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Mixed phosphine/*N*-heterocyclic carbene palladium complexes: synthesis, characterization and catalytic use in aqueous Suzuki–Miyaura reactions†

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A series of *N*-heterocyclic carbene (NHC)/PR_3 palladium(II) and palladium(0) complexes has been synthesized and fully characterized. X-ray crystallographic data have allowed comparison of ligand steric properties. The NHC ligand was found to vary its steric properties as a function of the phosphine co-ligand. These complexes display interesting catalytic properties in the Suzuki–Miyaura reaction performed in aqueous media. The pre-catalyst [$PdCl_2$(IPr)(XPhos)] (IPr = *N*,*N*′-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene; XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) was found to be the most efficient system, promoting the coupling of a wide range of aryl chlorides with boronic acids in aqueous media with a typical catalyst loading of 0.03 mol%.

Introduction

The 2010 Nobel Prize in Chemistry was awarded to Heck, Negishi and Suzuki for their seminal contributions to the field of C–C bond formation using palladium catalysis.[1] Recent developments in palladium-mediated cross-coupling catalysis have led to unprecedented advances in natural product, polymer and pharmaceutical compound syntheses.[2,3] Among cross-coupling reactions, the Suzuki–Miyaura reaction is one of the most popular and successful cross-coupling protocols,[4] allowing the efficient synthesis of pharmaceutically relevant biaryl compounds from non-toxic and versatile starting materials.[5] During the last decade, a major advance has been the development of catalysts enabling the coupling of boronic acids with chlorinated compounds.[6] Electron-rich phosphines[6b,e,f] and *N*-heterocyclic carbenes (NHC)[7] have been used as palladium catalyst modifiers in cross-coupling.[8,9] Combining both classes of ligands on the same metal has lead to highly active and stable catalysts.[10,11] The growing interest in sustainable development has triggered tremendous research activity in catalysis conducted in non-traditional media.[12] In particular, work has focused on the development of Suzuki–Miyaura coupling systems carried out in water.[13] The interest in this area of research primary resides in the potential of palladium cross-coupling catalysis to create C–C linkages required to generate novel bioactive molecules.[14] In this context, NHC-based systems have shown promising, but these studies are plagued by the need of very high catalyst loadings.[15] As part of our program exploring ligand synergism in catalysis, we wished to probe such potentially beneficial effects using PR_3/NHC mixed systems in the Suzuki–Miyaura reaction conducted in aqueous media. Herein, we report the synthesis and full characterization of well-defined mixed tertiary phosphine/NHC palladium systems and their corresponding catalytic performance in aqueous Suzuki–Miyaura reactions.

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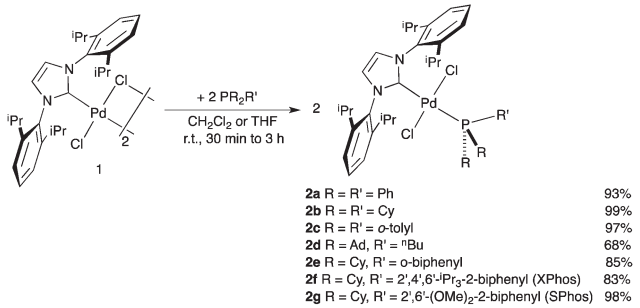
†Electronic supplementary information (ESI) available: Experimental details, kinetic experiments, NMR spectra, $\%V_{Bur}$ and mapping. CCDC 871882 **2a**, 871883 **2b**, 871884 **2c**, 871885 **2d**, 910518 **2e**, 871887 **2f**, 871888 **2g**, 913234 **5** and 871889 **6**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32858e

Results and discussion

Synthesis and characterization of [$PdCl_2$(IPr){P(R_2R')}] complexes

A series of [$PdCl_2$(IPr){P(R_2R')}] (IPr = *N*,*N*′-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene) complexes was straightforwardly synthesized by cleavage of [Pd(μ-Cl)(Cl)(IPr)]$_2$ (**1**)[16] with a tertiary phosphine. To test the generality of the method, several tertiary phosphine ligands possessing varied steric and electronic properties were selected and subjected to these reaction conditions (Scheme 1). As IPr-based complexes have proven best for the Suzuki–Miyaura coupling,[8c,17,18a] the IPr ligand was selected as the NHC of choice for the present study. Complexes **2a–g** are easily obtained in microanalytically pure form and in good to excellent yields (Scheme 1).

The aromatic protons of the phosphine appear as sharp signals for complexes **2a, b, d, f** and **2g** whereas complexes **2c** and **2e** show broad resonances. The broadness of the resonances suggested a restricted rotation of the phosphine ligand. This could be explained by the steric bulk of tri(*o*-tolyl)-phosphine for complex **2c**. In the case of **2e**, a palladium–arene interaction would explain a restricted rotation.[6e] Variable Temperature (VT) NMR experiments were carried out in $C_2D_2Cl_4$ at 298, 323, 348 and 373 K (see ESI†). A sharpening of the peaks was observed upon heating, permitting correct ^{1}H NMR assignments. Samples were then left to cool and again analyzed by NMR. The observed spectra were identical to the initial ones recorded at 298 K, confirming that these complexes conserved their integrity throughout the experiment. The electronic environment around the carbene carbon remains relatively constant across the series of complexes of type **2**, the carbenic carbon C^2 presenting a chemical shift within a narrow range of 170–174 ppm. The important $^2J_{CP}$ coupling constant (180 to 197 Hz) is characteristic of the *trans* position of the phosphorus ligand with respect to the NHC.[18] The imidazole backbone carbon atoms, C^4 and C^5, appear as a doublet (120–125.1 ppm, $^4J_{CP}$ = 5.1–5.7 Hz). ^{31}P–{^{1}H} NMR spectra of all complexes interestingly showed sharp singlets shifted downfield when compared to the free phosphine at room temperature. Table 1 summarizes selected ^{13}C–{^{1}H} and ^{31}P–{^{1}H} NMR data associated with complexes **2a–g**.



Scheme 1 Synthesis of [$PdCl_2$(IPr){$P(R_2R')$}] complexes.

