluene and trimethoxysilylbenzene^a

Entry	Palladium	Pd (mol %)	L	Pd/L	Solvent	Additive	Temperature (°C)	Time (h)	Yield ^b (%)
1	Pd(acac) ₂	5	1	1/1	NMP	TBAF	80	4	68
2	Pd(acac) ₂	5	1	1/1	DMF	TBAF	80	4	70
3	Pd(acac) ₂	5	1	1/1	Dioxane	TBAF	80	4	76
4	Pd(acac) ₂	5	1	1/1	Toluene	TBAF	80	4	76
5	Pd(acac) ₂	5	1	1/1	<i>p</i> -Xylene	TBAF	80	4	99
6	Pd(acac) ₂	5	2	1/1	<i>p</i> -Xylene	TBAF	80	4	82
7	Pd(acac) ₂	5	3	1/1	<i>p</i> -Xylene	TBAF	80	4	75
8	Pd(OAc) ₂	5	1	1/1	<i>p</i> -Xylene	TBAF	80	4	11
9	[PdCl(allyl)] ₂	5	1	1/1	<i>p</i> -Xylene	TBAF	80	4	10
10	Pd ₂ (dba) ₃	5	1	1/1	<i>p</i> -Xylene	TBAF	80	4	63
11	Pd(CH ₃ CN) ₂ Cl ₂	5	1	1/1	<i>p</i> -Xylene	TBAF	80	4	65
12	Pd(acac) ₂	5	1	1/0.5	<i>p</i> -Xylene	TBAF	80	4	85
13	Pd(acac) ₂	5	1	1/2	<i>p</i> -Xylene	TBAF	80	4	56
14	Pd(acac) ₂	2.5	1	1/1	<i>p</i> -Xylene	TBAF	80	6	95
15	Pd(acac) ₂	1	1	1/1	<i>p</i> -Xylene	TBAF	80	8	60
16	Pd(acac) ₂	0.1	1	1/1	<i>p</i> -Xylene	TBAF	140	12	8
17	Pd(acac) ₂	0.01	1	1/1	<i>p</i> -Xylene	TBAF	140	12	<1
18	Pd(acac) ₂	5	2	1/1	<i>p</i> -Xylene	TBAF	80	4	85
19	Pd(acac) ₂	5	3	1/1	<i>p</i> -Xylene	TBAF	80	4	75
20	Pd(acac) ₂	5	1	1/1	<i>p</i> -Xylene	TBACl	80	8	NR ^c
21	Pd(acac) ₂	5	1	1/1	<i>p</i> -Xylene	TBABr	80	8	NR ^c
22	Pd(acac) ₂	5	1	1/1	<i>p</i> -Xylene	CsF	80	8	NR ^c
23	Pd(CH ₃ CN) ₂ Cl ₂	5	1	1/1	Dioxane	NaOH	80	8	76

^a Reaction conditions: 1.0 mmol aryl halide, 1.2 mmol PhSi(OMe)₃, 3.0 ml solvent.

^b The yield was determined by GC by a comparison to an internal standard (naphthalene).

^c No reaction: only starting materials were appeared in GC.

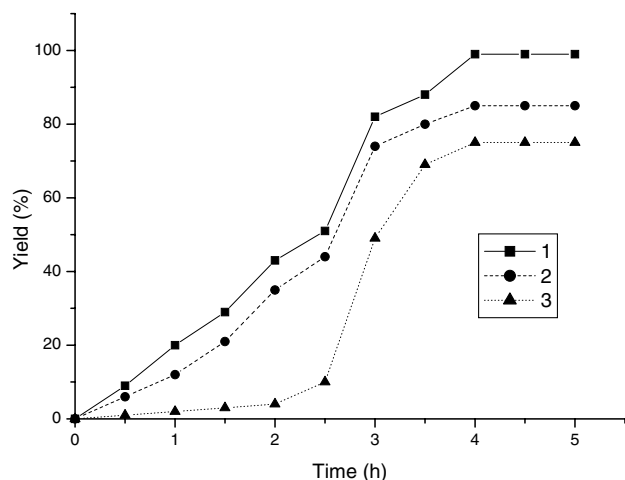


Figure 2. Reaction profile for the Hiyama cross-coupling reaction of 4-bromotoluene and trimethoxysilylbenzene using ligand **1** (■), **2** (●) and **3** (▲).

As shown in Figure 2, ligand **1** afforded the coupled product with an almost quantitative yield within 4 h. Comparable catalytic activity could also be obtained with ligand **2**, although the yield did not exceed 90% even after 8 h. Ligand **3** required an induction period and showed only 10% yield even

after 2.5 h. The maximum yield obtained with this ligand was 75%.

