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Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling of Various Aryl Halides Using *ortho*-Alkyl-Substituted Arylphosphanes and (*ortho*-Alkylphenyl)-alkylphosphanes under Microwave Heating

Sauli Vuoti,*[a] Juho Autio,[a] Minna Laitila,[a] Matti Haukka,[b] and Jouni Pursiainen[a]

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Mono- and dinuclear palladium(II) chloride complexes of various *ortho*-alkyl-substituted aryl- and alkylphosphanes were prepared. Subsequently, these were characterized by ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectroscopy, X-ray crystallographic studies and mass spectroscopy. The palladium complexes were screened as potential catalysts for the microwave-assisted Suzuki–Miyaura coupling reaction of several aryl halides under aerobic conditions. A preliminary study showed that excellent results can be obtained even for electron-rich bromides and unactivated aryl chlorides with an optimized solvent, base and catalyst loading using specific phosphane ligands.

Introduction

Transition-metal-catalyzed cross-coupling is now recognized to be one of the most powerful carbon–carbon bond forming reactions. Palladium-catalyzed carbon–carbon and carbon–nitrogen bond-forming reactions are widely used methods in modern organic chemistry. The Pd-catalyzed Suzuki–Miyaura coupling reaction is one of the most convenient methods for preparing biaryl compounds thanks to the advantages of wide functional group tolerance and the use of stable and nontoxic organoborane reagents.[1–7] The palladium-catalyzed coupling of aryl halides or their synthetic equivalents are very often used in the synthesis of biaryl molecules. These are key components in a growing number of pharmaceuticals, natural products and with axial chiral ligands highly efficient asymmetric catalysts.[2,4,8] Since the general catalytic procedures were discovered, efforts have been made toward increasing the substrate range and efficiency. Although the use of alternative bases or solvents can be beneficial, it is the electronic and steric improvement of the supporting ligand that has the most influence on increasing efficiency and reactivity in these processes.[9–16] Consequently, designing ligands that have the appropriate features with sufficient variety is decisive in dealing with the demanding substrates in this area. Typically, the electron-rich and sterically hindered ligands belonging to the trialkylphosphane, aryldialkyl- and diarylalkylphosphane classes have been studied for these reactions, with promising results.[17–18] The effectiveness of these types of ligands has been reported to be caused mainly by the high resistance towards oxidation.[19] However, there are also reports of ligand-free Pd/C catalysts, which bypass the waste formation caused by phosphane ligands.[20] Furthermore, De Vries et al. have successfully employed ultra low catalyst loadings in Suzuki coupling reactions.[21] Even if several new ligands with enhanced properties in assisting the palladium-catalyzed coupling have been developed, a universal method for the coupling of all substrates has not yet been entirely elucidated.[22]

Blettner et al. were the first to describe the use of the Suzuki coupling reaction for the coupling of various benzoates and phenylboronic acid using microwave irradiation.[23] Using microwave irradiation and metal catalysts has been often described in combination with green chemistry.[24] The choice of using microwave heating instead of conventional heating methods further enhances the effectiveness and rapidity of the coupling reactions. This in turn, creates new options and increases demand for the design of new ligands.[25] Access to new types of ligands is therefore a critical component of the design of novel homogeneous transition-metal catalysts. Even if the less demanding and less active furanones[26] and electron-rich aryl bromides have already been coupled with environmentally friendly solvents and ligand-free procedures using microwave irradiation,[27] research on the microwave-assisted Suzuki–Miyaura coupling reactions has been concentrated on the coupling of unactivated aryl chlorides, which are much cheaper starting materials. Unactivated aryl chlorides have been successfully coupled using recyclable PEG-catalysts[28] and even ligand-

[a] Department of Chemistry, University of Oulu,
P. O. Box 3000, 90014 Oulu, Finland
Fax: +358-8-5531603
E-mail: sauli.vuoti@oulu.fi
[b] Department of Chemistry, University of Joensuu,
P. O. Box 111, 80101 Joensuu, Finland

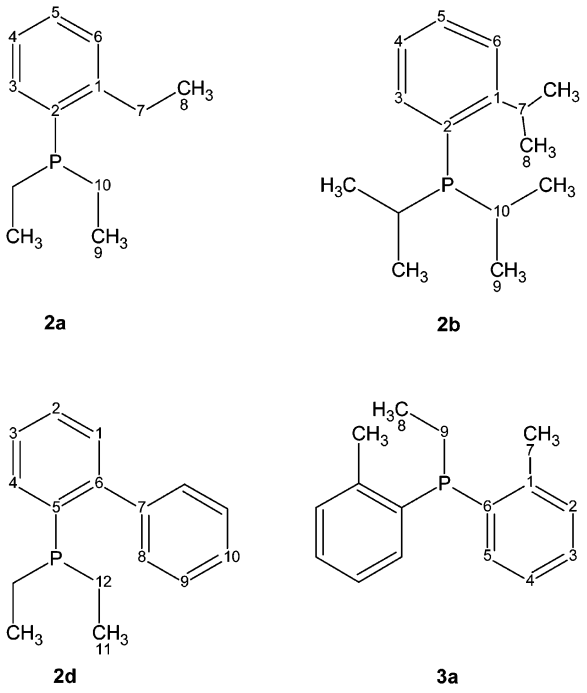
free processes,[29] but when microwave irradiation is employed, the coupling of unactivated aryl chlorides can only be achieved with limited success.[30]

In this study we synthesized and characterized four new *ortho*-alkyl-substituted arylalkylphosphanes and their corresponding palladium(II) complexes. Together with a selection of palladium(II) arylphosphane complexes characterized in our previous work,[31] and new palladium complexes prepared with previously known aryl(alkyl)phosphanes,[32–35] all these were screened and compared as potential catalysts for the Suzuki–Miyaura coupling of various aryl halides under microwave irradiation.

Results and Discussion

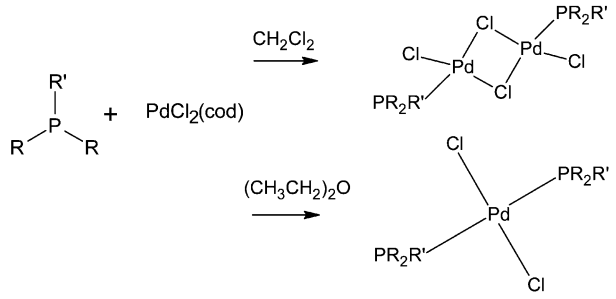
Syntheses and characterization of the *ortho*-alkyl-substituted arylalkylphosphane ligands and their corresponding palladium complexes

The new phosphane ligands **2a**, **2b**, **2d** and **3a** (Scheme 1) were prepared according to a modified method reported in the literature[34–35] by lithiating the substituted bromobenzenes with *n*-butyllithium followed by an overnight reaction between the matching dichloroalkyl- or dialkylchlorophosphane. The phosphanes were characterized by ^{1}H, ^{13}C, $^{31}P\{^{1}H\}$ NMR and mass spectroscopy.



Scheme 1. Structures of the new phosphanes **2a**, **2b**, **2d** and **3a**.

All the new and previously known mononuclear palladium(II) complexes were prepared by a simple 1:2 substitution of cyclooctadiene (cod) in $PdCl_2$(cod) with a preferred phosphane ligand in diethyl ether (Scheme 2). The dinuclear, chlorine-bridged palladium complexes were prepared by a similar 1:1 substitution reaction in dichloromethane. We have previously shown that depending on the solvent used *ortho*-alkyl-substituted arylphosphanes form mono- or dinuclear palladium complexes regardless of the Pd/P ratio.[31]



Scheme 2. A general reaction scheme for the preparation of the mono- and dinuclear palladium complexes.