Table 1 Selected ^{13}C–{^{1}H} and ^{31}P–{^{1}H} NMR data for complexes **2a–g** (δ in ppm, J in Hz)[a]

	C^4C^5		$C_{carbene}$		^{31}P
Complex (PR_2R')	δ_C	$^4J_{CP}$	δ_C	$^2J_{CP}$	δ_P
(**2a**) (PPh_3)	124.4	5.7	171.1	199.2	20.4
(**2b**) (PCy_3)	124.1	5.2	174.5	182.4	22.0
(**2c**) (P(*o*-tolyl)$_3$)	124.5	5.6	170.9	197.1	19.2
(**2d**) (P(Ad)$_2$(^{n}Bu))	124.0	5.1	171.9	181.9	28.6
(**2e**) (PCy_2(*o*-biph))	124.3	5.3	173.7	186.9	25.8
(**2f**) (XPhos)	124.0	5.3	174.1	187.8	42.5
(**2g**) (SPhos)	124.1	5.4	174.0	187.4	43.3

[a] ^{13}C–{^{1}H} spectra were recorded in $CDCl_3$; ^{31}P–{^{1}H} spectra were recorded in CD_2Cl_2. NMR were recorded at 298 K.

Structural features for complexes **2a–g** were unambiguously determined by single crystal X-ray diffraction studies.[19] Graphical representations are provided in Fig. 1 with selected bond distances and angles presented in Table 2. Complexes of type **2** show a slightly distorted square planar geometry, with angles between adjacent ligands ranging from 88.40(5)° to 94.26(7)°, displaying a *trans* configuration of the phosphine ligand to the *N*-heterocyclic carbene. The Pd–Cl bond distances of these

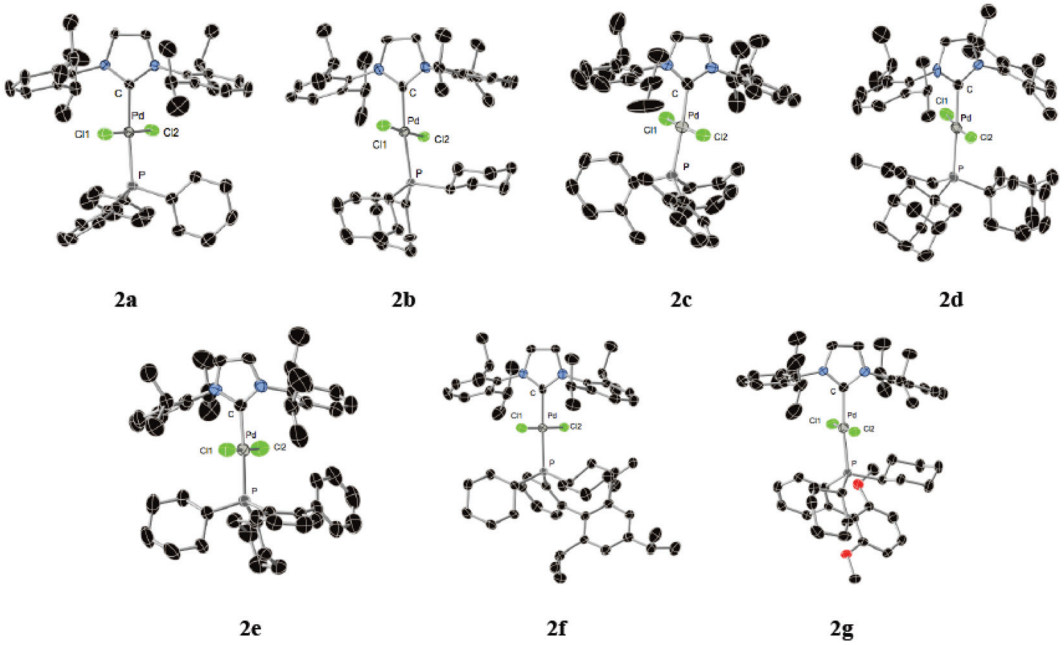


Fig. 1 Molecular representations of [$PdCl_2$(IPr)(PPh_3)] (**2a**), [$PdCl_2$(IPr)(PCy_3)] (**2b**), [$PdCl_2$(IPr){P(*o*-tolyl)$_3$}] (**2c**), [$PdCl_2$(IPr){P(1-Ad)$_2$(^{n}Bu)}] (**2d**), [$PdCl_2$(IPr){PCy_2-(*o*-biphenyl)}] (**2e**), [$PdCl_2$(IPr)(XPhos)] (**2f**) and [$PdCl_2$(IPr)(SPhos)] (**2g**). Solvent molecule (CH_2Cl_2 for **2c** and **2f**) and hydrogen atoms are omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) (esd) and $\%V_{Bur}$ values

	2a PPh_3	**2b** PCy_3	**2c** P(*o*-tol)$_3$	**2d** P(Ad)$_2$(*n*Bu)	**2e** PCy_2(*o*-biph)	**2f** XPhos	**2g** SPhos
Pd–C	2.032(5)	2.034(5)	2.032(6)	2.040(8)	2.036(3)	2.055(5)	2.054(3)
Pd–P	2.3054(13)	2.3344(12)	2.3547(15)	2.3671(19)	2.3359(10)	2.3211(14)	2.3319(9)
Pd–Cl1	2.2849(13)	2.3067(13)	2.3002(15)	2.3248(19)	2.3132(10)	2.3133(13)	2.3160(9)
Pd–Cl2	2.2873(14)	2.3136(13)	2.3127(15)	2.293(2)	2.2930(10)	2.3027(12)	2.2932(9)
C–Pd–P	173.95(14)	174.84(14)	175.67(18)	177.2(2)	173.19(9)	178.24(14)	174.73(9)
C–Pd–Cl1	87.30(13)	88.79(13)	90.73(15)	88.4(2)	85.75(9)	90.76(13)	88.61(9)
C–Pd–Cl2	92.57(13)	89.47(13)	88.89(15)	86.6(2)	92.82(9)	88.24(13)	91.46(9)
P–Pd–Cl1	87.06(5)	92.32(5)	92.37(5)	94.26(7)	87.46(4)	89.89(5)	91.20(3)
P–Pd–Cl2	93.11(5)	89.56(4)	88.40(5)	90.69(7)	93.98(4)	91.08(5)	88.74(3)
Cl1–Pd–Cl2	179.06(6)	177.58(5)	172.97(7)	174.28(7)	178.48(4)	178.38(5)	179.87(4)
NHC $\%V_{Bur}$[a]	34.3	32.1	32.8	33.2	33.7	33.8	32.3
PR_3 $\%V_{Bur}$[a]	31.8	35.2	39.0	37.2	38.0	36.2	35.6

[a] When two independent structures were found in single crystal X-ray diffraction experiments, $\%V_{Bur}$ were calculated for both. For clarity, only one value is given. Full details can be found in the ESI.

complexes fall between the values found for the Pd–(μ-Cl) and Pd–Cl distances of the parent dimer [Pd(μ-Cl)Cl(IPr)]$_2$: (Pd–(μ-Cl) = 2.4029(9) Å, Pd–Cl = 2.2715(9) Å).[16]

