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Palladium(II) complexes of 2-, 3-, and 4-quinolinyl(diphenyl) phosphane and di-(3-quinolinyl)phenylphosphane: Synthesis, characterization, and catalytic screening

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Abstract

One previously known and three novel quinolinyl phosphanes were synthesized by either a reaction between a lithiated diphenylphosphane and the appropriate chloroquinoline or by a reaction between a lithiated haloquinoline and an arylchlorophosphane. The reaction of the quinolinyl phenylphosphane ligands with $PdCl_2$(cod) produced monomeric palladium complexes in diethyl ether and dimeric, chlorine-bridged complexes in dichloromethane. Crystal structures of the palladium complexes confirm that the quinolinyl phenylphosphanes do not form chelated structures while bonded to the metal centre. 2-Quinolinyl(diphenyl)phosphane has a tendency to form a *cis*-isomer while bonded to the metal centre in the mononuclear complex due to attractive interactions between two ligands. A catalytic study showed that the quinolinyl phenylphosphane ligands are moderately active in the Suzuki–Miyaura coupling of various aryl halides in air.

Keywords: Palladium complexes; Cross-coupling reactions; Quinolinyl phosphane ligands; Crystal structures

1. Introduction

Quinoline and pyridine bearing moieties have been successfully used as building blocks for phosphane ligands working as catalysts in various reactions, such as polymerizations [1], hydroformylation reactions [2,3], alkyne additions [4,5], asymmetric synthesis [6,7] and phosphinations [8]. Other types of bidentate, N–P chelating ligands have been used as catalysts in asymmetric reactions [9], Suzuki couplings [10] and Heck reaction [11], where the yields have mostly been very high. However, other studies [2,3,8,12–14] report that the chelating effects between a transition metal complex and phosphane ligands with pyridine, quinoline and other nitrogen bearing groups have inhibited catalytic activity or describe a fast disintegration of the metal complex. On the other hand, it has been reported that the bidentate bonding of bulky aryl phosphanes [15] gave a complete catalysis with very high yields in Suzuki coupling reactions, when the appropriate substitutes had been introduced to the phenyl ring. Furthermore, biphenyl moieties among others have been a key factor in the success of these catalysts [16]. In contrast with other catalytic reactions, those involving ligands with quinoline moieties have not yet been extensively tested as potential catalysts for the Suzuki coupling reactions.

In this study we have prepared one previously known and three novel quinolinyl phosphanes, and synthesized their corresponding mono- and dinuclear palladium complexes to study the coordination chemistry of the ligands. The crystal structures of the palladium complexes have been studied for possible bidentate bonding between the Pd-atom and the phosphane. Furthermore, the quinolinyl phosphanes have been screened as potential catalysts in

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the Suzuki–Miyaura coupling reactions of various aryl bromides and chlorides under microwave irradiation.

2. Experimental

2.1. General details

The prepared phosphanes were air- and moisture sensitive in their pure solid compound forms. In solution, and without protection the phosphanes show observable oxidation within a few hours, and in some cases even within a few minutes. Therefore all reactions involving free phosphanes were carried out using standard Schlenk techniques in a nitrogen or argon atmosphere. 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 over sodium-benzophenone ketyl in nitrogen atmosphere before being used. Nitrogen was bubbled through dichloromethane, ethanol and *n*-hexane. Tetramethylethylenediamine (TMEDA) was distilled prior to use. Other commercial reagents were used as received. 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 on 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. Exact mass peaks of the free ligands were determined on a Micromass LCT, using an ESI+ method. C and H analyses were performed with a Perkin–Elmer 2400 CHNS analyzer from the purified, solid metal complex powders. The mass peaks for the coupling products were determined using a Hewlett Packard HP 6890 Series GC-system coupled with a 5973-MSD (Mass Selective Detector; quadrupole). Single crystals for X-ray crystallographical analyses were obtained by a slow evaporation of the dichloromethane–hexane solvent mixture at room temperature.

2.2. X-ray crystal structure determinations

The crystals were immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 120 K. The X-ray diffraction data were collected by means of a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The Denzo-Scalepack [17] program package was used for calculating cell refinements and data reductions. All of the structures were solved by direct methods using the SIR2004 [18] or SHELXS97 [19] with the WINGX [20] graphical user interface. An empirical absorption correction was applied to all of the data (SADABS [21] or XPREP in SHELXTL [22]). Structural refinements were carried out using SHELXL97 [23]. All hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H length range being = 0.95–0.99 Å and $U_{iso} = 1.2\ U_{eq}$ (parent atom). The crystallographic details are summarized in Table 1. Selected bond lengths and angles are shown in the figure captions.