The phosphane ligand **4b** forms a regular *trans*-isomer in the synthesis of the mononuclear palladium complex. However, a *cis-sym*-isomer was crystallized after the synthesis of the matching dinuclear complex. Variable temperature ^{31}P NMR measurements between –50 °C and 60 °C show just one NMR signal, which suggests the presence of only one isomer in solution. This is probably due to attractive interactions between two ligands. Such a phenomenon has been previously known.[36] To the best of our knowledge, this is the first time a dinuclear *cis-sym* palladium complex has been used successfully as a catalyst in Suzuki coupling reactions. However, the use of dinuclear Pd complexes in allyl substitutions reactions has been reported previously.[37] The palladium complexes were characterized by $^{31}P\{^{1}H\}$ NMR, elemental analysis and X-ray crystal diffraction (where applicable). The palladium complexes are not soluble enough to produce proper ^{1}H NMR spectra. However, overnight ^{1}H NMR measurements for a few mono- and dinuclear

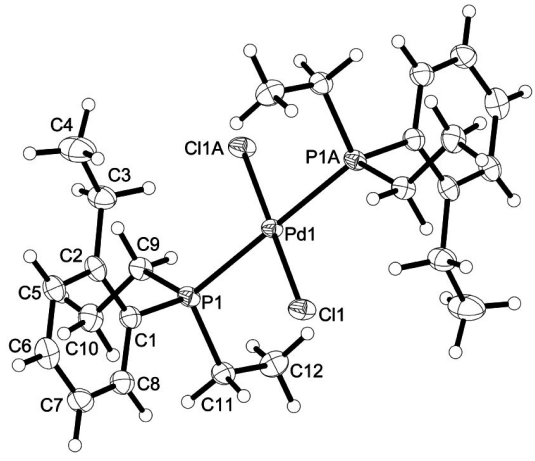


Figure 1. Thermal ellipsoid plot of the mononuclear palladium complex of ligand **2a**. Selected bond lengths (Å) and angles (°): Pd1–Cl1 2.2869(11), Pd1–P1 2.3189(12), P1–C11 1.806(5), P1–C1 1.817(5), P1–C9 1.830(5), Cl1–Pd1–P1 87.76(4), Cl1(A)–Pd1–P1 92.24(4). Symmetry transformations were used to generate equivalent atoms: (A) $-x + 2$, y, $-z + 2$.

complexes showed that the shifts of the hydrogen atoms had moved downfield only slightly, and therefore the measurements were not repeated for the other complexes.

In all complexes the Pd atoms have square planar or slightly disordered square-planar coordination geometry (see Figures 1, 2, 3, and 4). In the mononuclear complexes of ligands **4b**, **2c**, **2b**, **2a** and **2d** the Pd atom is located on an inversion center. In the complex of ligand **2d** the inversion center is located between the Pd atoms. The Pd–P [2.2224(13)–2.2397(11) Å], Pd–$Cl_{terminal}$ [2.2869(11)–2.3745(15) Å], Pd–$Cl_{bridging}$ [2.25(5)–2.4351(10) Å] and Pd–S [2.2550(13)–2.2710(16) Å] distances fall into the range of typical bond lengths. The short Pd–$Cl_{bridging}$ (2.25 Å) distance is most probably due to the elemental disorder in structure **2a**. In the dinuclear complexes of ligands **2d**, **4c** and **2c** the atoms bonded to the Pd centers form two square planes. The neighboring planes are nearly coplanar in **2d** and **2c**, but in **4c** the planes defined by Cl1, Cl2, P1, Cl3 and Cl1, Cl2, Cl4, P2 are slightly bent. The angle between the planes is 25.80(2)°.

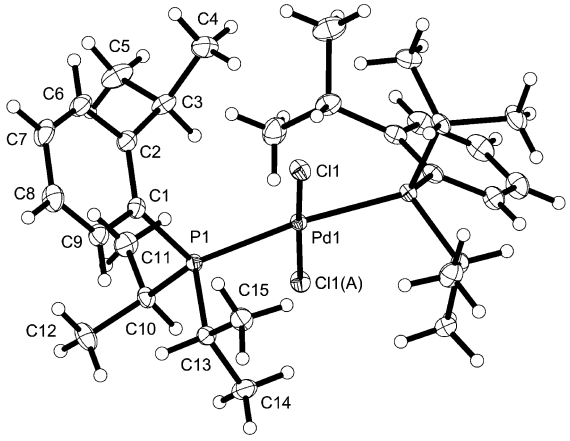


Figure 2. Thermal ellipsoid plot of the mononuclear palladium complex of ligand **2b**. Selected bond lengths (Å) and angles (°): Pd1–Cl1 2.3065(4), Pd1–P1 2.3373(4), P1–C1 1.842(2), P1–C10 1.855(2), P1–C13 1.858(2), Cl1–Pd1–P1 88.815(15), Cl1(A)–Pd(1)–P(1) 90.911(15). Symmetry transformations were used to generate equivalent atoms: $-x + 1$, y, $-z + 1/2$.

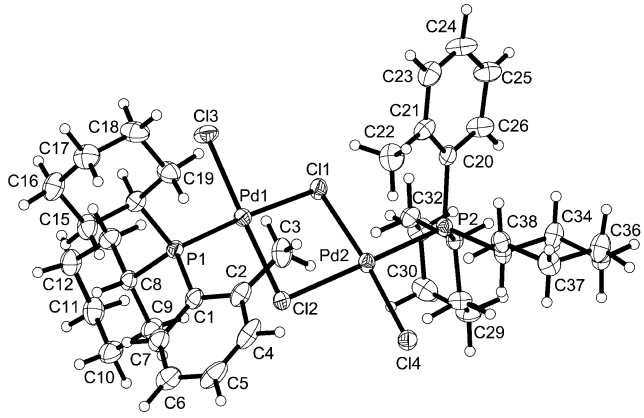


Figure 3. Thermal ellipsoid plot of the dinuclear palladium complex of ligand **2c**. Selected bond lengths (Å) and angles (°): Pd1–P1 2.2397(11), Pd1–Cl3 2.290011, Pd1–Cl2 2.3277(11), Pd1–Cl1 2.4351(10), Pd2–P2 2.2341(11), Pd2–Cl4 2.2922(11), Pd2–Cl1 2.3350(11), Pd2–Cl2 2.4106(10). Cl3–Pd1–Cl2 175.08(4), P1–Pd1–Cl1 175.90(4), Cl4–Pd2–Cl1 174.68(4), P2–Pd2–Cl2 177.82(4), Pd2–Cl1–Pd1 90.94(4), Pd1–Cl2–Pd2 91.73(4).