On the other hand, these Pd–Cl distances are similar to those found for phosphite analogues [$PdCl_2$(IPr){P(OR)$_3$}].[18a] The Pd–P bond distances found in complexes of type **2** are longer than those found in phosphite-containing Pd(II) complexes, a similar trend previously observed with Ru species.[18b] Buried volumes ($\%V_{Bur}$) calculated using the Samb*V*ca application[20] show that the NHC ligand adapts its bulkiness to the phosphine occupying a relative *trans* position.[18a] The highest value for the NHC $\%V_{Bur}$ is calculated in the PPh_3-containing complex **2a** (34.3 for the NHC moiety, 31.8 for the phosphine). Complex **2b**, featuring PCy_3, shows the smallest $\%V_{Bur}$ for the carbene ligand (32.1), while 35.2 is calculated for the phosphine. If no drastic differences in sterics were observed with the NHC ligands, the study brought in light the very different steric environments displayed by the phosphines (see ESI†). No clear trend with Pd–$C_{carbene}$ bond length and the $\%V_{Bur}$ or σ donating properties of the phosphine ligands were observed, suggesting that both *trans*-influence and steric properties do have an effect.

Synthesis of [Pd(μ-Cl)(Cl)(SPhos)]$_2$ (5)

In order to assess the synergy resulting from the presence of mixed ligands, the phosphine-based dimer [Pd(μ-Cl)(Cl)-(SPhos)]$_2$ (**5**) was synthesized (Scheme 2).

The $^{31}P–\{^1H\}$ NMR spectrum of the complex exhibits a singlet at 53.3 ppm. The Pd–P bond distance observed in the dimer is shorter than the one found in the IPr/SPhos Pd(II) complex **2g** (2.247(3) Å for **5**, 2.3319(9) for **2g**) (Fig. 2).[21]

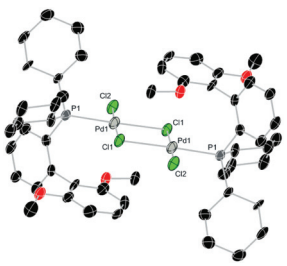
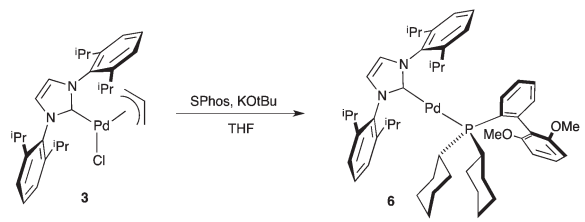


Fig. 2 Molecular representation of [Pd(μ-Cl)Cl(SPhos)]$_2$ (**5**). Selected bond distances (Å) and angles (°): Pd1–P1 2.247(3); Pd–Cl1 2.329(3); Pd–Cl2 2.283(3).

Synthesis of [Pd(IPr)(SPhos)] (6)

As [Pd(0)L$_n$] (n = 1 or 2)[22] complexes are believed to be the active species entering the catalytic cycle in cross coupling reactions, the synthesis of the mixed (NHC)/phosphine complex [Pd(IPr)(SPhos)] (**6**) was investigated. This compound was obtained using a one-pot reaction involving [Pd(η^3-allyl)Cl-(IPr)] **3**, SPhos and KO^{t}Bu (Scheme 3). [Pd(IPr)(SPhos)] (**6**) presents similar NMR features as its Pd(II) analogues: the backbone carbons C^4 and C^5 appear as a doublet (125.1 ppm, $^4J_{CP}$ = 17.2 Hz), the carbene carbon atom was shifted downfield when compared to the Pd(II) compounds and presented a much lower coupling constant with the phosphorus atom (199.5 ppm, $^2J_{CP}$ = 84.5 Hz).

Scheme 2 Synthesis of [Pd(μ-Cl)Cl(SPhos)]$_2$ (**5**).



Scheme 3 Synthesis of [Pd(IPr)(SPhos)] (**6**).

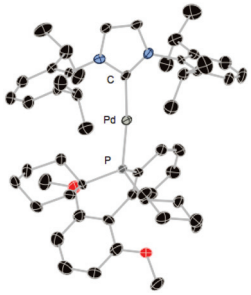


Fig. 3 Molecular representation of [Pd(IPr)(SPhos)] (**6**). Selected bond distances (Å) and angles (°): Pd–C: 2.022(8); Pd–P: 2.248(2); C–Pd–P: 172.9(2).

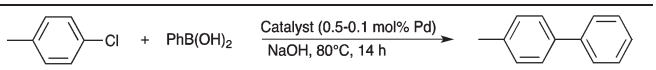
Finally, the $^{31}P–\{^{1}H\}$ NMR spectrum exhibits a sharp singlet at 66.9 ppm. An X-ray diffraction study on single crystal was performed on **6**. The molecular representation as well as selected bond distances and angles are presented in Fig. 3.

This complex presents a slightly distorted linear geometry and displays shorter Pd–C and Pd–P bond distances than its corresponding Pd(II) complex. The $\%V_{Bur}$ associated with the phosphine (36.3) varies only slightly from its Pd(II) counterpart (35.6), while the steric constrain of the NHC on the metal centre (43.9) is much larger in the absence of the chlorine atoms (32.3 for the Pd(II) analogue). The steric mapping of the Pd(0) clearly proves that the NHC ligand adapts its bulkiness in order to occupy the maximum area around the dicoordinated metal (see ESI†). This result further supports the non-negligible flexibility of the NHC ligands.

Catalytic studies

In order to gauge the effect of this mixed ligation about palladium, catalytic studies were performed in the Suzuki–Miyaura reaction in water. The benchmark coupling of 4-chlorotoluene with phenylboronic acid performed with a catalyst loading of 0.5 mol% was first investigated. Since NaOH was found to be the most efficient base in a previous study on carbene–phosphite Pd(II) pre-catalysts for Suzuki–Miyaura,[18a] the water-soluble and inexpensive base was selected for the present study.[23] Pre-catalysts **2a** and **2b** were first tested in pure water in reactions carried out for 14 hours at 80 °C (Table 3, entries 2 and 4). The rapid formation of palladium black was observed under these conditions, leading to limited conversions. Nolan and co-workers have successfully performed Suzuki–Miyaura couplings under mild conditions using technical grade isopropanol (containing amounts of water) as a solvent.[8a] Gratefully, using isopropanol as an additive (H_2O : ^{i}PrOH 9 : 1) resulted in a drastic improvement of the activity of **2a** and **2b** (Table 3, entries 3 and 5). The catalytic performance of our NHC/phosphine mixed system was then compared to that of the commercially available complexes [Pd(μ-Cl)(Cl)(IPr)]$_2$, (**1**),[16] [Pd(η^3-allyl)(Cl)(IPr)] (**3**),[24] [PdCl$_2$(IPr)(3-chloropyridine)] (**4**)[25] and the Buchwald phosphine-based dimer complex [Pd(μ-Cl)(Cl)-(SPhos)]$_2$ (**5**). Only poor to moderate conversions were obtained with 0.5 mol% Pd of the commercially available systems **1**, **3** and **4** (Table 3, entries 1, 11 and 12) and with the phenyl, cyclohexyl, tolyl and adamantyl phosphine-based complexes **2a–d** (Table 3, entries 3, 5–7). Noticeably, all biphenylphosphine-based catalysts led to complete conversion of the substrates with only 0.1 mol% Pd, regardless of the type of complexes (Table 3, entries 8–10 and 13–14).