Table 1
Crystal Data

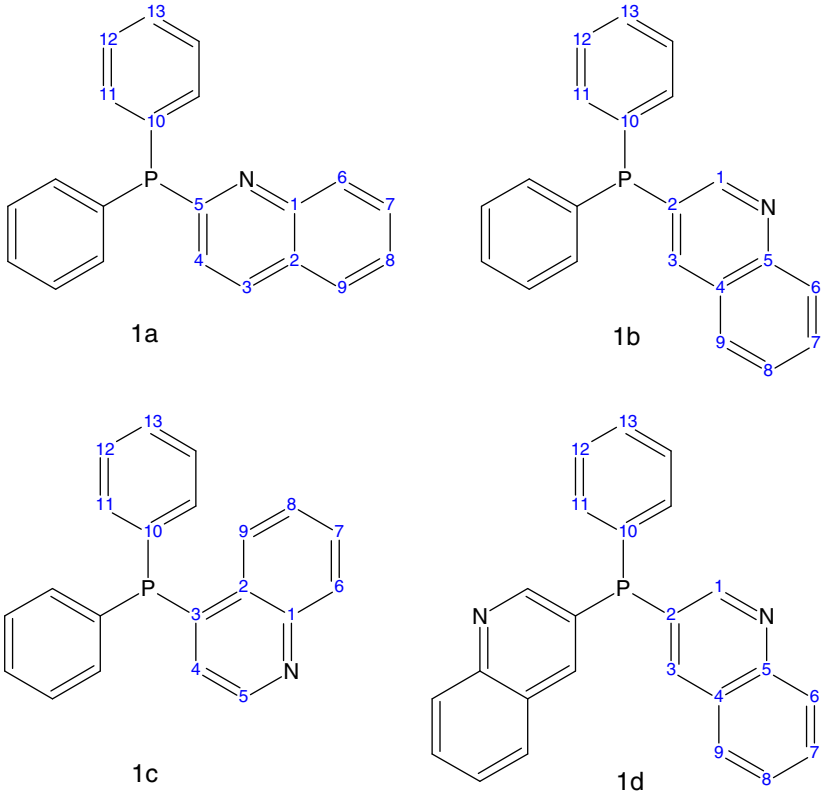
	2 · (CH_2Cl_2)	**3**
Empirical formula	$C_{43}H_{34}Cl_4N_2P_2Pd$	$C_{42}H_{32}Cl_4N_2P_2Pd_2$
Fw	888.86	981.24
Temperature (K)	120(2)	120(2)
λ (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/n$
a (Å)	13.7378(3)	8.6887(5)
b (Å)	10.5523(2)	14.2099(9)
c (Å)	13.8307(3)	14.9357(8)
β (°)	06.7670(10)	91.791(4)
V (Å^3)	1919.73(7)	1843.1(2)
Z	2	2
ρ_{calc} (Mg/m^3)	1.538	1.768
μ(Mo Kα) (mm^{-1})	0.880	1.388
Number of reflections	41 388	27 841
Unique reflections	8814	3571
R_1[a] ($I \geqslant 2\sigma$)	0.0275	0.0466
wR_2[b] ($I \geqslant 2\sigma$)	0.0525	0.0955

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

2.3. Synthesis of the ligands and starting materials

2.3.1. Preparation of 2-diphenylphosphanequinoline (*1a*)

The following reaction was conducted in the dark to prevent the decomposition of diphenylphosphane. A solution of *n*-buthyllithium in hexane (2.2 ml, 6.2 mmol) was added slowly to diphenylphosphane (1.3 ml, 7.5 mmol) dissolved in THF (40 ml) at −115 °C. The mixture was stirred for 15 min at −115 °C, and a solution of 2-chloroquinoline (1.00 g, 6.11 mmol) in THF (20 ml) was added dropwise to the mixture. The reaction mixture was then stirred at −115 °C for 2.5 h before it was allowed to gradually warm to room temperature overnight. The liquid was separated from the yellow precipitate by filtration and the precipitate was washed with THF (3 × 20 ml). The THF extracts were combined and the THF was removed in vacuo. The crude product was purified by column chromatography using silica gel and CH_2Cl_2/hexane/MeOH (10:3:1) as the eluent. The pure product **1a** was obtained as a white solid. Yield: 0.35 g, 18%. Exact mass (Micromass LCT ESI+): 314.1108 $(M+H)^+$ (calculated for $C_{21}H_{17}NP$, 314.1099). ^{1}H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering) δ_H (ppm): 7.15 (d, $^{3}J_{H-H} = 8.4$ Hz, 1H, H^4), 7.2–7.3 (m, 6H, H^{12}, H^{13}), 7.38 (t, $^{3}J_{H-H} = 7.6$ Hz, 1H, H^8), 7.4–7.5 (m, 4H, H^{11}), 7.57 (t, $^{3}J_{H-H} = 7.8$ Hz, 1H, H^7), 7.62 (d, $^{3}J_{H-H} = 8.4$ Hz, 1H, H^9), 7.85 (d, $^{3}J_{H-H} = 8.4$ Hz, 1H, H^3), 8.11 (d, $^{3}J_{H-H} = 8.8$ Hz, 1H, H^6). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ_C (ppm): 124.00 (d, $^{2}J_{C-P} = 15.09$ Hz, C^4), 126.41 (s, C^2), 126.48 (s, C^8), 127.31 (s, C^9), 126.41 (d, $^{3}J_{C-P} = 7.04$ Hz, C^{12}), 128.70 (s, C^{13}), 129.28 (s, C^7), 129.30 (s, C^6) 133.88 (d, $^{2}J_{C-P} = 20.12$ Hz, C^{11}), 134.94 (s, C^3), 136.11 (d, $^{1}J_{C-P} = 12.07$ Hz, C^{10}), 148.30 (d, $^{3}J_{C-P} = 15.09$ Hz, C^1), 164.56 (d, $^{1}J_{C-P} = 3.02$ Hz, C^5). $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$) δ_P (ppm): −0.1.