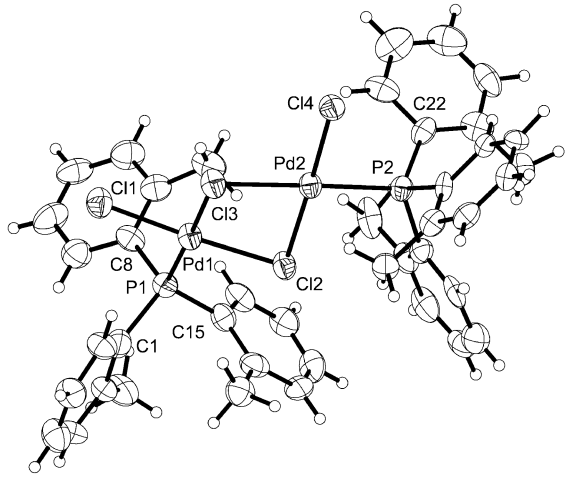


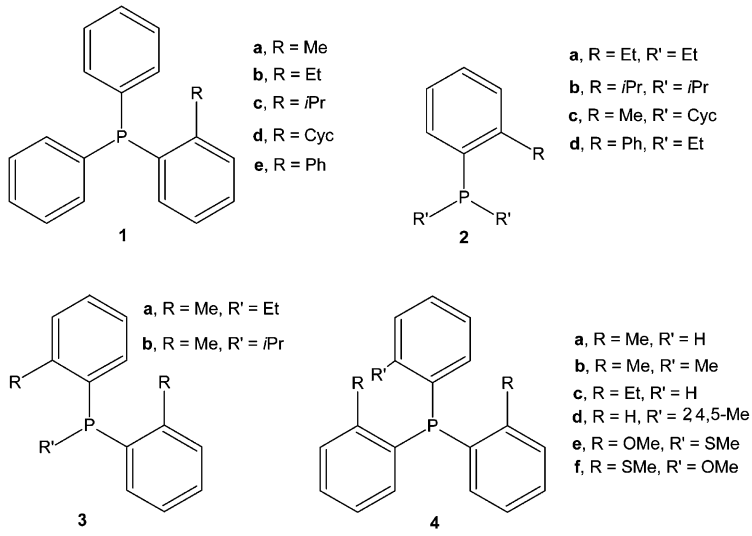
Figure 4. Thermal ellipsoid plot of the dinuclear palladium complex of ligand **4b**. The solvent has been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–P1 2.244(3), Pd1–Cl1 2.286(4), Pd1–Cl2 2.342(3), Pd1–Cl3 2.399(3), Pd2–P2 2.244(3), Pd2–Cl4 2.287(3), Pd2–Cl2 2.318(3), Pd2–Cl3 2.406(3), Pd1–Cl2–Pd2 91.67(12), Pd1–Cl3–Pd2 88.17(11), P1–Pd1–Cl1 86.80(13), P2–Pd2–Cl4 87.37(12).

Suzuki Coupling of Arylboronic Acids with Aromatic Halides

To create the optimum conditions for the coupling reactions, the catalyst loading, base and solvent were screened using the simple coupling reaction of 4-bromotoluene and phenylboronic acid (Scheme 3). Using 0.5 mol-% of the palladium catalyst provided the best result whereas using larger or smaller amounts of the catalyst did not improve the yield further (see Table 1). We also tested a series of bases for the aforementioned coupling reaction. According to a report by Bele et al.,[38] K_2CO_3 is an effective base for many Pd-catalyzed coupling reactions under microwave irradiation. Our results confirmed this by showing that both K_2CO_3 and K_3PO_4 were indeed effective bases (see Table 2, Entries 1 and 3). Our solvent screening data revealed that DMF and THF were the most effective solvents for the coupling reaction (see Table 3, entries 4 and 5).

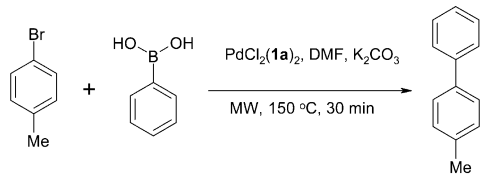
Utilizing the optimized reaction conditions, we evaluated the scope of the coupling of various aryl and heteroaryl halides with phenylboronic acid and biphenylboronic acid using palladium catalysts with a variety of phosphane ligands. The results are presented in Tables 4 and 5. All yields were reported as isolated yields after separation of the products by column chromatography.

The results show that the palladium complexes of the arylphosphane ligands produce high yields when simple substrates such as 3-bromotoluene or 3-bromopyridine are



Scheme 3. Structures of the phosphanes used in the coupling reactions.

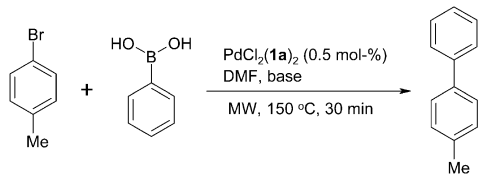
Table 1. Screening of the catalyst loading for the reaction of 4-bromotoluene and phenylboronic acid.[a]



Entry	mol-%	% Yield[b]
1	0.05	41
2	0.1	73
3	0.5	99
4	1.0	77
5	2.5	90
6	5.0	92
7	10.0	81

[a] Reaction conditions: 4-bromotoluene (1.45 mmol, 1.0 equiv.), phenylboronic acid (1.65 mmol, 1.14 equiv.), K_2CO_3 (3.0 mmol, 2.1 equiv.), DMF (2.5 mL).. [b] Isolated yield after column chromatography.

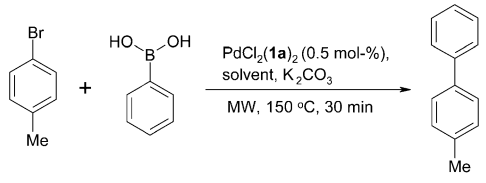
Table 2. Screening of bases for the reaction of 4-bromotoluene and phenylboronic acid.[a]



Entry	Base	% Yield[b]
1	K_3PO_4	88
2	Na_2CO_3	63
3	K_2CO_3	99
4	KOH	59
5	KF	55
6	K_2CO_3[c]	94

[a] Reaction conditions: 4-bromotoluene (1.45 mmol, 1.0 equiv.), phenylboronic acid (1.65 mmol, 1.14 equiv.), base (3.0 mmol, 2.1 equiv.), DMF (2.5 mL). [b] Isolated yield after column chromatography. [c] 4.0 mmol, 2.8 equiv.

Table 3. Screening of solvents for the reaction of 4-bromotoluene and phenylboronic acid.[a]



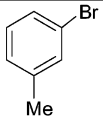
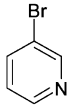
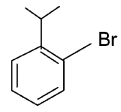
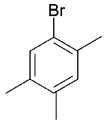
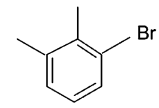
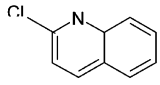
Entry	Solvent	% Yield[b]
1	water	26
2	toluene	68
3	ethanol	83
4	tetrahydrofuran	87
5	DMF	99

[a] Reaction conditions: 4-bromotoluene (1.45 mmol, 1.0 equiv.), phenylboronic acid (1.65 mmol, 1.14 equiv.), K_2CO_3 (3.0 mmol, 2.1 equiv.), solvent (2.5 mL). [b] Isolated yield after column chromatography.

coupled, but the yields start to decrease when more demanding substrates such as bromoxylenes or trimethylbromobenzenes are used. The palladium complexes of the hetero-atom substituted phosphane ligands **4e** and **4f** are only mildly active as catalysts in all reactions. The aryl-(alkyl)phosphane ligands produce high yields in all reactions with only minor differences between the yields. The various size *ortho*-substituents influenced the yields only slightly. The dinuclear palladium complexes produced lower yields than the corresponding mononuclear complexes in all reactions.