Table 3 Catalysts screening[a]



Entry	Catalyst	Loading (mol%)	Conv.[b] (%)
1	[Pd(μ-Cl)(Cl)(IPr)]$_2$ **1**	0.5	37
2	[PdCl$_2$(IPr)(PPh$_3$)] **2a**	0.5	22[c]
3	[PdCl$_2$(IPr)(PPh$_3$)] **2a**	0.5	42
4	[PdCl$_2$(IPr)(PCy$_3$)] **2b**	0.5	6[c]
5	[PdCl$_2$(IPr)(PCy$_3$)] **2b**	0.5	19
6	[PdCl$_2$(IPr){P(*o*-tolyl)$_3$}] **2c**	0.5	43
7	[PdCl$_2$(IPr){P(1-Ad)$_2$(^{n}Bu)}] **2d**	0.5	22
8	[PdCl$_2$(IPr){PCy$_2$(*o*-biphenyl)}] **2e**	0.1	>99
9	[PdCl$_2$(IPr)(XPhos)] **2f**	0.1	>99
10	[PdCl$_2$(IPr)(SPhos)] **2g**	0.1	>99
11	[Pd(η^3-allyl)(Cl)(IPr)] **3**	0.5	42
12	[PdCl$_2$(IPr)(3-chloropyridine)] **4**	0.5	57
13	[Pd(μ-Cl)(Cl)(SPhos)]$_2$ **5**	0.1	>99
14	[Pd(IPr)(SPhos)] **6**	0.1	96

[a] Reaction conditions: 4-chlorotoluene (1 mmol), PhB(OH)$_2$ (1.05 mmol), NaOH (1.5 mmol), catalyst 0.5–0.1 mol% Pd, H_2O : ^{i}PrOH (9 : 1) (0.5 mL), 80 °C, 14 h. [b] Conversion to coupling product, based on 4-chlorotoluene, determined by GC (average of two runs). [c] Performed in H_2O.

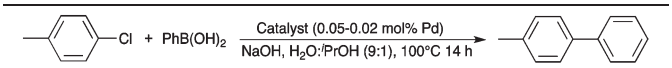
Interestingly and not surprisingly, [PdCl$_2$(IPr)(SPhos)] (**2g**) and its Pd(0) analogue led to similar conversions (Table 3, entries 10 and 14), supporting the existence of the same active species in the catalytic cycle. In order to study this case in more details, a comparative reaction profiling was performed. At 80 °C, a slight induction period was observed for the Pd(II) complex [PdCl$_2$(IPr)(SPhos)] **2g** whereas the Pd(0) species [Pd(IPr)(SPhos)] **6** reacted immediately (see ESI†). Considering the air-sensitive nature of **6** and the difficulty associated with its handling, the remainder of this study was carried out with Pd(II) precursors.

To test the limits of the biphenylphosphine-based complexes, low catalyst loading (0.05–0.02 mol%) experiments were performed (Table 4). At a catalyst loading of 500 ppm, mixed NHC/Buchwald phosphine ligand based complexes **2e–g** displayed higher activities than the corresponding dimer **5** (Table 4, entries 1–4). Decreasing the catalyst loading to 200 ppm (Table 4, entries 5–7), [PdCl$_2$(IPr)(XPhos)] (**2f**) was found to be the best catalyst among the NHC/phosphine complexes (TON of 4300) and was therefore selected to further explore the scope of the Suzuki–Miyaura reaction under these optimized reaction conditions.

Scope of the reaction

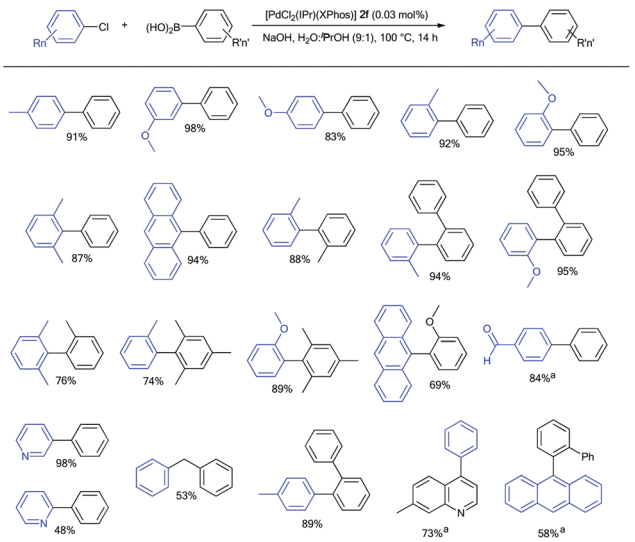
In order to investigate the efficiency and versatility of [PdCl$_2$(IPr)(XPhos)] **2f** under aqueous conditions, various aryl

Table 4 Low catalyst loading study[a]



Entry	Catalyst	Load. (mol%)	Conv.[b] (%)	TON
1	[$PdCl_2$(IPr){PCy_2(*o*-biphenyl)}] **2e**	0.05	93	1860
2	[$PdCl_2$(IPr)(XPhos)] **2f**	0.05	>99	>1980
3	[$PdCl_2$(IPr)(SPhos)] **2g**	0.05	>99	>1980
4	[Pd(μ-Cl)(Cl)(SPhos)]$_2$ **5**	0.05	51	1020
5	[$PdCl_2$(IPr){PCy_2(*o*-biphenyl)}] **2e**	0.02	36	1800
6	[$PdCl_2$(IPr)(XPhos)] **2f**	0.02	86	4300
7	[$PdCl_2$(IPr)(SPhos)] **2g**	0.02	53	2650

[a] Reaction conditions: 4-chlorotoluene (1 mmol), $PhB(OH)_2$ (1.05 mmol), NaOH (1.5 mmol), pre-catalyst injected from a 0.01 mol L^{-1} stock solutions (THF was used due to the poor solubility of the catalyst in isopropanol), solvent: H_2O : ^{i}PrOH, 9 : 1 (0.5 mL), 100 °C, 14 h. [b] Conversion to coupling product, based on 4-chlorotoluene, determined by GC (average of two runs).