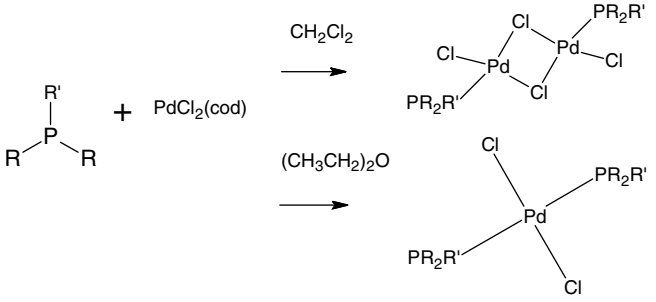


Scheme 1. Structures of phosphanes **1a**, **1b**, **1d** and **1d**.

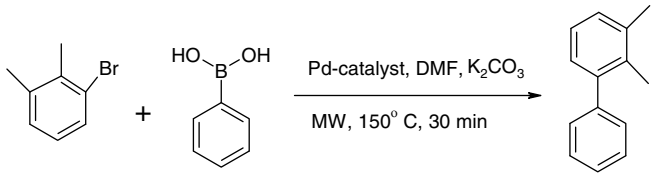
*2.3.2. Preparation of 3-diphenylphosphanequinoline (**1b**), 4-diphenylphosphanequinoline (**1c**), and di-(3-quinolinyl)-phenylphosphane (**1d**)*

A solution of *n*-buthyllithium in hexane (7.1 ml, 20 mmol) was added slowly to dry TMEDA (3.1 ml, 20 mmol). The solution was stirred for 15 min and then cooled to −115 °C by adding cold diethyl ether (50 ml). A solution of 3-bromoquinoline (4.17 g, 20 mmol) in cold diethyl ether (20 ml) was added dropwise to the reaction mixture at −115 °C. The colour of the solution turned from yellow to orange and a white precipitate was formed. After stirring for 5 min, chlorodiphenylphosphane (4.40 g, 20.0 mmol) in diethyl ether (20 ml) was added dropwise to the mixture at −115 °C. The colour of the reaction mixture turned from orange to yellow and a white precipitate was formed. The reaction mixture was then stirred at −115 °C for 2.5 h, before it was allowed to gradually warm to room temperature overnight. The solution was then extracted by H_2SO_4 (2 M, 3 × 10 ml) and the combined extracts were made alkaline with the addition of NaOH (20%). The resulting aqueous phase was extracted by CH_2Cl_2(3 × 20 ml), and the extracts were then combined and dried with $MgSO_4$. The solvent was removed in vacuo. The crude product was washed with ethanol/*n*-hexane (1:1) solution and purified by column chromatography using CH_2Cl_2/*n*-hexane/MeOH (10:3:1) as the eluent. The crude solid was recrystallized from CH_2Cl_2 to give **1b**. The yield of the phosphane as a white solid was 3.0 g, 9.4 mmol, 47%. Exact mass (Micromass LCT ESI+): 314.1093 $(M+H)^+$ (calc. for $C_{21}H_{17}NP$, 314.1099). ^1H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering) δ_H (ppm): 7.3–7.45 (m, 10H, H^{11}, H^{12}, H^{13}), 7.53 (t, $^3J_{H-H} = 7.47$ Hz, 1H, H^8), 7.67–7.79 (m, 2H, H^9, H^7), 8.00 (d, $^3J_{H-P} = 6.76$ Hz, 1H, H^3), 8.09 (d, $^3J_{H-H} = 8.31$ Hz, 1H, H^6), 8.81 (m, 1H, H^1). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C (ppm): 126.90 (s, C^8), 127.85 (s, C^9), 128.79 (d, $^3J_{C-P} = 7.19$ Hz, C^{12}), 129.20 (s, C^{13}), 129.32 (s, C^6), 130.11 (s, C^7), 131.00 (d, $^4J_{C-P} = 16.08$ Hz, C^5), 132.04 (d, $^3J_{C-P} = 9.97$ Hz, C^4), 133.77 (d, $^2J_{C-P} = 19.78$ Hz, C^{11}), 135.78 (d, $^1J_{C-P} = 10.28$ Hz, C^{10}), 141.53 (d, $^2J_{C-P} = 17.74$ Hz, C^3), 147.79 (s, C^2), 154.02 (d, $^2J_{C-P} = 22.28$ Hz, C^1). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ_P (ppm): −10.0.

