Palladium/Phosphite Catalyst Systems for Efficient Cross Coupling of Aryl Bromides and Chlorides with Phenylboronic Acid**

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Dedicated to Professor Wilhelm Keim (RWTH Aachen) on the occasion of his 65th birthday

Abstract: The Suzuki reaction of aryl bromides is efficiently catalyzed by palladium/phosphite complexes generated in situ. The influence of ligand, base, and different additives is examined. The process tolerates various functional groups and catalyst turnover numbers up to 820000 are obtained even with deactivated aryl bromides. For the first time it is shown that palladium/phosphite complexes also catalyze efficiently the Suzuki reaction of aryl chlorides.

Keywords: aryl chlorides · homogeneous catalysis · palladium · phosphite ligands · Suzuki reaction

Introduction

Biaryls are important building blocks for the synthesis of numerous pharmaceutically active compounds[1] and herbicides.[2] In addition, biaryl compounds are applied as chiral ligands,[3] liquid crystals,[4] and organic electric wires.[5] Among the various methods known to synthesize substituted biaryls, probably the most powerful method for the construction of an unsymmetrical biaryl axis is through palladium-catalyzed coupling reaction of arylboronic acid derivatives with aryl halides (Suzuki reaction).[6] So far, mostly aryl bromides, iodides, and triflates have been used as starting materials for Suzuki reactions. Due to the industrial interest in the functionalization of economically attractive aryl chlorides[7] there is currently a great deal of interest in the coupling of aryl chlorides with arylboronic acids. While Indolese[8] and Saito et al.[9] demonstrated that nickel catalysts are useful for this purpose, most studies focussed on palladium catalysts. After initial work by us,[10] and others,[11] Fu,[12] Buchwald,[13] and Nolan[14] recently developed significant breakthroughs in this area. However, all palladium catalysts known to date for the Suzuki reaction of neutral or non-activated chloroarenes make use of significant amounts of expensive basic phosphine ligands or carbenes. Simple palladium/triarylphosphine complexes can only by applied for coupling of arylboronic acids with *heteroaryl* chlorides due to the higher reactivity of the latter.[15]

As a result of our efforts on activation of C–Cl bonds we discovered that phosphites in combination with palladium(II) acetate form productive catalysts for Heck reaction of aryl bromides and electron deficient aryl chlorides.[16] This finding is contrary to the general belief that electron rich ligands are necessary to generate highly nucleophilic palladium(0) species for insertion into C–Cl bonds. Parallel to our investigations[17] Bedford et al. reported the first Suzuki reactions of aryl bromides in the presence of phosphite ligands.[18] Here, the orthopalladated complex from tris(2,4-di-*tert*-butylphenyl)-phosphite and palladium(II) acetate gave high yields and turnover numbers using activated bromoarenes (e. g. 4-bromoacetophenone) but lower with 4-bromoanisole. The conversion of chloroarenes was not described.

In this full paper we describe for the first time phosphites as a class of ligands for Suzuki reactions of various aryl chlorides. In addition, an industrially feasible solution for the Suzuki reaction of aryl bromides is shown.

Results and Discussion

Based on our recent success with palladium(II)acetate and tris(2,4-di-*tert*-butylphenyl)phosphite as catalyst system in Heck reactions of aryl chlorides, we employed a similar protocol for the Suzuki coupling of 4-trifluoromethylchlorobenzene and phenylboronic acid (Scheme 1). In early experiments toluene was chosen as solvent and sodium carbonate as base.

In the absence of phosphite we observed little or no coupling products. Without any co-catalyst 52% of 4-tri-

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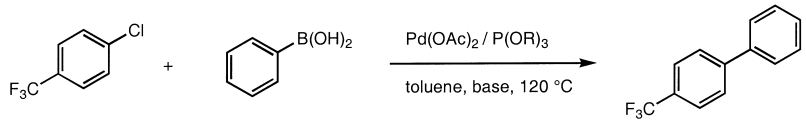


Scheme 1. Suzuki coupling of 4-trifluoromethylchlorobenzene and phenylboronic acid.

fluoromethyl biphenyl is obtained after 18 h at 120 °C (Table 1, entry 1). The addition of tetra-*n*-butylammonium bromide which is known to activate palladium(0) for oxidative addition by formation of at-complexes led to a significant drop in yield of the desired product (12%). In order to accelerate the transmetallation of the phenyl group to palladium the addition of nucleophiles which might form borate complexes was investigated (Table 1). The addition of