Scheme 4 Substrate scope using **2f** (isolated yields; [a]0.06 mol% Pd used).

chlorides were reacted with a number of boronic acids (Scheme 4).

Phenylboronic acid could be coupled in excellent yields with a number of deactivated aryl chloride substrates, namely, methyl or methoxy groups in *ortho*, *meta* and *para* positions. 2-Chloro-*m*-xylene as well as 9-chloroanthracene were also reacted with phenylboronic acid and reactions provided yields of 87% and 94%, respectively. *Ortho*-substituted boronic acids and *ortho*-substituted aryl chlorides could be coupled to yield a number of bi- and tri-*ortho*-substituted biaryls as well as terphenyl derivatives in good to quantitative yields. Finally, this methodology also proved efficient for the coupling of heteroaromatic compounds, which are regarded as challenging substrates, as well as benzyl chloride. Notably, 2-chloropyridine and 3-chloropyridine were reacted with phenylboronic acid and provided quite different reaction outcomes: no starting material could be observed by GC, but 2-phenylpyridine could only be isolated in 48% yield, and 3-phenylpyridine was isolated in quantitative yield in pure form using a simple aqueous workup followed by a filtration through a pad of silica. This reactivity difference could be explained by a more facile dehalogenation of 2-chloropyridine under the catalytic conditions, with 3-chloropyridine undergoing the Suzuki coupling at a higher rate. The hydrodehalogenation reaction has indeed been observed with NHC-based catalytic systems.[26] Of note, electron-poor substrates were found to give lower conversions and require higher catalyst loadings than electron-rich deactivated substrates.

Conclusions

In summary, a series of mixed NHC/tertiary phosphine palladium complexes has been successfully synthesized and fully characterized. The structural data emerging from single crystal X-ray diffraction studies permit an analysis of ligand steric properties. These palladium complexes were tested for catalytic activity in the Suzuki–Miyaura cross-coupling in an aqueous medium comprised of water–isopropanol as a 9 : 1 mixture, using NaOH as the operational base. The best catalyst among those examined is [$PdCl_2$(IPr)(XPhos)] (**2f**). This pre-catalyst permits the successful synthesis of a broad range of biaryls from aryl chlorides using a typical catalyst loading of 0.03 mol%. Sterically hindered biaryls, including tri-*ortho*-substituted species and terphenyls, were synthesized in high yields from aryl chlorides and boronic acids. Further studies aimed at exploring catalytic behaviour in aqueous media are currently being studied in our laboratories.

Experimental section

General considerations

All reactions were performed under an inert atmosphere of argon or nitrogen using standard Schlenk line and glovebox techniques. Solvents were dispensed from a solvent purification system from Innovative Technology. Flash column chromatography was performed on silica gel 60 (230–400 mesh). ^{1}H, ^{13}C{^{1}H} and ^{31}P–{^{1}H} nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC300 or on a Bruker Avance 400 Ultrashield spectrometer at 298 K unless otherwise stated. All reagents and commercial catalysts were purchased and used as received unless otherwise stated. HRMS samples were submitted to EPSRC National Mass Spectrometry Service Centre (http://www.swan.ac.uk/nmssc/index.html).

General procedure for the synthesis of complexes of the type [$PdCl_2$(IPr)(PR_2R')].

Synthesis of complexes 2a–e. In a glovebox, a Schlenk flask was charged with [Pd(μ-Cl)(Cl)(IPr)]$_2$ (200 mg, 0.177 mmol) and the appropriate phosphine (0.344 mmol) and closed with

a septum. Outside the glovebox, CH_2Cl_2 (3 mL) was injected through a septum and the reaction mixture was stirred at room temperature until the solution became clear. The solvent was reduced *in vacuo* (1 mL) and absolute ethanol (3 mL) was added. The solvent was reduced *in vacuo* until the appearance of a precipitate. The supernatant solution was removed and the resulting powder was dried under vacuum.

[$PdCl_2$(IPr)(PPh_3)] (2a). The procedure yielded 272 mg (93%) of the analytically pure product as a microcrystalline yellow powder. ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K) δ (ppm) = 1.09 (d, $^3J_{H-H}$ = 6.7 Hz, 12H, CH–CH_3), 1.31 (d, $^3J_{H-H}$ = 6.7 Hz, 12H, CH–CH_3), 3.19 (sept, $^3J_{H-H}$ = 6.7 Hz, 4H, CH–CH_3), 7.18 (d, J = 1.6 Hz, 2H, H^4 H^5), 7.21–7.30 (m, 12H, CH PPh_3), 7.32–7.37 (m, 3H, CH PPh_3), 7.40 (d, $^3J_{H-H}$ = 7.8 Hz, 4H, Ar CH), 7.58 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, Ar CH). ^{13}C–{^{1}H} NMR ($CDCl_3$, 75.47 MHz, 298 K) δ (ppm) = 23.1 (s, CH–CH_3), 26.4 (s, CH–CH_3), 28.8 (s, CH–CH_3), 123.9 (s, CH), 124.4 (d, $^4J_{C-P}$ = 5.3 Hz, C^4 C^5), 127.7 (d, J = 10.6 Hz, CH), 129.8 (d, J_{C-P} = 2.3 Hz, CH), 129.9 (s, CH), 130.5 (d, $^1J_{C-P}$ = 44.5 Hz, C–P), 135.1 (d, J_{C-P} = 10.6 Hz, CH), 135.7 (s, C^{IV}), 149.0 (s, C^{IV}), 171.1 (d, $^2J_{C-P}$ = 199.2 Hz, C^2). ^{31}P–{^{1}H} NMR (CD_2Cl_2) δ (ppm) = 20.4. Anal. calcd for $C_{45}H_{51}N_2Cl_2PPd$: C, 65.26; H, 6.21; N, 3.38. Found: C, 65.42; H, 6.09; N, 3.54.