Phosphane **1c** was synthesized by a similar method as phosphane **1b** by reacting *n*-buthyllithium (6.2 ml, 18 mmol), 4-chloroquinoline (2.95 g, 18 mmol) and



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



Scheme 3. A standard reaction scheme for the couplings showing the reaction used for the optimization for the amount of the Pd-catalyst.

chlorodiphenylphosphane (3.96 g, 18 mmol). The yield of **1c**, a white solid, was 2.94 g, 9.4 mmol, 52%. Exact mass (Micromass LCT ESI+): 314.1080 $(M+H)^+$ (calc. for $C_{21}H_{17}NP$, 314.1099). ^1H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering) δ_H (ppm): 6.82 (t, $^3J_{H-H} = 2.25$ Hz, 1H, H^5), 7.25–7.43 (m, 11H, H^8, H^{11}, H^{12}, H^{13}), 7.62–7.75 (m, 1H, H^7) 8.13 (d, $^3J_{H-H} = 8.42$ Hz, 1H, H^6), 8.20–8.25 (m, 1H, H^9), 8.76 (d, $^3J_{H-H} = 4.30$ Hz, 1H, H^4).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C (ppm): 125.24 (s, C^5), 126.01 (d, $^3J_{C-P} = 22.24$ Hz, C^9), 126.62 (s, C^8), 128.79 (d, $^3J_{C-P} = 7.5$ Hz, C^{12}), 129.41 (s, C^{13}), 129.82 (d, $^3J_{C-P} = 19.19$ Hz, C^2), 130.04 (s, C^6), 134.27 (d, $^2J_{C-P} = 20.23$ Hz, C^{11}), 134.29 (d, $^1J_{C-P} = 8.65$ Hz, C^{10}), 146.56 (d, $^2J_{C-P} = 20.83$ Hz, C^1), 147.59 (s, C^3), 149.59 (s, C^4). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ_P (ppm): −13.8.

Phosphane **1d** was synthesized by a similar method as phosphanes **1b** and **1c** by reacting *n*-buthyllithium (10.7 ml, 30 mmol), 3-bromoquinoline (6.24 g, 30 mmol) and dichlorophenylphosphane (2.68 g, 15 mmol). The yield of **1d**, a white solid, was 3.17 g, 8.7 mmol, 58%. Exact mass (Micromass LCT ESI+): 365.1217 $(M+H)^+$ (calc. for $C_{24}H_{17}N_2P$, 365.1208). ^1H NMR (400 MHz, $CDCl_3$, see Scheme 1 for numbering) δ_H (ppm): 7.35–7.50 (m, 5H, H^{11}, H^{12}, H^{13}), 7.53 (t, $^3J_{H-H} = 7.53$ Hz, 2H, H^8), 7.7 (d, $^3J_{H-H} = 8.71$ Hz, 2H, H^9), 7.73–7.75 (m, 2H, H^7), 8.00 (d, $^3J_{H-P} = 8.07$ Hz, 2H, H^3), 8.12 (d, $^3J_{H-H} = 8.46$ Hz, 2H, H^6), 8.9 (m, 2H, H^1). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ_C (ppm): 127.07 (s, C^8), 127.80 (s, C^9), 129.03 (d, $^3J_{C-P} = 7.41$ Hz, C^{12}), 129.31 (s, C^6), 129.48 (d, $^3J_{C-P} = 15.6$ Hz, C^5), 129.64 (s, C^{13}), 130.37 (s, C^7), 131.91 (d, $^3J_{C-P} = 10.28$ Hz, C^4), 133.75 (d, $^3J_{C-P} = 20.16$ Hz, C^{11}), 134.31 (d, $^3J_{C-P} = 9.77$ Hz, C^{10}), 141.85 (d, $^3J_{C-P} = 23.84$ Hz, C^3), 147.00 (s, C^2), 153.58 (d, $^3J_{C-P} = 23.29$ Hz, C^1). $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ_P (ppm): −13.9.

2.4. Synthesis of the palladium complexes

All palladium complexes were prepared by a substitution of cyclooctadiene (cod) in $PdCl_2$ (cod) with a preferred phosphane ligand in dichloromethane or diethyl ether, See Scheme 2 and purification by silica gel and dichloromethane/hexane (1:2) solvent mixture as reported previously [24].

2.4.1. Dichlorobis(2-diphenylphosphanequinoline)palladium (*2*)

An overnight reaction between 2-diphenylphosphanequinoline (0.988 g, 3.2 mmol) **1a** and $PdCl_2$(cod) (0.472 g, 1.7 mmol) in diethylether (30 ml) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was 0.745 g, 0.9 mmol, 57.9%. *Anal.* Calc. $C_{42}H_{32}N_2P_2Cl_2Pd$: C, 62.74; H, 4.01. Found: C, 62.29; H, 3.89%. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ_P (ppm): 23.8.

2.4.2. Di-μ-chlorodichlorobis(2-diphenylphosphanequinoline)di-palladium (*3*)

An overnight reaction between 2-diphenylphosphanequinoline**1a** (0.986 g, 3.2 mmol) and $PdCl_2$(cod) (0.941 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 1.101 g, 1.1 mmol, 70.1%. *Anal.* Calc. $C_{42}H_{32}N_2P_2Cl_4Pd_2$: C, 51.40; H, 3.29. Found: C, 51.13; H, 3.26%. δ_P (ppm): 31.0.

2.4.3. Dichlorobis(3-diphenylphosphanequinoline)palladium (*4*)

An overnight reaction between 3-diphenylphosphanequinoline (0.985 g, 3.2 mmol) **1b** and $PdCl_2$(cod) (0.469 g, 1.7 mmol) in diethylether (30 ml) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was 0.819 g, 1.0 mmol, 63.7%. *Anal.* Calc. $C_{42}H_{32}N_2P_2Cl_2Pd$: C, 62.74; H, 4.01. Found: C, 62.43; H, 3.71%. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ_P (ppm): 28.2.