On the basis of these results, we next investigated the scope of the Hiyama coupling reactions using phosphite **1** as the ligand for a series of aryl bromides and chlorides possessing different steric and electronic properties. These studies showed that equimolar amounts of Pd(acac)₂ and phosphite **1** (5 mol % each) in *p*-xylene at 80 °C with TBAF as an additive formed the coupled compound in a high yield in less than 4 h.

As shown in Table 3, the coupling reaction is tolerant of functional groups in the case of aryl bromides. The reactions with both electron-withdrawing and electron-donating substituents gave the desired biaryl products in moderate to excellent yields. Bromobenzene and aryl bromides having alkyl substituents at the *para* position showed almost quantitative yields (entries 1–3). Bromonaphthalene and aryl bromides with amino substituents at the *para* position also gave the corresponding cross-coupled products in excellent yields (entries 4 and 5). The substrates with *ortho* mono substituents also cross-coupled to afford the desired biaryls in high yields (entry 6). However, the more hindered 2-phenylbromobenzene and 2,4,6-trimethylbromobenzene coupled to give the corresponding biaryls in low yield (entries 7 and 8). 3-Methoxy, 4-methoxy, 4-nitro substituted aryl

Table 3. Hiyama cross-coupling reactions with arylbromides and trimethoxysilylbenzene by catalyst **1**^a

Entry	ArBr	Conversion (%)	Yield ^b (%)	Entry	ArBr	Conversion (%)	Yield ^b (%)
1		100	98	9		100	70
2		100	99	10		100	77
3		100	98	11		100	83
4		100	95	12		100	87
5		100	98	13		100	93
6		97	95	14		66	35
7		43	32	15		38	11
8		15	9	16		32	25

^a Reaction conditions: 1.0 equiv of aryl halide, 1.2 equiv of PhSi(OMe)₃, 5 mol % **1**, 5 mol % Pd(acac)₂, 2.0 equiv of TBAF, *p*-xylene (0.3 M).

^b The isolated yields of compounds are an average of at least two runs. All compounds are characterized by comparison of ¹H and ¹³C NMR spectra with authentic samples or literature data.

bromides reacted to give the products in moderate yields (entries 9–11). Carbonyl group substituted aryl bromides showed good yields (entries 12 and 13). We found that this catalyst/ligand system was not suitable for the coupling of heteroaryl halide such as bromopyridines and bromothiophenes. 2-Bromopyridine gave the coupled product in a 35% yield and 3-bromopyridine showed a yield of 11%. 2-Bromothiophene also gave a yield of 25% (entries 14–16). Their yields were little improved when the reactions were carried out at 120 °C.

Encouraged by the above success, we extended our work to aryl chlorides, which are more challenging substrates. However, as shown in Table 4, 4-chloro acetophenone and 4-chlorophenyl acetic acid coupled to afford the corresponding biaryl products in good yields (entries 1 and 4). As in the case of the arylbromides, Pd(acac)₂ was the best palladium source. Low yields were observed with aryl chlorides having electron neutral substituents or

electron-donating ones (entries 5–7). There were only a few examples that moderate yields were observed with aryl chlorides and aryltrialkoxysilanes in the Hiyama cross-coupling reactions.^{6f,j,n}

In conclusion, we showed that phosphite ligand **1** coordinated catalyst exhibited the highest activities in the palladium-catalyzed Hiyama coupling reactions. To the best of our knowledge, phosphite **1** has never before been used as a ligand in palladium-catalyzed cross-coupling reactions. This is the first example in which phosphite **1** is used as a ligand. We found that the palladium source, solvent and additive are also important to obtain the coupled products in high yields. This catalytic system can be used without resorting to dry reagents or anaerobic conditions. In addition, considering the very low cost of arylphosphites as ligands and the stability of arylsiloxanes as substrates, this method should be of a great value as a convenient route to functionalized unsymmetrical biaryl compounds.

Table 4. Hiyama cross-coupling reactions with arylchlorides and trimethoxysilylbenzene by catalyst **1**^a

Entry	ArCl	Conversion (%)	Yield ^c (%)	Entry	ArCl	Conversion (%)	Yield ^c (%)
1		100	93	5		35	27
2 ^a		42	32	6		34	25
3 ^b		11	7				
4		100	78	7		18	15

^a Pd₂(dba)₃.^b Pd(OAc)₂.^c The isolated yields of compounds are an average of at least two runs. All compounds are characterized by comparison of ¹H and ¹³C NMR spectra with authentic samples or literature data.

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