When the more challenging biphenylboronic acid is used, the results are similar as the ones received in the reactions with phenylboronic acid. The palladium complexes of the aryl(alkyl)phosphane ligands produce higher yields than the complexes of the arylphosphanes. The yields produced with

Table 4. Coupling of aryl halides with phenylboronic acid.[a]

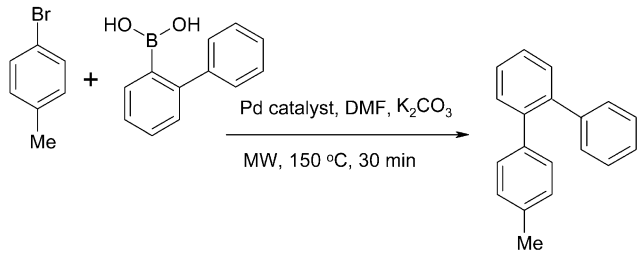
Entry	Aryl halide	Pd catalyst	% Yield
			
1		**1b**	92
2		**1a**	90
3		**1c**	87
4		**3b**[b]	87
5		**2c**	85
6		**2b**	82
7		**4b**[b]	82
8		**3b**	80
9		**2a**	70
10		**2d**	68
11		**2c**[b]	64
12		**1e**[b]	53
13		**$PdCl_2$cod**	11
			
14		**3a**	93
15		**2b**	92
16		**2d**	90
17		**1b**	84
18		**4f**	64
19		**1c**	60
20		**4b**	53
21		**3b**	52
22		**1e**	48
23		**2c**	37
24		**2a**	29
25		**1a**	27
26		**1d**	24
27		**4b**[b]	17
28		**$PdCl_2$cod**	no reaction
			
29		**2b**	96
30		**2a**	91
31		**3b**	90
32		**2c**	88
33		**3a**	87
34		**1c**	87
35		**1a**	85
36		**4b**	85
37		**1b**	83
38		**1e**	83
39		**2d**	72
40		**4d**	70
41		**1d**	65
42		**4a**	62
43		**4e**	55
44		**4c**[b]	41
45		**$PdCl_2$cod**	no reaction
			
46		**2b**	96
47		**2a**	94
48		**3a**	93
49		**1a**	90
50		**2c**	90
51		**1d**	89
52		**1e**	89
53		**4**[a]	87
54		**1b**	86
55		**2d**	86
56		**3b**	81
57		**1c**	80
58		**4b**	66
59		**1a**[b]	64
60		**4c**	54
			
61		**2a**	96
62		**4b**	86
63		**3a**	82
64		**2d**	82
65		**2b**	80
66		**4a**	70
67		**4d**	60
68		**1b**	51
69		**1c**	24
70		**4e**	11
			
71		**2b**	96
72		**3b**	91
73		**2a**	86
74		**4d**	80
75		**2c**	79
76		**3b**[b]	77
77		**3a**	75
78		**4b**	71
79		**4c**[b]	69
80		**2d**	61
81		**1a**	53

[a] Standard reaction conditions: aryl halide (1.45 mmol, 1.0 equiv.), phenylboronic acid (1.65 mmol, 1.15 equiv.), K_2CO_3 (3.0 mmol, 2.0 equiv.), DMF (2.5 mL), 0.5 mol-% of Pd catalyst, MW (150 °C, 30 min). [b] Dinuclear palladium complex of the $Pd_2Cl_4L_2$-type.

the complexes of the bulkier aryl alkyl ligands **3a**, **3b** and **2d** were somewhat lower than the ones produced with the smaller ligands **2a**–**2c**.

The palladium complexes of the mixed aryl(alkyl)phosphane ligands **2a**–**3b** gave the highest yields in most coupling reactions with only small differences between the yields.

Table 5. Pd-catalyzed coupling of 4-bromotoluene and 2-biphenylboronic acid.[a]



Entry	Pd catalyst	Isolated yield (%)
1	**2b**	96
2	**2c**	90
3	**2a**	86
4	**3a**	77
5	**3b**	77
6	**4d**	76
7	**2d**	70
8	**4a**[b]	68
9	**4b**	64
10	**1a**	51
11	**4f**	40

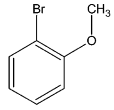
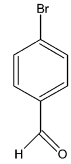
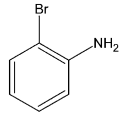
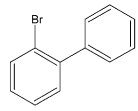
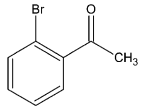
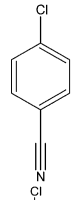
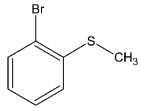
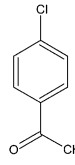
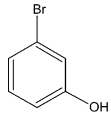
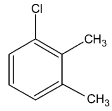
[a] Reaction conditions: 4-bromotoluene (1.45 mmol, 1.0 equiv.), biphenylboronic acid (1.64 mmol, 1.14 equiv.), K_2CO_3 (3.0 mmol, 2.1 equiv.), DMF (2.5 mL), 0.5 mol-% of Pd catalyst. [b] Dinuclear palladium complex of the $Pd_2Cl_4L_2$-type.

Overall, ligand **2b** was observed to be the most efficient catalyst for most couplings, although the other aforementioned ligands gave almost equally as high yields in several reactions. The combination of two isopropyl groups directly connected to the phosphorus atom with one *ortho*-isopropyl-substituted phenyl ring seemed to be the optimal structure even for the most demanding coupling reactions in our screening. Increasing the size of the isopropyl groups directly connected to the phosphorus atom to cyclohexyl groups or decreasing the size to ethyl groups was observed to lower the yields. Altering the *ortho*-substituent on the phenyl ring from methyl to isopropyl only slightly affected the yields. However, increasing the size of the substituent to a phenyl ring somewhat lowered the yield.

The palladium complexes with classic triphenylphosphane moieties worked well in simple coupling reactions, but mostly produced only low to mediocre yields in the more demanding couplings. The triphenylphosphane palladium complexes with thiomethyl and methoxy groups in the *ortho* position produced only low to mediocre yields, which was probably due to the respective chelated structure. Such a phenomenon has been previously observed in various hydroformylation reactions.[32] The dinuclear palladium complexes produced average yields in the simplest reactions, but a fast disintegration of the complexes was detected and therefore high yields were not achieved.

Due to promising results with the coupling reactions presented above, our studies continued using a series of more challenging, electron-rich aryl bromides and unactivated aryl chlorides in the coupling reactions. The results are presented in Table 6.

Table 6. Coupling of aryl halides with phenylboronic acid.[a]

Entry	Aryl halide	% Yield	Entry	Aryl halide	% Yield
1		98	6		65
2		96	7		93
3		97	8		90
4		99	9		97
5		96	10		98

[a] Standard reaction conditions: aryl halide (1.45 mmol, 1.0 equiv.), phenylboronic acid (1.65 mmol, 1.15 equiv.), K_2CO_3 (3.0 mmol, 2.0 equiv.), DMF (2.5 mL), H_2O (0.5 mL), 0.5 mol-% of $PdCl_2(\mathbf{2b})_2$, MW (150 °C, 30 min).

All the coupling reactions conducted by using the mononuclear palladium complex of ligand **2b** as the catalyst produced high yields. The coupling reaction between the 4-bromobenzaldehyde and phenylboronic acid was the only exception, only a 65% yield was achieved by our method. The coupling reactions seem to produce high yields regardless of the functional group of the aryl substrate. Even the unactivated aryl chlorides, which of the 3-bromo-*o*-xylene is the most demanding one, were coupled successfully with high yields.

Preliminary testing showed that some of the starting materials remained unreacted in the reaction mixture. Consequently, the reaction was further enhanced by the addition of a small amount of water, which is reported to enhance the yields even further.[39] In our studies it also improved the purity of the coupling products and prevented homocoupling of the phenylboronic acid.

The coupling of various more demanding aryl and heteroaryl halides with phenylboronic acid by using K_2CO_3 (2 equiv.)/Pd catalyst (**2b**) (0.5%) system in DMF/H_2O gave good to excellent yields of the corresponding bi and terphenyls. Even the normally mildly reactive aryl chlorides were successfully coupled providing high yields. Further testing for these potential catalysts are currently underway in our laboratory.