[$PdCl_2$(IPr)(PCy_3)] (2b). The procedure yielded 298 mg (99%) of the analytically pure product as a colourless powder. ^{1}H NMR (CD_2Cl_2, 400 MHz, 278 K) δ (ppm) = 1.06 (d, $^3J_{H-H}$ = 6.6 Hz, 12H, CH–CH_3), 1.08 (br s, 8H, Cy CH_2), 1.25–1.33 (m, 7H, Cy CH_2), 1.36 (d, $^3J_{H-H}$ = 6.6 Hz, 12H, CH–CH_3), 1.58 (br s, 15H, Cy CH_2), 2.09 (dt, $^2J_{H-P}$ = 12.0 Hz, $^3J_{H-H}$ = 12.0 Hz, 3H, P–CH), 3.18 (sept, $^3J_{H-H}$ = 6.6 Hz, 4H, CH–CH_3), 7.11 (d, J = 1.6 Hz, 2H, H^4, H^5), 7.31 (d, $^3J_{H-H}$ = 7.6 Hz, 4H, Ar CH), 7.44 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, Ar CH). ^{13}C–{^{1}H} NMR ($CDCl_3$, 100.62 MHz, 298 K) δ (ppm) = 22.9 (s, CH–CH_3), 26.5 (s, Cy CH_2), 26.6 (s, CH–CH_3), 27.6 (d, J_{C-P} = 10.5 Hz, Cy CH_2), 28.7 (s, CH–CH_3), 29.3 (s, Cy CH_2), 31.3 (d, $^1J_{C-P}$ = 20 Hz, P–CH), 123.4 (s, Ar CH), 124.1 (d, $^4J_{C-P}$ = 5.3 Hz, C^4, C^5), 129.7 (s, Ar CH), 135.7 (s, C^{IV}), 147.1 (s, C^{IV}), 174.5 (d, $^2J_{C-P}$ = 182.4 Hz, C^2). ^{31}P–{^{1}H} NMR (CD_2Cl_2) δ (ppm) = 22.1. Anal. calcd for $C_{45}H_{69}Cl_2N_2PPd$: C, 63.86; H, 8.22; N, 3.31. Found: C, 63.74; H, 8.29, N, 3.45.

[$PdCl_2$(IPr){P(*o*-tolyl)$_3$}] (2c). The procedure yielded 298 mg (97%) of the analytically pure product, as a yellow powder. ^{1}H NMR ($C_2D_2Cl_4$, 300 MHz, 348 K) δ (ppm) = 1.07 (d, $^3J_{H-H}$ = 6.7 Hz, 12H, CH–CH_3), 1.25 (d, $^3J_{H-H}$ = 6.7 Hz, 12H, CH–CH_3), 1.87 (br s, 9H, C–CH_3), 3.22 (sept, $^3J_{H-H}$ = 6.7 Hz, 4H, CH–CH_3), 6.94–7.03 (m, 7H, Ar CH), 7.13 (d, J = 1.3 Hz, 2H, H^4 H^5), 7.23 (br t, $^3J_{H-H}$ = 7.4 Hz, 4H, Ar CH), 7.38 (d, $^3J_{H-H}$ = 7.7 Hz, 4H, Ar CH), 7.56 (t, $^3J_{H-H}$ = 7.7 Hz, 2H, Ar CH). ^{13}C–{^{1}H} NMR ($CDCl_3$, 75 MHz, 298 K) δ (ppm) = 22.7 (s, CH–CH_3), 23.7 (br s, C–CH_3), 26.7 (s, CH–CH_3), 28.8 (s, CH–CH_3), 123.7 (s, Ar CH), 124.5 (d, $^4J_{C-P}$ = 5.6 Hz, C^4 C^5), 124.8 (br s, Ar CH), 129.7 (br s, Ar CH), 130.0 (s, Ar CH), 131.1 (d, J_{C-P} = 7.8 Hz, Ar CH), 133.1 (br s, Ar CH), 135.7 (s, C^{IV}), 143.4 (d, J_{C-P} = 7.3 Hz, C^{IV}), 147.4 (s, C^{IV}), 170.9 (d, $^2J_{C-P}$ = 197.1 Hz, C^2). ^{31}P–{^{1}H} NMR (CD_2Cl_2) δ (ppm) = 19.2. Anal. calcd for $C_{48}H_{57}N_2Cl_2PPd$: C, 66.24; H, 6.40; N, 3.22. Found: C, 65.87; H, 6.79; N, 3.34.

[$PdCl_2$(IPr){P(1-adamantyl)$_2$(^{n}Bu)}] (2d). The procedure yielded 221 mg (68%) of the analytically pure product as a white powder. (CD_2Cl_2, 400 MHz, 278 K) δ (ppm) = 0.81 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, CH_2–CH_3), 1.05 (d, $^3J_{H-H}$ = 6.7 Hz, 12H, CH–CH_3), 1.17–1.32 (m, 4H, CH_2), 1.37 (d, $^3J_{H-H}$ = 6.7 Hz, 12H, CH–CH_3), 1.52–1.62 (m, 2H, CH_2), 1.59 (br s, 12H, Ad-H), 1.77 (br s, 6H, Ad-H), 1.96–2.08 (m, 12H, Ad-H), 3.22 (br s, 4H, CH–CH_3), 7.12 (d, J = 1.4 Hz, 2H, H^4, H^5), 7.31 (d, $^3J_{H-H}$ = 7.7 Hz, 4H, Ar CH), 7.44 (t, $^3J_{H-H}$ = 7.7 Hz, 2H, Ar CH). ^{13}C–{^{1}H} NMR ($CDCl_3$, 75.47 M Hz, 298 K) δ (ppm) = 14.1 (s, CH_3), 15.3 (d, J_{C-P} = 19.5 Hz, CH_2), 22.8 (s, CH–CH_3), 25.4 (d, J_{C-P} = 13.3 Hz, CH_2), 26.7 (s, CH–CH_3), 27.8 (d, J_{C-P} = 8.9 Hz, CH), 28.8 (s, CH–CH_3), 28.8 (s, CH), 28.9 (s, CH), 29.1 (s, CH_2), 36.6 (d, J_{C-P} = 6.9 Hz, CH), 36.8 (s, CH_2), 39.9 (s, CH_2), 40.2 (d, $^1J_{C-P}$ = 11.5 Hz, Ad C^{IV}), 123.4 (s, Ar CH), 124.0 (d, $^4J_{C-P}$ = 5.1 Hz, C^4, C^5), 129.7 (s, Ar CH), 135.8 (s, C^{IV}), 147.2 (s, C^{IV}), 171.9 (d, $^2J_{C-P}$ = 181.9 Hz, C^2). ^{31}P–{^{1}H} NMR (CD_2Cl_2) δ (ppm) = 26.6. Anal. calcd for $C_{51}H_{75}N_2Cl_2PPd$: C, 66.26; H, 8.18; N, 3.03. Found: C, 66.15; H, 8.27; N, 3.14.