Table 1. Effect of various additives on the coupling reaction of 4-trifluoromethylchlorobenzene and phenylboronic acid.[a]

Entry	Additive (mol-%)	Yield [%][b]
1	–	52
2	Bu_4NBr (20)	12
3	CsF (1)	58
4	$Bu_4NF \cdot 3H_2O$ (10)	56
5	CaF_2 (10)	77
6	EtOH (10)	60
7	H_2O (50)	70

[a] 8.2 mmol 4-Trifluoromethylchlorobenzene, 9 mmol phenylboronic acid, 10 mmol sodium carbonate, 1 mol-% palladium(II) acetate, 10 mol-% tris(2,4-di-*tert*-butylphenyl)phosphite, 8 mL toluene, 120 °C, 18 h. [b] Determined by GC with hexadecane as internal standard.

fluoride salts has a reproducible beneficial effect on the yield of 4-trifluoromethyl biphenyl (entries 3–5). Interestingly, cesium fluoride has a small positive effect only if applied in small quantities. If it is used in stoichiometric amount the yield of desired product is lowered to 44%. To our surprise, calcium fluoride was the best promoter under the investigated reaction conditions. Here, 77% of 4-trifluoromethyl biphenyl is formed upon addition (10 mol-%) of this almost insoluble source of fluoride. The addition of catalytic amounts of ethanol or water also leads to improved product yields (60 and 70%, respectively; Table 1, entries 6–7). We suggest that ethoxide and hydroxide ions, which are generated to some extent in the presence of sodium carbonate activate phenylboronic acid for the transmetallation reaction.

From previous studies[6] it is known that the base is of significant importance for the rate and yield of Suzuki couplings. In contrast to most Suzuki couplings only a slight excess (1.2 equiv) of base is used throughout our study. We were pleased to find that NaOH which is the most attractive base for larger scale applications gives the best results (71%). Among the bases listed in Table 2, K_3PO_4 and Na_2CO_3 led to slightly lower yields (61 and 52%, respectively). Interestingly, the reaction using Cs_2CO_3 produced 4-trifluoromethyl biphenyl in 26% yield, albeit Cs_2CO_3 was superior to other bases in the presence of basic phosphine ligands.[15] Weak bases such as NaOAc or Et_3N are not efficient. Regarding the influence of the base it is clear that not only basicity but also solubility of the base is crucial for the success of the reaction.

Next, we investigated the influence of the electronic and steric nature of the phosphite ligand. It became apparent that only sterically hindered phosphites are useful as ligands. Simple phosphites such as triethylphosphite or triphenylphosphite give only low yields (<10% yield) of the coupling product. The reason for this seems to be the lower stability of these phosphites.

Table 2. Reaction of 4-trifluoromethylchlorobenzene and phenylboronic acid in the presence of various bases.[a]

Entry	Base	Yield [%][b]
1	NaOAc	12
2	Na_2CO_3	52
3	Cs_2CO_3	26
4	K_3PO_4	61
5	LiOH	34
6	NaOH	71
7	KOH	44
8	NEt_3	26

[a] 8.2 mmol 4-Trifluoromethylchlorobenzene, 9 mmol phenylboronic acid, 10 mmol base, 1 mol-% palladium(II) acetate, 10 mol-% tris(2,4-di-*tert*-butylphenyl)phosphite, 8 mL toluene, 120 °C, 18 h. [b] Determined by GC with hexadecane as internal standard.

As shown in Table 3 the correct combination of base, additive, and sterically hindered phosphite ligand is decisive for the success of the catalysis. Applying tris(2,4-di-*tert*-butylphenyl)phosphite the best results were obtained with

Table 3. Variation of reaction conditions for the coupling of 4-trifluoromethylchlorobenzene and phenylboronic acid.[a]

Entry	$P(OR)_3$	Additive (mol-%)	Yield [%][b]	
			Na_2CO_3	NaOH
1	$P(O\text{-}2,4\text{-}tBu_2C_6H_3)_3$	–	52	71
2	$P(O\text{-}2,4\text{-}tBu_2C_6H_3)_3$	CaF_2 (10)	77	67
3	$P(O\text{-}2,4\text{-}tBu_2C_6H_3)_3$	H_2O (50)	70	63
4	$P(O\text{-}i\text{Pr})_3$	–	79	9
5	$P(O\text{-}i\text{Pr})_3$	CaF_2 (10)	88	48
6	$P(O\text{-}i\text{Pr})_3$	H_2O (50)	21	30

[a] 8.2 mmol 4-Trifluoromethylchlorobenzene, 9 mmol phenylboronic acid, 10 mmol base, 1 mol-% palladium(II) acetate, 10 mol-% phosphite, 8 mL toluene, 120 °C, 18 h. [b] Determined by GC with hexadecane as internal standard.