Conclusions

In conclusion, we prepared four new ligands suitable for microwave -assisted Pd-catalyzed Suzuki–Miyaura coupling of aryl bromides and chlorides with phenylboronic acids. The ligands are relatively cheap due to the low catalyst loadings and can be readily prepared from commercially available reagents. To avoid difficulties caused by in situ generated systems,[40] such as the requirement for an excess of expensive ligands, we have used air- and moisture-stable palladium(II) complexes, which allow strict control over the palladium/ligand ratio and remain stable in organic solvents at high temperatures. Furthermore, the reactions can take place in air. Microwave heating provides several advantages in comparison to conventional heating methods. Microwave heating gives shorter reaction times, and in most cases improves product yields.[23,27,39–40] Other advantages include: new avenues for synthesis not achieved by using conventional heating methods and the avoidance of lengthy metal catalyst extraction steps.[41] The addition of a small amount of water into the reaction mixture further enhances the yields and the purity of the coupling products. The catalyst system can therefore be used even for the electron-rich bromides and unactivated aryl chlorides. Further testing is currently underway in our laboratory.

Experimental Section

General: The prepared phosphanes are air- and moisture sensitive, both as pure solid compounds and in solution. Without protection they undergo observable oxidation within a few hours. Therefore all reactions involving these free phosphanes were carried out using standard Schlenk techniques under either nitrogen or argon. The palladium complexes are stable in air, both as solid compounds and in solution, and were therefore isolated and characterized in air. Diethyl ether was distilled from sodium-benzophenone ketyl under nitrogen before use. Nitrogen was bubbled through dichloromethane, ethanol and *n*-hexane. Other commercial reagents were used as obtained. The characterization of the new phosphanes and the palladium complexes was based on ^{1}H-, ^{31}P{^{1}H} and ^{13}C-NMR spectroscopy. NMR spectra were recorded with a Bruker DPX400 or DPX200 spectrometer at room temperature in $CDCl_3$ (99.8% D, 0.03% TMS). 85% H_3PO_4 was used as an external standard for ^{31}P{^{1}H} NMR spectroscopy. Exact mass peaks of the free ligands were determined on a Micromass LCT, using an ESI+ method. C and H analyses were made using a Perkin–Elmer 2400 CHNS analyzer from the purified, solid metal complex powders. The mass peaks for the coupling products were determined by a Hewlett Packard HP 6890 Series GC-system coupled to a 5973-MSD (Mass Selective Detector, quadrupole). Single-crystals for X-ray crystallographic analysis were obtained by slow evaporation of the dichloromethane/hexane solvent mixture at room temperature.

The microwave system was Biotage Initiator Eight. The microwave reactor was from Biotage (personal Chemistry) Emrys syntheziser, where temperature, pressure and microwave power can be controlled. The reaction vessel used was a 2–5 mL closed tube. The maximum pressure was 21 bar, the maximum temperature 250 °C and the maximum microwave power 300 W. Temperatures were measured with an IR thermometer. The reactor was a single mode reactor, where the microwave cavity is tuned for each sample, so that absorption of microwaves is at the highest possible level. The microwave cavity was tuned for 2–5 mL samples. The sample was heated to the desired temperature using 150 W power. The power was set 0 W immediately after reaching the preset temperature, and the sample was irradiated as needed to maintain the temperature. The 30 min heating period was started when the temperature of the sample had reached 150 °C. Cooling was not used while heating the sample. After the preset heating period, the reaction vessel was cooled to room temperature using airflow.

X-ray Crystal Structure Determinations: The crystals were immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 110 or 120 K. The X-ray diffraction data were collected by means of a Nonius KappaCCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å) resolution. The DENZO-SCALEPACK[42] or EvalCCD[43] program packages were used for cell refinements and data reductions. All of the structures were solved by direct methods using the SHELXS97,[44] SIR92,[45] SIR97,[46] SIR2004[47] with the WinGX[48] or X-SEED[49] graphical user interface. An empirical absorption correction factor was applied to all of the data (SADABS,[50] XPREP in SHELXTL v.6.14-1[51]). Structural refinements were carried out using SHELXL97.[52] The crystallographic data of **2a**, **2b**, **2c**, and **4b** are summarized in Table 7. The thermal ellipsoid plots of three representative palladium complexes of ligands **2a**–**c** and **4b** are shown in Figures 1–4. The crystallographic data for the Pd^{II} complexes of ligands **2a**–**2d**, **3a**–**b**, **4a**–**4c** and **4e**–**f** have been deposited with the Cambridge Crystallographic Data Centre under supplementary publication numbers: CCDC-644388 (for **2a**), -644389 (for **2d**), -644390 (for **3a**), -644391 (for **3b**), -644392 (for **4a**), -644393 (for **4b**), -644394 (for **4c**), -644395 (for **4e**), -644396 (for **4f**), -644397 (for **2d**), -644398 (for **3a**), -652017 (for **4e**), and -652018 (for **4f**). Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1ET, UK [Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk].

A General Method for the Preparation of the *ortho*-Alkyl-Substituted Aryl(alkyl)phosphane Ligands 2a, 2b, 2d, and 3a: A solution of *n*-butyllithium was transferred dropwise by a cannula to a freshly prepared solution of 1-bromo-2-alkylbenzene in diethyl ether (30 mL) at –10 °C→0 °C (salted ice bath). After stirring for 3 h, a solution of dialkylchlorophosphane or dichloroalkylphosphane in diethyl ether (25 mL) was slowly added to the mixture, and the mixture was stirred at room temperature overnight. The liquid was removed, and the solid was extracted three times with diethyl ether (10 mL). The liquid layers were combined and the solvent was removed in vacuo. The crude product was recrystallized from ethanol, and if necessary, purified by column chromatography using dichloromethane/hexane (1:2) mixture as eluent. The pure products were bright viscous oils or white solids. The previously known phosphanes were prepared according to methods reported in the literature.[34–35]

Diethyl(*o*-ethylphenyl)phosphane (2a): Following the general procedure described above, reactions of 1-bromo-2-ethylbenzene (7.373 g, 39.8 mmol), *n*-butyllithium (16 mL, 2.5 M, 40.0 mmol) and chlorodiethylphosphane (5 g, 40.1 mmol) yielded a bright viscous oil after recrystallization from ethanol and purification by column chromatography. The yield of the pure product was 7.503 g, 38.6 mmol, 97.0%. Exact mass (Micromass LCT, ESI+): 195.1333 $[M + H]^+$ (calculated for $C_{12}H_{20}P$, 195.1303). ^{1}H NMR (200 MHz, $CDCl_3$, see Scheme 1 for numbering): δ = 1.14 (t, $^{3}J_{H,H}$ = 4.6 Hz, 3 H, H^8), 1.36 (t, $^{3}J_{H,H}$ = 5.2 Hz, 6 H, H^9), 2.02 (m, 4 H, H^{10}), 2.95 (m, 2 H, H^7), 7.15–7.55 (m, 4 H, H^3, H^4, H^5, H^6) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 5.82 (s, 1 C, C^9), 5.86 (s, 1 C, C^9), 16.32 (s, 1 C, C^8), 22.26 (s, 1 C, C^{10}), 22.95 (s, 1 C, C^{10}),

Table 7. Crystallographic data for the mononuclear palladium complexes **2a**–**b** and dinuclear **2c** and **4b**.