[$PdCl_2$(IPr){PCy_2(*o*-biphenyl)}] (2e). The procedure yielded 268 mg (85%) of the analytically pure product as a yellow powder. ^{1}H NMR ($C_2D_2Cl_4$, 300 MHz, 373 K) δ (ppm) = 0.79–1.17 (m, 10H, Cy), 1.09 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH–CH_3), 1.36 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH–CH_3), 1.47–1.51 (m, 8H, Cy), 1.81–1.93 (m, 4H, Cy), 3.28 (sept, $^3J_{H-H}$ = 6.8 Hz, 4H, CH–CH_3), 7.01–7.06 (m, 3H, Ar CH), 7.08 (m, 2H, H^4, H^5), 7.17–7.38 (m, 5H, Ar CH), 7.35 (m, 4H, Ar CH), 7.45–7.55 (m, 3H, Ar CH). ^{13}C–{^{1}H} NMR ($CDCl_3$, 75.47 MHz, 298 K) δ (ppm) = 22.8 (s, CH–CH_3), 26.4 (s, Cy CH_2), 26.5 (s, CH–CH_3), 27.4 (s, Cy CH_2), 27.6 (s, Cy CH_2), 27.8 (s, Cy CH_2), 28.7 (s, CH–CH_3), 29.3 (d, J_{C-P} = 5.2 Hz, Cy CH_2), 30.7 (d, J_{C-P} = 3.4 Hz, Cy CH_2), 31.3 (d, $^1J_{C-P}$ = 25.2 Hz, Cy CH), 123.8 (s, Ar CH), 124.3 (d, $^4J_{C-P}$ = 5.2 Hz, C^4, C^5), 125.7 (d, J_{C-P} = 8.5 Hz, Ar CH), 126.5 (d, $^2J_{C-P}$ = 31.4 Hz, C^{IV}), 126.6 (s, Ar CH), 128.4 (d, J_{C-P} = 6.3 Hz, Ar CH), 129.8 (s, Ar CH), 130.0 (s, Ar CH), 131.4 (d, J_{C-P} = 8.5 Hz, Ar CH), 135.3 (d, J_{C-P} = 8.7 Hz, Ar CH), 135.9 (s, C^{IV}), 141.7 (s, C^{IV}), 145.9 (d, J_{C-P} = 4.9 Hz, C^{IV}), 147.2 (s, C^{IV}), 173.69 (d, $^2J_{C-P}$ = 186.9 Hz, C^2). ^{31}P–{^{1}H} NMR (CD_2Cl_2) δ (ppm) = 25.8. Anal. calcd for $C_{51}H_{67}Cl_2N_2PPd$: C, 66.84; H, 7.37; N, 3.06. Found C, 66.84; H, 7.70; N, 3.14.

[$PdCl_2$(IPr)(XPhos)] (2f). In a glovebox, a Schlenk flask was charged with [Pd(μ-Cl)(Cl)(IPr)]$_2$ (283 mg, 0.25 mmol), XPhos (238.4 mg, 0.5 mmol) and THF (3 mL) was added. The reaction mixture was stirred for 3 hours. The solvent was evaporated, the resulting solid dissolved in CH_2Cl_2 (1 mL) and isopropanol (3 mL) was then added. The volume was reduced *in vacuo* until the appearance of a precipitate, the suspension cooled to −15 °C and the supernatant solution was removed. The resulting solid was dried under vacuum to give analytically pure **2f** (432 mg, 83%) as a pale yellow solid. ^{1}H NMR ($C_2D_2Cl_4$, 300 MHz, 373 K) δ (ppm) = 0.59–0.80 (m, 3H, CH–CH_3), 0.85 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, CH–CH_3), 0.91–1.20 (m, 10H, Cy), 1.10 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH–CH_3), 1.27–1.57 (m, 12H, Cy), 1.28 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, CH–CH_3), 1.39 (d, $^3J_{H-H}$ = 6.6 Hz, 12H, CH–CH_3), 1.98 (br s, 3H, CH–CH_3), 2.74 (sept, $^3J_{H-H}$ = 6.7 Hz, 2H, CH–CH_3), 2.90 (sept, $^3J_{H-H}$ = 6.9 Hz, 1H, CH–CH_3),

3.26 (sept, $^3J_{H-H}$ = 6.6 Hz, 4H, C*H*–CH_3), 6.83–6.86 (m, 1H, Ar CH), 6.95 (s, 2H, Ar CH), 6.98–7.07 (m, 1H, Ar CH), 7.09 (d, $^5J_{H-P}$ = 1.2 Hz, 2H, H^4, H^5), 7.17 (m, 1H, Ar CH), 7.33 (d, $^3J_{H-H}$ = 7.7 Hz, 4H, Ar CH), 7.48 (t, $^3J_{H-H}$ = 7.7 Hz, 2H, Ar CH), 7.82–7.90 (m, 1H, Ar CH). $^{13}C-\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 298 K) δ (ppm) = 22.8 (br s, CH–*C*H_3), 24.2 (s, CH–*C*H_3), 25.9 (s, Cy CH_2), 26.1 (s, CH–*C*H_3), 26.7 (br s, CH–*C*H_3), 27.0 (d, J_{C-P} = 12.6 Hz, Cy CH_2), 27.6 (d, J_{C-P} = 10.8 Hz, Cy CH_2), 28.8 (br s, CH–CH_3), 29.9 (d, J_{C-P} = 13.4 Hz, Cy CH_2), 30.0 (br s, *C*H–CH_3), 34.5 (s, *C*H–CH_3), 120.7 (br s, Ar CH), 123.4 (s, Ar CH), 124.0 (d, $^4J_{C-P}$ = 5.3 Hz, C^4, C^5), 124.6 (d, J_{C-P} = 13.6 Hz, Ar CH), 127.2 (d, J_{C-P} = 2.0 Hz, Ar CH), 129.6 (s, Ar CH), 130.0 (s, C^{IV}), 133.2 (d, J_{C-P} = 6.1 Hz, Ar CH)), 135.8 (s, C^{IV}), 137.1 (s, C^{IV}), 139.0 (d, J_{C-P} = 21.0 Hz, Ar CH), 142.7 (s, C^{IV}), 147.2 (s, C^{IV}), 148.2 (s, C^{IV}), 174.1 (d, $^2J_{C-P}$ = 187.8 Hz, C^2). $^{31}P-\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) = 42.5. Anal. calcd for $C_{60}H_{85}Cl_2N_2PPd$: C, 69.12; H, 8.22; N, 2.69. Found: C, 69.14; H, 7.92; N, 2.82.