2.4.4. Di-μ-chlorodichlorobis(3-diphenylphosphanequinoline)di-palladium (*5*)

An overnight reaction between 3-diphenylphosphanequinoline **1b** (0.985 g, 3.2 mmol) and $PdCl_2$(cod) (0.940 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 1.008 g, 1.0 mmol, 63.9%. *Anal.* Calc. $C_{42}H_{32}N_2P_2Cl_4Pd_2$: C, 51.40; H, 3.29. Found: C, 51.13; H, 3.26%. δ_P (ppm): 36.1.

2.4.5. Dichlorobis(4-diphenylphosphanequinoline)palladium (*6*)

An overnight reaction between 4-diphenylphosphanequinoline (0.985 g, 3.2 mmol) **1c** and $PdCl_2$(cod) (0.470 g, 1.7 mmol) in diethylether (30 ml) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was 0.801 g, 1.0 mmol, 62.3%. *Anal.* Calc. $C_{42}H_{32}N_2P_2Cl_2Pd$: C, 62.74; H, 4.01. Found: C, 62.39; H, 3.88%. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ_P (ppm): 19.9.

2.4.6. Di-μ-chlorodichlorobis(4-diphenylphosphanequinoline)di-palladium (*7*)

An overnight reaction between 4-diphenylphosphanequinoline **1c** (0.983 g, 3.2 mmol) and $PdCl_2$(cod) (0.938 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 0.996 g, 1.0 mmol,

63.2%. *Anal.* Calc. $C_{42}H_{32}N_2P_2Cl_4Pd_2$: C, 51.40; H, 3.29. Found: C, 51.06; H, 3.07%. δ_P (ppm): 28.7.

2.4.7. Dichlorobis(di-(3-quinolinyl)phenylphosphane) palladium (**8**)

An overnight reaction between di-(3-quinolinyl)phenylphosphane (0.915 g, 2.5 mmol) **1d** and $PdCl_2$(cod) (0.359 g, 1.3 mmol) in diethylether (30 ml) yielded a yellow solid product after purification by column chromatography. The yield of the pure product was 0.819 g, 0.9 mmol, 72.3%. *Anal.* Calc. $C_{48}H_{34}N_2P_2Cl_2Pd$: C, 63.62; H, 3.78. Found C, 63.40; H, 3.55%. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$) δ_P (ppm): 17.2.

2.4.8. Di-μ-chlorodichlorobis(di-(3-quinolinyl) phenylphosphane)di-palladium (**9**)

An overnight reaction between di-(3-quinolinyl)phenylphosphane **1d** (0.914 g, 2.5 mmol) and $PdCl_2$(cod) (0.360 g, 1.3 mmol) in dichloromethane (20 ml) yielded an orange solid product after purification by column chromatography. The yield of the pure product was 0.615 g, 0.6 mmol, 45.4%. *Anal.* Calc. $C_{48}H_{34}N_2P_2Cl_4Pd_2$: C, 53.21; H, 3.16. Found C, 53.06; H, 3.02%. δ_P (ppm): 23.8.

2.5. A general procedure for the Suzuki–Miyaura coupling reactions

A microwave pressure vessel (2–5 ml) was charged with the aryl halogen, phenylboronic acid, K_2CO_3 and the corresponding palladium complex. DMF (2.5 ml) (and in some cases H_2O (0.5 ml)) were added to the vessel, and the vessel was pre-stirred for 5 min. The resulting solution was warmed at 150 °C for 30 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 by diethyl ether (30 ml) three times. 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 were reported as an average of the two measurements. The coupling products were identified by ^1H and ^{13}C NMR spectroscopy and gas chromatography. See Scheme 3.

2.5.1. 2,3-Dimethylbiphenyl

White solid, mp 97–99 °C (lit. 98–100 °C). ^1H NMR ($CDCl_3$) δ 7.5–7.35 (m, 2H), 7.35–7.25 (m, 3H), 7.2–7.05 (m, 3H), 2.33 (s, 3H); 2.15 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$) 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^+).

2.5.2. 2-Phenylquinoline

White solid, mp 81–83 °C (lit. 82–84 °C). ^1H NMR ($CDCl_3$) δ 8.24–8.1 (m, 4H), 7.87 (d, $J = 8.57$ Hz, 1H), 7.82–7.75 (m, 1H), 7.75–7.65 (m, 1H), 7.6–7.4 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$) 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^+).

2.5.3. 2-Isopropylbiphenyl

White solid, mp 80 °C (lit. 82 °C). ^1H NMR ($CDCl_3$) δ 7.75–7.4 (m, 7H), 7.3–7.4 (m, 2H), 3.05 (sep, $J = 6.80$ Hz, 1H), 1.15 (d, $J = 6.80$ Hz, 6 H) ppm; ^{13}C NMR ($CDCl_3$) 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^+).

2.5.4. 2,4,5-Trimethylbiphenyl

Yellow oil. ^1H NMR ($CDCl_3$) δ 7.42–7.35 (m, 2H), 7.35–7.22 (m, 3H), 7.05–7.02 (m, 2H), 2.22–2.28 (m, 9H) ppm; ^{13}C NMR ($CDCl_3$) 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^+).