	2a	**2b**	**2c**	**4b**
Empirical formula	$C_{24}H_{38}Cl_2P_2Pd$	$C_{30}H_{50}Cl_2P_2Pd$	$C_{34}H_{42}Br_2Cl_6P_2Pd_2$	$C_{43}H_{43}Cl_7P_2Pd_2$
Fw	565.78	649.94	1097.94	1082.66
Temperature [K]	120(2)	120(2)	120(2)	120(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic	monoclnic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/c$
a [Å]	7.4317(3)	17.8026(5)	7.63530(10)	18.4500(17)
b [Å]	8.7296(5)	10.7622(3)	21.3959(5)	12.2249(13)
c [Å]	10.5167(6)	18.1899(3)	12.4927(3)	21.012(2)
α [°]	75.711(2)	90	90	90
β [°]	74.582(3)	111.748(2)	90.654(2)	113.374(5)
γ [°]	82.901(4)	90	90	90
V [Å^3]	636.15(6)	3237.04(15)	2040.73(7)	4350.2(8)
Z	1	4	2	4
ρ_{calc} [Mg/m^3]	1.477	1.334	1.787	1.653
μ (Mo-K_α) [mm^{-1}]	1.075	0.854	3.335	1.362
Number of collected reflections	10419	22864	27952	46424
Number of unique reflections	2626	3717	4674	7653
$R_{int.}$	0.0621	0.0418	0.0435	0.2702
R_1[42] [$I \geq 2\sigma$]	0.0499	0.0260	0.0436	0.0826
wR_2[44] [$I \geq 2\ \sigma$]	0.1312	0.0570	0.1124	0.1575

27.58 (d, $^3J_{C,P}$ = 16 Hz, 1 C, C^7), 125.46 (s, 1 C, C^4), 125.48 (s, 1 C, C^5), 129.96 (s, 1 C, C^6), 130.06 (s, 1 C, C^3), 131.69 (d, $^1J_{C,P}$ = 8 Hz, 1 C, C^2), 131.84 (d, $^2J_{C,P}$ = 10 Hz, 1 C, C^1) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = –31.5 ppm.

Diisopropyl(*o*-isopropylphenyl)phosphane (2b): Following the general procedure described above, reactions of 1-bromo-2-isopropylbenzene (4.903 g, 24.6 mmol), *n*-butyllithium (9.8 mL, 2.5 M, 24.5 mmol) and chlorodiisopropylphosphane (3.710 g, 24.3 mmol) yielded a white solid product after recrystallization from ethanol. The yield of the pure product was (5.434 g, 23.0 mmol, 94.6%). Exact mass (Micromass LCT, ESI+): 237.1766 $[M + H]^+$ (calculated for $C_{15}H_{26}P$, 237.1772). ^1H NMR (200 MHz, $CDCl_3$, see Scheme 1 for numbering): δ = 0.89 (dd, $^3J_{H,H}$ = 7.4, $^3J_{H-P}$ = 11.6 Hz, 12 H, H^9), 1.05 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, H^8), 2.08 (m, 2 H, H^{10}), 4.09 (sep, $^3J_{H,H}$ = 9.6 Hz, 1 H, H^7), 7.01 (m, 1 H, H^3), 7.11–7.22 (m, 1 H, H^4), 7.34–7.46 (m, 2 H, H^5, H^6) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 20.35 (d, $^2J_{C,P}$ = 21.4 Hz, 4 C, C^9), 24.24 (d, $^1J_{C,P}$ = 28.5 Hz, 2 C, C^{10}), 25.94 (m, 2 C, C^8), 30.66 (d, $^3J_{C,P}$ = 27 Hz, 1 C, C^7), 125.03 (s, 1 C, C^4), 125.13 (s, 1 C, C^5), 125.19 (s, 1C C^6), 128.92 (s, 1 C, C^3), 132.22 (s, 1 C, C^2), 132.25 (s, 1 C, C^1) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = –7.4 ppm.

Diethyl(*o*-phenylphenyl)phosphane (2d): Following the general procedure described above, reactions of 1-bromo-2-biphenyl (4.701 g, 20.2 mmol), *n*-butyllithium (8.2 mL, 2.5 M, 20.5 mmol) and chlorodiethylphosphane (2.516 g, 20.2 mmol) yielded a bright viscous oil after recrystallization from ethanol and purification by column chromatography. The yield of the pure product was (4.749 g, 19.6 mmol, 97.0%). Exact mass (Micromass LCT, ESI+): 381.1768 $[M + H]^+$ (calculated for $C_{27}H_{26}P$, 381.1772). ^1H NMR (200 MHz, $CDCl_3$, see Scheme 1 for numbering): δ_H () = 1.03 (t, $^3J_{H,H}$ = 9.0 Hz, 6 H, H^{11}) 1.46 (m, 4 H, H^{12}), 7.21–7.44 (m, 9 H, H$^{1-4,8-10}$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 9.52 (s, 2 C, C^{11}), 19.09 (s, 2 C, C^{12}), 126.89 (s, 1 C, C^3), 127.14 (s, 1 C, C^2), 127.35 (m, 2 C, C^9), 127.81 (m, 1 C, C^{10}), 128.13 (s, 2 C, C^8), 128.76 (d, $^3J_{C,P}$ = 16.9 Hz, 1 C, C^1), 129.20 (s, 1 C, C^4), 129.84 (d, $^1J_{C,P}$ = 23.0 Hz, 1 C, C^5), 131.18 (s, 1 C, C^7), 148.18 (d, $^2J_{C,P}$ = 30.6 Hz, 1 C, C^6) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = –25.5 ppm.

Ethylbis(*o*-methylphenyl)phosphane (3a): Following the general procedure described above, reactions of 1-bromo-2-methylbenzene (4.61 g, 27.0 mmol), *n*-butyllithium (10.8 mL, 2.5 M, 27.0 mmol) and dichloroethylphosphane (3.522 g, 26.9 mmol) yielded a bright viscous oil after recrystallization from ethanol and purification by column chromatography. The yield of the pure product was (5.839 g, 24.1 mmol, 89.6%). Exact mass (Micromass LCT, ESI+): 243.1296 $[M + H]^+$ (calculated for $C_{16}H_{20}P$, 243.1303). ^1H NMR (200 MHz, $CDCl_3$, see Scheme 1 for numbering): δ = 1.18 (m, 3 H, H^8), 1.34 (m, 2 H, H^9), 2.60 (s, 6 H, H^7), 7.16 (m, 2 H, H^5), 7.30–7.43 (m, 6 H, H$^{2-4,6}$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 10.42 (d, $^2J_{C,P}$ = 18.4 Hz, 1 C, C^8), 20.14 (s, 1 C, C^9), 21.51 (d, $^3J_{C,P}$ = 20.7 Hz, 2 C, C^7), 126.27 (s, 2 C, H^4), 128.55 (s, 2 C, H^3), 130.23 (s, 2 C, H^2), 131.22 (s, 2 C, H^5), 137.39 (d, $^1J_{C,P}$ = 13 Hz, 2 C, H^6), 142.51 (d, $^2J_{C,P}$ = 26.1 Hz, 2 C, H^1) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = –31.9 ppm.

Preparation of the Palladium Complexes: All palladium complexes were prepared as reported previously; by a substitution of cyclooctadiene (cod) in $PdCl_2$ (cod) with a preferred phosphane ligand in dichloromethane or diethyl ether, and purification by dichloromethane/hexane (1:2) solvent mixture if necessary.[31] The previously known palladium complexes were prepared by a similar method. All the synthesized mononuclear Pd complexes are *trans*-isomers.

Dichlorobis[diethyl(*o*-ethylphenyl)phosphane]palladium: A reaction between diethyl(*o*-ethylphenyl)phosphane (0.978 g, 5 mmol) (**2a**) and $PdCl_2$(cod) (0.704 g, 2.5 mmol) in diethyl ether (30 mL) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was (0.745 g, 1.3 mmol, 52.7%). $C_{24}H_{38}Cl_2P_2Pd$ (565.82): calcd. C 50.94, H 6.77; found C 51.20, H 6.89. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ_P = 11.1 ppm.

Dichlorobis[diisopropyl(*o*-isopropylphenyl)phosphane]palladium: A reaction between **2b** (0.976 g, 4.0 mmol) and $PdCl_2$(cod) (0.581 g, 2.0 mmol) in diethyl ether (30 mL) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was (1.072 g, 1.7 mmol, 82.5%). $C_{30}H_{49}Cl_2P_2Pd$ (648.97): calcd. C 55.43, H 7.60; found C 55.20, H 7.39. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ_P = 24.6 ppm.