Na_2CO_3 and 10 mol-% CaF_2. If sodium hydroxide instead of sodium carbonate is used as base a higher yield is obtained without co-catalyst. Tri-isopropylphosphite is even more effective as ligand in this coupling reaction. Almost 90% of 4-trifluoromethyl biphenyl is formed in the presence of Na_2CO_3 as base and 10 mol-% CaF_2 as co-catalyst! As expected, water or hydroxide ions have a detrimental effect on catalyst productivity when applying tri-isopropylphosphite due to the easier hydrolysis of the alkyl phosphite.

Not only the nature of the ligand but also the P/Pd ratio is an important parameter for catalyst productivity (Table 4). In the presence of NaOH only four equivalents of tris(2,4-di-*tert*-

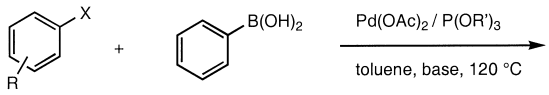
Table 4. Effect of P/Pd ratio on the reaction of 4-trifluoromethylchlorobenzene and phenylboronic acid in the presence of palladium(II) acetate and tris(2,4-di-*tert*-butylphenyl)phosphite.[a]

Entry	P/Pd	Yield [%][b]	
		Na_2CO_3	NaOH
1	2	3	48
2	4	47	82
3	6	51	78
4	10	52	71
5	50	40	8

[a] 8.2 mmol 4-Trifluoromethylchlorobenzene, 9 mmol phenylboronic acid, 10 mmol base, 1 mol-% palladium(II) acetate, 8 mL toluene, 120 °C, 18 h. [b] Determined by GC with hexadecane as internal standard.

butylphenyl)phosphite (with respect to Pd) are required to give an optimum yield (82%) for the test reaction. On the other hand using sodium carbonate as base ten equivalents of tris(2,4-di-*tert*-butylphenyl)phosphite per palladium give the best result. Lower ratios do not lead to stabile catalysts, a higher excess of ligand blocks free coordination sites of the palladium(0) complex prone to oxidative addition of the aryl halide.

With efficient catalyst systems for the test reaction at hand the reactivity of various aryl halides in the Suzuki reaction was tested (see Scheme 2). A survey of catalytic cross-coupling of aryl chlorides and aryl bromides with phenylboronic acid is provided in Table 5. Electron-poor 4-trifluoromethylchlorobenzene, 3-trifluoromethylchlorobenzene, and 4-chloroacetophenone are coupled in good to very good yields (71–94%). Remarkably, even non-activated chlorobenzene and deactivated 4-chlorotoluene give the desired biarylic products in substantial yield (45–54%) in the presence of only 1 mol-% of palladium(II) acetate. The resulting turnover numbers (ca. 50) are comparable even to most of the recent palladium/basic ligand systems.[14, 15, 17] 4-Chloronitrobenzene and 2-chlorobenzonitrile are much more active substrates for C–C coupling reactions. Thus, comparable or even higher yields of products are formed at catalyst loadings one order of magnitude lower (0.1 mol-%).



Scheme 2. Suzuki reaction of various aryl halides **1**–**6**.

Table 5. Coupling of various aryl halides and phenylboronic acid.[a]