2.5.5. 2,5-Dimethyl-3′,5′-dimethylbiphenyl

Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.2 (s, 3H), 2.33 (s, 3H), 2.34–2.37 (m, 6H), 6.91–6.94 (m, 2H), 7.02–7.07 (m, 4H), 7.11–7.16 (m 1H). $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm): 19.97, 20.89, 21.35, 125.10, 126.98, 127.71, 128.25, 130.14, 130.46, 132.08, 135.01, 137.42, 141.94, 142.03. GC–MS: m/z 210 (M^+).

2.5.6. 2,5-Dimethylbiphenyl

White solid, mp 105–107 °C (lit. 107–109 °C). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.2 (s, 3H), 2.30 (s, 3H), 7.0–7.05 (m, 2H), 7.09–7.17 (m, 2H), 7.23–7.3 (m, 2H), 7.3–7.4 (m, 2H). $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm): 19.90, 20.85, 126.60, 127.80, 127.89, 127.96, 130.20, 130.48, 132.05, 135.03, 141.71, 142.05. GC–MS: m/z 182 (M^+).

2.5.7. 3-Methylbiphenyl

Colorless oil. ^1H NMR ($CDCl_3$) δ 7.6–7.5 (m, 2H), 7.45–7.35 (m, 3H), 7.35–7.19 (m, 2H), 7.18–7.0 (m, 2H), 2.39 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$) 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^+).

2.5.8. 3,4-Dimethyl-3′,5′-dimethylbiphenyl

Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.27 (s, 3H) 2.30 (s, 3H), 2.35 (s, 6H), 6.94 (s, 1H), 7.1–7.24 (m, 3H), 7.27–7.33 (m, 1H), 7.34 (s, 1H). $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm): 19.39, 19.89, 21.39, 124.52, 124.91, 128.41, 128.53, 129.92, 135.42, 136.69, 138.07, 139.05, 141.28. GC–MS m/z 210 (M^+).

2.5.9. 3,4-Dimethylbiphenyl

Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 2.28 (s, 3H) 2.30 (s, 3H), 7.16–7.19 (m, 1H), 7.25–7.34 (m, 2H), 7.34–7.45 (m, 3H), 7.53–7.58 (m, 2H). $^{13}C\{H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm): 19.39, 19.88, 124.46, 126.83,

126.93, 128.37, 128.61, 130.00, 135.60, 136.81, 138.80, 141.22. GC–MS m/z 182 (M^+).

2.5.10. 4-Methyl-o-terphenyl

White solid, mp 60–62 °C. ^{1}H NMR ($CDCl_3$) δ 7.5–7.25 (m, 7H), 7.25–7.06 (m, 4H), 7.06–6.95 (m, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$) 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^+).

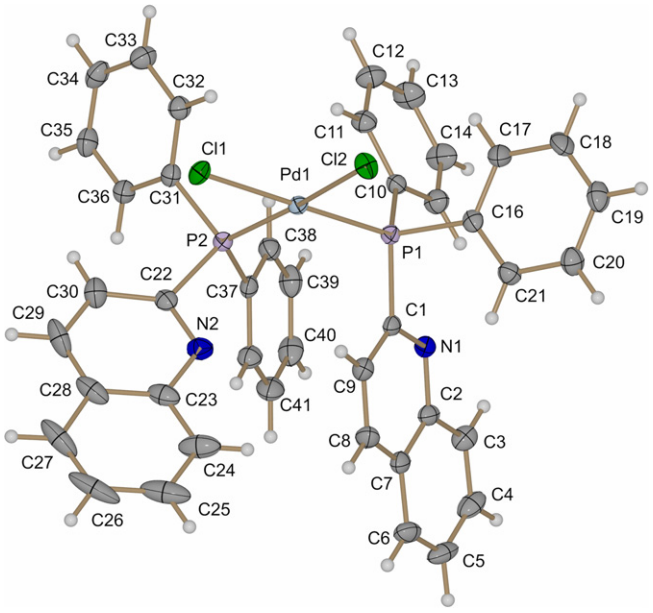


Fig. 1. Thermal ellipsoid plot (50% probability level) of **2**. The CH_2Cl_2 solvent molecule has been omitted for clarity. Selected bond lengths (Å) and angles (deg.): Pd1–P1 2.2631(6), Pd1–P2 2.2711(6), Pd1–Cl2 2.3428(6), Pd1–Cl1 2.3617(6), P1–Pd1–P2 94.83(2), Cl1–Pd1–Cl2 90.86(2).

2.5.11. 2,6-Dimethyl-o-terphenyl

White solid, mp 40–42 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.92 (s, 6H), 6.85–7.00 (m, 2H), 7.00–7.22 (m, 4H), 7.22–7.50 (m, 4H), 7.50–7.65 (m, 2H). ^{13}C{H} NMR ($CDCl_3$, 100 MHz) δ (ppm): 126.60, 126.97, 127.17, 127.21, 127.29, 127.37, 127.48, 127.65, 128.80, 128.83, 130.20, 130.40, 136.13, 139.00, 140.81, 140.85, 141.29, 141.32. GC–MS m/z 258 (M^+).