Dichlorobis[diethyl(*o*-phenylphenyl)phosphane]palladium: A reaction between **2d** (0.962 g, 4.0 mmol) and $PdCl_2$(cod) (0.580 g, 2.0 mmol)

in diethyl ether (30 mL) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was (1.122 g, 1.7 mmol, 84.8%). $C_{32}H_{38}Cl_2P_2Pd$ (661.91): calcd. C 58.06, H 5.79; found C 57.88, H 5.49. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ_P = 27.6 ppm.

Dichlorobis[ethylbis(*o*-methylphenyl)phosphane]palladium: A reaction between **3a** (0.955 g, 3.9 mmol) and $PdCl_2$(cod) (0.560 g, 2.0 mmol) in diethyl ether (30 mL) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was (1.043 g, 1.6 mmol, 82.9%). $C_{32}H_{38}Cl_2P_2Pd$ (661.91): calcd. C 58.06, H 5.79; found C 58.01, H 5.44. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ_P = 20.3 ppm.

Dichlorobis[dicyclohexyl(*o*-methylphenyl)phosphane]palladium: A reaction between (*o*-methylphenyl)dicyclohexylphosphane (**2c**) (0.972 g, 3.4 mmol) and $PdCl_2$(cod) (0.582 g, 2.0 mmol) in diethyl ether (30 mL) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was (1.153 g, 1.5 mmol, 88.2%). $C_{38}H_{60}Cl_2P_2Pd$ (756.15): calcd. C 60.35, H 8.00; found C 59.88, H 8.29.$^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ_P = 20.5 ppm.

Dichlorobis[isopropylbis(*o*-methylphenyl)phosphane]palladium: A reaction between **3b** (0.959 g, 3.7 mmol) and $PdCl_2$(cod) (0.566 g, 2.0 mmol) in diethyl ether (30 mL) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was (1.143 g, 1.7 mmol, 91.9%). $C_{34}H_{44}Cl_2P_2Pd$ (691.98): calcd. C 59.19, H 6.43; found C 59.03, H 6.11. ^{31}P NMR: δ_P = 27.9 ppm.

Dichlorobis[diphenyl(2,4,5-trimethylphenyl)phosphane]palladium: A reaction between **4d** (0.915 g, 3.0 mmol) and $PdCl_2$(cod) (0.510 g, 1.8 mmol) in diethyl ether (30 mL) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was (0.843 g, 1.1 mmol, 71.5%). $C_{42}H_{44}Cl_2P_2Pd$ (788.06): calcd. C 64.17, H 5.64; found C 63.65, H 5.44. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ_P = 20.4 ppm.

Dichlorobis[*o*-thiomethylphenylbis(*o*-methoxyphenyl)phosphane]palladium: A reaction between *o*-thiomethylphenylbis(*o*-methoxyphenyl)phosphane (**4e**) (0.700 g, 1.9 mmol) and $PdCl_2$(cod) (0.516 g, 1.8 mmol) in diethyl ether (30 mL) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was (0.662 g, 1.2 mmol, 67.4%). $C_{21}H_{22}Cl_2O_2PPdS$ (546.74): calcd. C 46.21, H 4.06; found C 46.00, H 4.23. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ_P = 54.3 ppm.

Dichlorobis[*o*-methoxyphenylbis(*o*-thiomethylphenyl)phosphane]palladium: A reaction between **4f** (0.766 g, 2.0 mmol) and $PdCl_2$(cod) (0.518 g, 1.8 mmol) in diethyl ether (30 mL) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was (0.687 g, 1.2 mmol, 67.9%). $C_{21}H_{22}Cl_2OPPdS_2$ (562.80): calcd. C 44.89, H 3.95; found C 44.55, H 3.81. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ_P = 57.4 ppm.

Di-μ-chlorodichlorobis[dicyclohexyl(*o*-methylphenyl)phosphane]dipalladium: A reaction between **2c** (0.970 g, 3.4 mmol) and $PdCl_2$(cod) (1.164 g, 4.1 mmol) in dichloromethane (20 mL) yielded an orange solid product after purification by column chromatography. The yield of the pure product was (1.266 g, 1.35 mmol, 79.6%). $C_{38}H_{60}Cl_4P_2Pd_2$ (933.45): calcd. C 48.79, H 6.47; found C 48.86, H 6.16. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ_P = 44.3 ppm.

Di-μ-chlorodichlorobis[isoprophylbis(*o*-methylphenyl)phosphane]dipalladium: A reaction between **3b** (0.952 g, 3.7 mmol) and $PdCl_2$(cod) (1.130 g, 4.0 mmol) in dichloromethane (20 mL) yielded an orange solid product after purification by column chromatography. The yield of the pure product was (1.317 g, 1.5 mmol, 81.8%). $C_{34}H_{44}Cl_4P_2Pd_2$ (869.28): calcd. C 46.87, H 5.09; found C 46.55, H 5.43. ^{31}P NMR: δ_P = 40.2 ppm.

Di-μ-chlorodichlorobis[bis(*o*-methylphenyl)phenylphosphane]dipalladium: A reaction between **4a** (1.165 g, 4.0 mmol) and $PdCl_2$(cod) (1.146 g, 4.0 mmol) in dichloromethane (20 mL) yielded an orange solid product after purification by column chromatography. The yield of the pure product was (1.560 g, 1.7 mmol, 85.6%). $C_{40}H_{38}Cl_4P_2Pd_2$ (935.30): calcd. C 51.39, H 4.10; found C 51.55, H 4.43. δ_P = 37.0 ppm.

Di-μ-chlorodichlorobis(tri-*o*-tolylphosphane)dipalladium: A reaction between **4b** (1.044 g, 3.4 mmol) and $PdCl_2$(cod) (0.979 g, 3.4 mmol) in dichloromethane (20 mL) yielded an orange solid product after purification by column chromatography. The yield of the pure product was (1.408 g, 1.5 mmol, 85.2%). $C_{42}H_{42}Cl_4P_2Pd_2$ (963.35): calcd. C 52.38, H 4.40; found C 52.11, H 4.42. ^{31}P NMR: δ_P = 28.9 ppm.

Di-μ-chlorodichlorobis[bis(*o*-ethylphenyl)phenylphosphane]dipalladium: A reaction between bis(*o*-methylphenyl)isopropylphosphane **4c** (1.061 g, 3.3 mmol) and $PdCl_2$(cod) (0.951 g, 3.3 mmol) in dichloromethane (20 mL) yielded an orange solid product after purification by column chromatography. The yield of the pure product was (1.486 g, 1.5 mmol, 90.1%). $C_{44}H_{46}Cl_4P_2Pd_2$ (991.41): calcd. C 53.32, H 4.68; found C 53.17, H 4.35. ^{31}P NMR: δ_P = 36.7 ppm.

A General Procedure for the Suzuki–Miyaura Coupling Reactions: A microwave pressure vessel (2–5 mL) was charged with the aryl halogenide, phenylboronic acid, K_2CO_3 and with the corresponding palladium complex. DMF (2.5 mL) and in some cases H_2O (0.5 mL) was added to the vessel, and the vessel was pre-stirred for 5 min. The resulting solution was warmed at 150 °C for 30–50 min under standard irradiation mode. The reaction mixture was cooled to room temperature, and water (30 mL) was added to the mixture. The organic layer was separated, and the water extracted three times with diethyl ether (30 mL). The ether extracts were combined with the organic layer and dried with $MgSO_4$, and the solvent was removed in vacuo. The remaining residue was separated by column chromatography using silica gel and dichloromethane/hexane (1:3) mixture. Each experiment was repeated twice and the yields are reported as an average of two measurements.