Entry	X	R	P(OR′)$_3$	P/Pd	Pd(OAc)$_2$ [mol-%]	Base	Yield [%][b]
1	Cl	4-CF_3	P(O-2,4-*t*Bu$_2$C$_6$H$_3$)$_3$	10	1	NaOH	71
2	Cl	3-CF_3	P(O-*i*Pr)$_3$	10	1	Na_2CO_3	78
3	Cl	4-Ac	P(O-*i*Pr)$_3$	10	1	Na_2CO_3	94
4	Cl	H	P(O-2,4-*t*Bu$_2$C$_6$H$_3$)$_3$	10	1	NaOH	54
5[c]	Cl	4-CH_3	P(O-2,4-*t*Bu$_2$C$_6$H$_3$)$_3$	10	1	NaOH	45
6	Cl	4-NO_2	P(O-2,4-*t*Bu$_2$C$_6$H$_3$)$_3$	10	0.1	Na_2CO_3	57
7	Cl	2-CN	P(O-*i*Pr)$_3$	20	0.1	NaOH	89
8	Br	4-F	P(O-2,4-*t*Bu$_2$C$_6$H$_3$)$_3$	100	0.0001	NaOH	66
9	Br	H	P(O-2,4-*t*Bu$_2$C$_6$H$_3$)$_3$	100	0.0001	NaOH	85
10	Br	4-Me	P(O-2,4-*t*Bu$_2$C$_6$H$_3$)$_3$	100	0.0001	NaOH	69
11	Br	[d]	P(O-*i*Pr)$_3$	100	0.0001	NaOH	82

[a] 8.2 mmol Aryl halide, 9 mmol phenylboronic acid, 10 mmol base, 8 mL toluene, 120 °C, 18 h. [b] Determined by GC with hexadecane as internal standard. [c] 140 °C. [d] 2-Bromo-6-methoxynaphthalene.

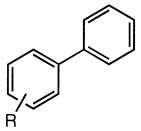
Activated and deactivated aryl bromides can be coupled efficiently with the palladium/phosphite catalyst systems at very low catalyst loadings (0.0001 mol-%). Turnover numbers in between 660000 and 850000 (66–85%) are obtained without further optimization of the reaction conditions.

In summary, we have shown that mixtures of palladium(II) acetate and sterically hindered phosphites are highly efficient catalysts for the coupling reaction of aryl bromides and aryl chlorides with phenylboronic acid. Crucial for the success of the reaction is the choice of the right ligand, the phosphite/palladium ratio, and the use of NaOH or Na_2CO_3 as base. Optimum yields of the products may be obtained in the presence of CaF_2 as additive. As ligands phosphites are advantageous compared with phosphines for several reasons. They are significantly cheaper for large scale applications and more easily accessible. Thus, a quick fine tuning of catalyst properties is possible. In addition, phosphites are more stable towards oxygen. Hence, they can be handled and stored on air without problems. Due to the steric bulk of the ligands hydrolysis of phosphites is not a problem in these reactions except almost stoichiometric quantities of water or hydroxide ions are present.

Experimental Section

General: All chemicals were commercially available and used without further purification. Dry toluene (stored on molecular sieves) was purchased from Fluka. Due to the fact that all synthesized biphenyls are known they were characterized by means of GC/MS, ^{1}H-, and ^{13}C-NMR spectroscopy.

General procedure: In an ACE pressure tube (Aldrich) aryl halide (8.2 mmol), phenylboronic acid (9 mmol), base (10 mmol), hexadecane (400 μL) (as internal standard), an appropriate amount of additive (if necessary), phosphite, and palladium(II) acetate is suspended in dry toluene (8 mL) under an atmosphere of argon. The tube is sealed and put in a 120 °C hot bath of silicon oil. After 18 h the mixture is cooled to room temperature and CH_2Cl_2 (10 mL) and 2N NaOH (10 mL) are added. The organic phase is analyzed by gas chromatography. After washing the organic phase with water and brine, drying and evaporating the solvents the products are isolated by crystallization from methanol/acetone mixtures or by column chromatography (silica gel, hexane/ethyl acetate mixtures).



Analytical data

4-Trifluoromethylbiphenyl: ^{1}H NMR (360 MHz, $CDCl_3$, 21 °C): $\delta = 7.69$ (m, 4H), 6.60 (d, ^2J(H,H) = 6.8 Hz, 2H), 7.47 (m, 2H), 7.40 (m, 1H); ^{13}C{^{1}H} NMR (91 MHz, $CDCl_3$, 21 °C): $\delta = 144.7$, 139.8, 129.3 (q, ^2J(C,F) = 32 Hz), 129.0, 128.2, 127.4, 127.3, 125.7 (q, ^3J(C,F) = 3.8 Hz), 124.4 (q, ^1J(C,F) = 272 Hz); MS (70 eV, EI): *m*/*z*: 222 [*M*]$^+$, 201, 153, 152.