3. Results and discussion

3.1. Ligand syntheses

The synthesis of 2-diphenylphosphanequinoline (**1a**) See Scheme 1 has been previously described in the literature, but using a different method and obtaining a different yield [25]. In our study phosphane **1a** was prepared by lithiating diphenylphosphane followed by an overnight reaction with 2-chloroquinoline. The starting material for ligand **1d**, 4-chloroquinoline, was prepared according to the method involving the chlorination of 4-quinoline by phosphorous oxychloride [26]. The novel phosphane ligands **1b**, **1c** and **1d** were prepared according to a modification of a method reported in the literature. This involved lithiating the haloquinolines by *n*-butyl lithium followed by an overnight reaction between the matching dichlorophenyl or diphenylchlorophosphane [2]. The phosphanes were characterized by ^{1}H, ^{13}C, ^{31}P–{^{1}H} NMR and mass spectroscopy.

3.2. Palladium(II) complex syntheses

The mononuclear palladium(II) complexes were prepared by a 1:2 substitution reaction of cyclooctadiene (cod) in $PdCl_2$(cod) with a preferred phosphane ligand in diethyl ether. The dinuclear, chlorine-bridged palladium complexes were prepared by a 1:1 similar reaction in dichlo-

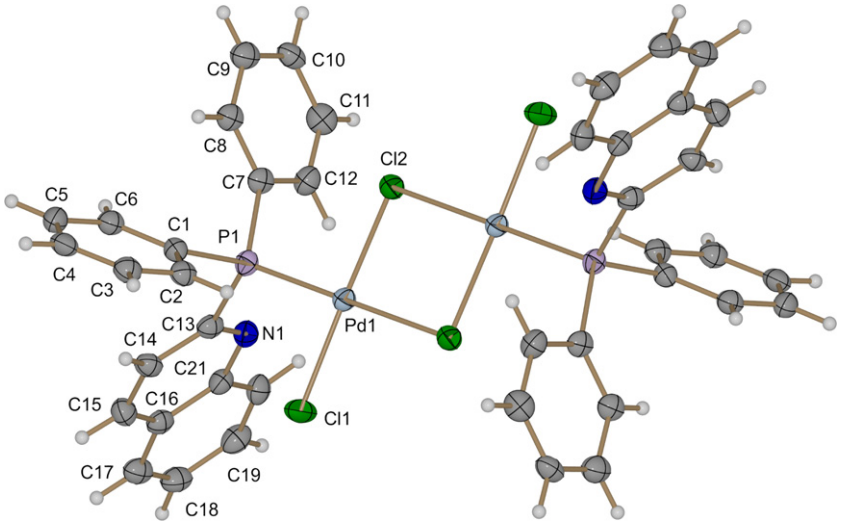


Fig. 2. Thermal ellipsoid plot (50% probability level) of **3**. Selected bond lengths (Å) and angles (deg.): Pd1–P1 2.2383(14), Pd1–Cl1 2.2671(14), Pd1–Cl2 2.3235(14), P1–Pd1–Cl1 88.75(5), Cl2–Pd1–Cl2# 84.58(5), Pd1–Cl2–Pd1# 95.42(5). Symmetry transformations used to generate equivalent atoms: # $-x$, $-y+1$, $-z$.

romethane. We have previously reported that *ortho*-alkyl substituted arylphosphanes form mono- or dinuclear palladium complexes regardless of stoichiometric factors and the nuclearity of the complexes depends on the solvent used [24]. The same occurs with the prepared quinolinyl phosphanes; dinuclear complexes were formed in dichloromethane and mononuclear complexes in diethyl ether regardless of the Pd:P ratio. Interestingly, phosphane **1a** forms a *cis*-isomer (see Fig. 1) in the synthesis of the mononuclear complex **2** but a *trans*-isomer (see Fig. 2) in the synthesis of the dinuclear complex **3**. It has been previously shown that various pyridyl phosphanes behave similarly and tend to form *cis*-isomers in tungsten carbonyl complexes. This is due to the attractive interactions within the molecules [27]. The crystal structure of the mononuclear palladium complex **2** revealed an offset π-stacking interaction between the quinolinyl and phenyl moieties. The centroid to centroid contact between the rings being 3.831 Å and the angle between the planes 10.86°. The typical distance range between two π-stacked rings is 3.3 and 3.8 Å, and contact angles usually lie from parallel displacement up to 40° [28]. 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 of complexes **2**, **3** and **4** showed that the shifts of the hydrogen atoms had moved downfield only slightly; therefore the measurements were not repeated for the other complexes.

3.3. Catalytic testing

As a starting point, we utilized the widely used K_2CO_3 as the base and DMF as the solvent for our catalytic screening. In some cases a small amount of water was added to the reaction mixture to enhance further the yield and the purity of the coupling products [29]. The amount of the Pd-catalyst was optimized to 0.5%. The catalyst system is extremely simple and the reactions can be done in air due to the stability of the palladium (II) complexes. Additionally, the palladium(II) complexes allow strict control for the palladium/ligand ratio and therefore an excess of the ligands is not required.

Microwave heating was chosen as the heating method in our studies for practical reasons. Microwave heating is an adaptable heating method, which shortens the reaction times and increases yields [30]. The results for each individual aryl halide are presented in Tables 2–4. All yields have been reported as isolated yields after separation of the products by column chromatography.

Early on in our studies we observed that the dinuclear palladium(II) complexes produced only low to mediocre yields in the simplest coupling reactions. Apparently the dinuclear palladium complex decomposes under the reaction conditions. Therefore these catalysts were not tested in more complicated coupling reactions. Similarly, the mononuclear complex **8** seemed to produce only low yields, which was probably due to the bulky, highly sterically hindered structure. For this reason, it was not further tested.