3-Methylbiphenyl: Colourless oil, (ref.[53] m.p. 4–5 °C). ^1H NMR ($CDCl_3$): δ = 7.6–7.5 (m, 2 H), 7.45–7.35 (m, 3 H), 7.35–7.19 (m, 2 H), 7.18–7.0 (m, 2 H), 2.39 (s, 3 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.289, 141.168, 138.245, 128.642, 128.619, 127.948, 127.918, 127.118, 124.222, 21.50 ppm. GC-MS: *m*/*z* = 168 [M^+].

3-Phenylpyridine: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.84–8.8 (m, 1 H), 8.57 (d, *J* = 3.5 Hz, 1 H), 7.83–7.8 (m, 1 H), 7.6–7.5 (m, 2 H), 7.5–7.4 (m, 2 H), 7.4–7.33 (m, 1 H), 7.33–7.25 (m, 1 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 148.246, 148.108, 137.598, 136.386, 134.057, 128.851, 127.870, 126.908, 123.294 ppm. GC-MS: *m*/*z* = 155 [M^+].

2-Phenylquinoline: White solid, m.p. 81–83 °C (ref.[54] 82–84 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.24–8.1 (m, 4 H), 7.87 (d, *J* = 8.57 Hz, 1 H), 7.82–7.75 (m, 1 H), 7.75–7.65 (m, 1 H), 7.6–7.4 (m, 5 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 157.31, 136.73, 129.70, 129.61, 129.27, 128.81, 127.53, 127.42, 127.11, 126.24, 118.96 ppm. GC-MS: *m*/*z* = 205 [M^+].

2-Isopropylbiphenyl: White solid, m.p. 80 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.4 (m, 7 H), 7.3–7.4 (m, 2 H), 3.05 (sep, *J* =

6.80 Hz, 1 H), 1.15 (d, J = 6.80 Hz, 6 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 146.286, 142.059, 141.040, 129.912, 129.273, 127.934, 127.631, 126.651, 125.485, 125.257, 29.309, 24.261 ppm. GC-MS: m/z = 196 [M^+].

4-Methyl-*o*-terphenyl: White solid, m.p. 60–62 °C (ref.[55] 74–75 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.5–7.25 (m, 7 H), 7.25–7.06 (m, 4 H), 7.06–6.95 (m, 2 H), 2.29 (s, 3 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.614, 140.442, 138.454, 130.548, 129.799, 129.662, 128.540, 127.790, 127.388, 126.303, 21.04 ppm. GC-MS: m/z = 244 [M^+].

2,3-Dimethylbiphenyl: White solid, m.p. 97–99 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.5–7.35 (m, 2 H), 7.35–7.25 (m, 3 H), 7.2–7.05 (m, 3 H), 2.33 (s, 3 H) ppm. 2.15 (s, 3 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 142.560, 142.244, 137.134, 133.969, 129.385, 128.821, 127.955, 127.660, 126.580, 125.211, 20.690, 16.947 ppm. GC-MS: m/z = 182 [M^+].

2,4,5-Trimethylbiphenyl: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.35 (m, 2 H), 7.35–7.22 (m, 3 H), 7.05–7.02 (m, 2 H), 2.22–2.28 (m, 9 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 141.972, 139.402, 135.452, 133.755, 132.438, 131.695, 131.108, 129.253, 127.975, 126.497, 22.724, 19.309, 19.180 ppm. GC-MS: m/z = 196 [M^+].

2-Methoxybiphenyl: Colourless oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.75 (s, 3 H), 6.92–6.96 (m, 1 H), 6.97–7.20 (m, 1 H), 7.22–7.28 (m, 3 H), 7.28–7.42 (s, 2 H), 7.48–7.55 (m, 2 H) ppm. $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 55.42, 111.13, 120.75, 126.84, 127.91, 128.54, 129.48, 130.62, 130.81, 138.48, 156.37 ppm. GC-MS: m/z = 184 [M^+].

2-Aminobiphenyl: Orange oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (s, 2 H), 6.69–6.72 (m, 1 H), 6.76–6.82 (m, 1 H), 7.08–7.15 (m, 2 H), 7.27–7.31 (m, 1 H), 7.32–7.44 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 115.49, 118.51, 127.05, 127.48, 128.39, 128.70, 128.98, 130.34, 139.42, 143.41 ppm. GC-MS: m/z = 169 [M^+].

2-Acetylbiphenyl: White solid, m.p. 52–54 °C (ref.[56] 53–56 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.62 (s, 3 H), 7.30–7.42 (m, 1 H), 7.43–7.49 (m, 1 H), 7.59–7.64 (m, 3 H), 7.65–7.7 (s, 2 H), 8.0–8.4 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 26.60, 127.13, 127.19, 128.17, 128.85, 128.89, 135.75, 139.76, 145.68, 197.67 ppm. GC-MS: m/z = 196 [M^+].

3′,5′-Dimethyl-2-(methylsulfanyl)biphenyl: White solid, m.p. 41–43 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 2.31–2.35 (m, 6 H), 6.95–6.96 (m, 1 H), 7.0–7.3 (m, 1 H), 7.05–7.3 (s, 5 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 15.65, 21.22, 124.31, 124.54, 126.93, 127.58, 129.00, 129.67, 136.94, 137.34, 140.23, 140.85 ppm. GC-MS: m/z = 228 [M^+].

3′,5′-Dimethylphenyl-3-phenol: Red oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 6 H), 6.64 (s, 1 H), 6.78–6.83 (m, 1 H), 7.04–7.06 (m, 1 H), 7.08–7.14 (m, 4 H), 7.18–7.25 (m, 1 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.23, 114.12, 119.53, 124.91, 128.97, 129.76, 138.08, 140.66, 143.05, 155.76, 163.49 ppm. GC-MS: m/z = 198 (M^+).

4-(3,5-Dimethylphenyl)benzaldehyde: White solid, m.p. 49–51 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 6 H), 6.98 (s, 2 H), 7.07 (s, 1 H), 7.39–7.50 (m, 2 H), 7.57–7.63 (m, 1 H), 7.98–8.30 (m, 1 H), 10.00 (s, 1 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.23, 127.29, 127.46, 127.98, 129.65, 130.62, 133.38, 133.66, 137.56, 137.93, 146.26 192.64 ppm. GC-MS: m/z = 210 [M^+].

3,5-Dimethyl-*o*-terphenyl: Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 6 H), 6.72–6.75 (m, 2 H), 6.77–6.80 (m, 1 H), 7.08–7.20 (m, 5 H), 7.3–7.42 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 21.19, 126.30, 127.22, 127.32, 127.71, 127.79, 128.00, 129.79, 130.45, 130.47, 137.09, 140.51, 140.70, 141.30, 141.65 ppm. GC-MS: m/z = 258 [M^+].

4-Cyanobiphenyl: White solid, m.p. 85–87 °C (ref.[57] 86–87 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.5 (m, 3 H), 7.53–7.6 (m, 2 H), 7.62–7.73 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 110.76, 118.84, 127.10, 127.60, 128.56, 129.00, 132.47, 139.02, 145.52 ppm. GC-MS: m/z = 179 [M^+].

4-Acetylbiphenyl: White solid, m.p. 122–123 °C (ref.[56] 118–123 °C). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.62 (s, 3 H), 7.35–7.50 (m, 3 H), 7.58–7.69 (m, 4 H), 7.99–8.04 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 26.58, 127.12, 127.17, 128.15, 128.83, 128.88, 135.74, 139.75, 145.65, 197.66 ppm. GC-MS: m/z = 196 [M^+].

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