3-Trifluoromethylbiphenyl: ^{1}H NMR (360 MHz, $CDCl_3$, 21 °C): $\delta = 7.95$–7.49 (m, 9H); ^{13}C{^{1}H} NMR (91 MHz, $CDCl_3$, 21 °C): $\delta = 142.0$, 139.7, 131.2 (q, ^2J(C,F) = 32 Hz), 130.4, 129.2, 129.0, 128.0, 127.2, 124.3 (q, ^1J(C,F) = 272 Hz), 123.9 (m, 2C); MS (70 eV, EI): *m*/*z* 222 [*M*]$^+$, 201, 153, 152.

4-Acetylbiphenyl: ^{1}H NMR (360 MHz, $CDCl_3$, 21 °C): $\delta = 8.02$ (d, ^2J(H,H) = 8.0 Hz, 2H), 7.67 (d, ^2J(H,H) = 8.0 Hz, 2H), 7.61 (d, ^2J(H,H) = 7.3 Hz, 2H), 7.46 (m, 2H), 7.39 (m, 1H), 2.62 (s, 3H); ^{13}C{^{1}H} NMR

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(91 MHz, $CDCl_3$, 21 °C): $\delta = 197.7$, 145.8, 139.9, 135.9, 128.9, 128.9, 128.2, 127.2, 127.2, 26.6; MS (70 eV, EI): m/z: 196 $[M]^+$, 181, 152, 76.

Biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta = 7.68$ (d, ^2J(H,H) = 7.3 Hz, 4H), 7.52 (m, 4H), 7.42 (m, 2H); ^{13}C{^{1}H} NMR (91 MHz, $CDCl_3$, 21 °C): $\delta = 141.2$, 128.2, 127.2, 127.1; MS (70 eV, EI): m/z: 154 $[M]^+$, 76.

4-Methylbiphenyl: ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta = 7.63$ (m, 2H), 7.54 (m, 2H), 7.47 (m, 2H), 7.36 (m, 1H), 7.29 (m, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 21 °C): $\delta = 141.1$, 138.3, 137.0, 129.5, 128.7, 127.0, 126.9, 126.9, 21.1; MS (70 eV, EI): m/z: 168 $[M]^+$, 152.

4-Nitrobiphenyl: ^{1}H NMR (360 MHz, $CDCl_3$, 21 °C): $\delta = 8.25$ (d, ^2J(H,H) = 8.0 Hz, 2H), 7.70 (d, ^2J(H,H) = 8.2 Hz, 2H), 7.61 (d, ^2J(H,H) = 6.4 Hz, 2H), 7.47 (m, 3H); ^{13}C{^{1}H} NMR (91 MHz, $CDCl_3$, 21 °C): $\delta =$ 147.4, 146.9, 138.6, 129.2, 128.8, 127.6, 127.2, 123.9; MS (70 eV, EI): m/z: 199 $[M]^+$, 169, 152, 141.

2-Cyanobiphenyl: ^{1}H NMR (360 MHz, $CDCl_3$, 21 °C): $\delta = 7.72 - 7.47$ (m, 9H); ^{13}C{^{1}H} NMR (91 MHz, $CDCl_3$, 21 °C): $\delta = 145.1$, 137.9, 133.4, 132.6, 129.8, 128.5 (3C), 127.3, 118.5, 110.9; MS (70 eV, EI): m/z: 179 $[M]^+$, 152, 151, 76.

4-Fluorobiphenyl: ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta = 7.55$ (m, 4H), 7.45 (m, 2H), 7.36 (m, 1H), 7.14 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 21 °C): $\delta = 162.4$ (d, ^1J(C,F) = 247 Hz), 140.2, 137.3, 128.8, 128.7 (d, ^3J(C,F) = 8.6 Hz), 127.2, 127.0, 115.6 (d, ^2J(C,F) = 21 Hz); MS (70 eV, EI): m/z: 172 $[M]^+$, 85.

2-Methoxy-6-phenylnaphthalene: ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C): $\delta =$ 7.87 (d, ^4J(H,H) = 1.6 Hz, 1H), 7.69 (m, 2H), 7.61 (m, 3H), 7.36 (m, 2H), 7.25 (m, 1H), 7.06 (m, 2H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 21 °C): $\delta = 157.7$, 141.2, 136.3, 133.7, 129.7, 129.1, 128.8, 127.2, 127.2, 127.0, 126.0, 125.6, 119.1, 105.5, 55.3; MS (70 eV, EI): m/z: 234 $[M]^+$, 219, 191, 189.

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