Table 2
Coupling of aryl halides with phenyl boronic acid[a]

Entry	Aryl halide	Pd-catalyst	Yield (%)
	3-Br-o-xylene		
1		6	75
2		4	70
3		2	69
4		5	51
5		9	35
6		3	20
7		8	10
	2-Chloroquinoline		
8		6	80
9		4	72
10		2	55
11		8	46
	2-Isopropylbromobenzene		
12		6	81
13		2	80[b]
14		4	71[b]
15		2	59
16		4	54
17		3	50
18		8	16
	2,4,5-Trimethylbromobenzene		
19		4	82[b]
20		2	79[b]
21		6	70
22		8	60
23		7	58
	4-Br-o-xylene		
24		4	80[b]
25		6	66[b]
26		2	62[b]
27		5	50
28		8	45
29		9	40
30		6	19
	2-Br-p-xylene		
31		2	84[b]
32		6	78[b]
33		4	77[b]

[a] Standard reaction conditions: aryl halide (1.45 mmol, 1.0 equiv), phenyl boronic 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.
[b] 0.5 ml H_2O added into the reaction mixture.

Our preliminary testing showed that the mononuclear palladium(II) complexes **2**, **4** and **6** produced average to high yields in most coupling reactions. In our screening the reactions between biphenyl boronic acid and 4-bromotoluene, or 2-bromo-*m*-xylene were the most demanding reactions involving aryl bromides. The complexes only produced low to mediocre yields in these reactions. We observed that some of the biphenyl boronic acid remained unreactive in these reactions. Therefore coupling reactions with even more complex aryl bromides were not conducted.

The differences in the catalytic efficiencies of complexes **2**, **4** and **6** were mostly insignificant as all the ligands

Table 3
Coupling of aryl halides with 3,5-dimethylphenyl boronic acid[a]

Entry	Aryl halide	Pd-catalyst	Yield (%)
	4-Br-o-xylene		
1		4	86[b]
2		2	80[b]
3		6	79[b]
	2-Br-p-xylene		
4		4	85[b]
5		2	84[b]
6		6	68[b]
7		3	40[b]
8		8	40
9		6	27

[a] Reaction conditions: aryl halide (1.50 mmol, 1.0 equiv), 3,5-dimethyl phenyl boronic acid (1.65 mmol, 1.1 equiv), K_2CO_3 (3.0 mmol, 2.0 equiv), DMF (2.5 ml), 0.5 mol% of Pd-catalyst.
[b] 0.5 ml H_2O added into the reaction mixture.

Table 4
Coupling of aryl halides with 2-biphenyl boronic acid[a]

Entry	Aryl halide	Pd-catalyst	Yield (%)
	4-Bromotoluene		
1		2	68[b]
2		4	51[b]
3		6	49[b]
4		6	35
5		8	8[b]
	2-Br-m-xylene		
6		2	49[b]
7		4	39[b]
8		6	38[b]

[a] Reaction conditions: aryl halide (1.45 mmol, 1.0 equiv), 2-biphenyl boronic 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.
[b] 0.5 ml H_2O added into the reaction mixture.

produced similar results. Therefore in our study, it can be concluded that the position of the nitrogen atom in the quinoline ring does not seem to have an influence on the catalytic efficiencies of the tested ligands. The addition of water seemed to increase the yields in all reactions and for all complexes as expected.

Due to the promising results with the activated aryl chloride 2-chloroquinoline, the testing was further extended to more demanding inactivated aryl chlorides, which so far have been produced with only limited success under microwave irradiation under these conditions [31]. Unfortunately the coupling reactions between phenyl boronic acid and 2-chlorotoluene, 2-chloroxylene and 4-chloromethoxybenzene either failed or produced less than 10% yields with all mononuclear complexes **2**, **4** and **6**. Consequently, further testing was not conducted.

4. Conclusion

The quinolinyl phenyl and diphenylphosphanes can be prepared by a reaction between the haloquinoline and aryl phosphane by lithiating either. The quinolinyl phenyl and diphenylphosphane complexes readily coordinate with palladium(II) under standard reaction conditions. It is possible to prepare either mono- or dinuclear palladium complexes with these ligands depending on the choice of solvent. The mononuclear palladium complex of 2-quinolinyl diphenylphosphane forms a *cis*-isomer due to the attractive forces between the two ligands. The nitrogen atoms in the quinoline rings of the quinolinyl phenylphosphane ligands do not form a bond with the palladium atom and the structures remain non-chelated, which is also reflected in the catalytic activity of the complexes. The prepared mononuclear palladium complexes are moderately active in the Suzuki–Miyaura coupling of various simple and moderately demanding aryl halides and phenyl boronic acids. They also produce high yields in most reactions. The reaction setup is simple and can be conducted in air using low catalyst loadings. Microwave heating enables fast reaction times. The addition of a small amount of water to the reaction mixture further increases the yields in all coupling reactions. No reaction, or only a small yield is observed when bulky substrates or inactivated aryl chlorides are used.

Appendix A. Supplementary material

CCDC 650409 and 650410 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.09.009.

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