[$PdCl_2$(IPr)(SPhos)] (2g). In a glovebox, a Schlenk flask was charged with $[Pd(\mu\text{-}Cl)(Cl)(IPr)]_2$ (283 mg, 0.25 mmol) and SPhos (205.3 mg, 0.5 mmol). THF (3 mL) was added and the solution was stirred for 3 hours. Addition of pentane (15 mL) led to a precipitate. The solid was collected by filtration and washed with hexanes (10 mL), leading to the analytically pure **2g** as a pale yellow solid (477 mg, 98%). ^1H NMR (CD_2Cl_2, 400 MHz, 278 K) δ (ppm) = 0.69–0.92 (m, 6H, Cy), 0.93–1.05 (m, 4H, Cy), 1.06 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH–CH_3), 1.28–1.42 (br s, 6H, Cy), 1.35 (d, $^3J_{H-H}$ = 6.6 Hz, 12H, CH–CH_3), 1.43–1.54 (br s, 4H, Cy), 1.71 (m, 2H, Cy), 3.19 (sept, $^3J_{H-H}$ = 6.7 Hz, 4H, C*H*–CH_3), 3.52 (s, 6H, O–CH_3), 6.50 (d, $^3J_{H-H}$ = 8.4 Hz, 2H, Ar CH), 6.77–6.82 (m, 1H, Ar CH), 7.04 (m, 1H, Ar CH), 7.14 (d, 2H, $^5J_{H-P}$ = 1.2 Hz, H^4, H^5), 7.19–7.30 (m, 2H, Ar CH), 7.34 (d, $^3J_{H-H}$ = 7.7 Hz, 4H, Ar CH), 7.41–7.46 (m, 1H, Ar CH), 7.48 (t, $^3J_{H-H}$ = 7.7 Hz, 2H, Ar CH). $^{13}C-\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 298 K) δ (ppm) = 22.9 (s, CH–*C*H_3), 26.1 (s, Cy CH_2), 26.7 (s, CH–*C*H_3), 27.1 (d, $^2J_{C-P}$ = 11.7 Hz, Cy CH_2), 27.3 (d, $^2J_{C-P}$ = 12.1 Hz, Cy CH_2), 28.2 (s, Cy CH_2), 28.7 (s, *C*H–CH_3), 30.3 (s, Cy CH_2), 31.9 (d, $^1J_{C-P}$ = 21.1 Hz, Cy CH), 55.0 (s, O–CH_3), 103.1 (s, Ar CH), 119.4 (s, C^{IV}), 123.4 (s, Ar CH), 124.1 (d, $^4J_{C-P}$ = 5.4 Hz, C^3, C^4), 124.3 (d, J_{C-P} = 14.2 Hz, Ar CH), 127.6 (d, $^1J_{C-P}$ = 33.2 Hz, C^{IV}), 128.5 (s, Ar CH), 128.9 (s, Ar CH), 129.7 (s, Ar CH), 131.8 (d, J_{C-P} = 5.7 Hz, Ar CH), 135.8 (s, Ar–C), 138.5 (d, J_{C-P} = 2.5 Hz, C^{IV}), 140.0 (d, J_{C-P} = 21.2 Hz, Ar CH), 147.4 (s, C^{IV}), 158.0 (s, C^{IV}), 175.0 (d, $^2J_{C-P}$ = 187.4 Hz, C^2). $^{31}P-\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) = 43.3. Anal. calcd for $C_{52}H_{71}Cl_2N_2PPd$: C, 65.19; H, 7.33; N, 2.87. Found: C, 64.84; H, 7.67; N, 3.18.

[Pd(μ-Cl)(Cl)(SPhos)]$_2$ (5). A Schlenk flask was charged with $[PdCl_2(NCPh)_2]$ (200 mg, 0.52 mmol), SPhos (211.3 mg, 0.515 mmol) and THF–toluene (2 mL, 1 : 1) was added. The reaction mixture was stirred for 2 hours. The precipitate was collected by filtration and washed with pentane (3 × 5 mL). The resulting orange solid was dried under vacuum to afford analytically pure **5** (250 mg, 83%) as an orange powder. ^1H NMR (CD_2Cl_2, 300 MHz, 278 K) δ (ppm) = 1.05–1.33 (m, 12H, Cy), 1.47–1.59 (m, 4H, Cy), 1.61–1–83 (m, 16H, Cy), 1.88–2.07 (br s, 4H, Cy), 2.11–2.42 (m, 8H, Cy), 3.72 (s, 12H, O–CH_3), 6.69 (d, $^3J_{H-H}$ = 8.4 Hz, 4H, Ar CH), 7.06–7.09 (m, 2H, Ar CH), 7.39–7.50 (m, 6H, Ar CH), 7.91–7.97 (m, 2H, Ar CH). $^{13}C-\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz, 298 K) δ 26.5 (s, Cy CH_2), 27.8 (d, $^2J_{C-P}$ = 11.2 Hz, Cy CH_2), 29.6 (s, Cy CH_2), 31.7 (s, Cy CH_2), 37.2 (d, $^1J_{C-P}$ = 25.5 Hz, Cy CH), 55.9 (s, O–CH_3), 68.1 (s, *C*–OCH_3), 104.3 (s, Ar CH), 118.2 (d, $^3J_{C-P}$ = 2.2 Hz, Ar C^{IV}), 126.3 (d, J_{C-P} = 10.3 Hz, Ar CH), 130.5 (s, Ar CH), 130.7 (d, J_{C-P} = 2.3 Hz, Ar CH), 133.9 (d, J_{C-P} = 9.1 Hz, Ar CH), 135.9 (d, J_{C-P} = 9.0 Hz, Ar CH), 139.7 (d, J_{C-P} = 4.4 Hz, Ar C^{IV}), 158.3 (s, Ar C^{IV}). $^{31}P-\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) = 53.3. Anal. calcd for $C_{52}H_{70}Cl_4O_4P_2Pd_2$: C, 53.12; H, 6.00. Found: C, 53.15; H, 6.11.

[Pd(IPr)(SPhos)] (6). In a glovebox, a flask was charged with $[Pd(\eta^3\text{-allyl})(Cl)(IPr)]$ (150 mg, 0.262 mmol), SPhos (107.6 mg, 0.262 mmol) and KO^{t}Bu (64.7 mg, 0.577 mmol). Toluene (3 mL) and isopropanol (3 mL) were then added. The reaction mixture was stirred during 5 days at room temperature. The solvent was evaporated under vacuum and isopropanol (2 mL) was added. The resulting solid was collected by filtration and washed with isopropanol (3 × 2 mL). The product was dried under vacuum to afford **6** (88.5 mg, 37%) as a yellow solid. ^1H NMR (C_6D_6, 400 MHz, 298 K) δ (ppm) = 0.94–1.64 (m, 22H, Cy), 1.23 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH–CH_3), 1.72 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, CH–CH_3), 3.11 (sept, $^3J_{H-H}$ = 6.8 Hz, 4H, C*H*–CH_3), 3.14 (s, 6H, O–CH_3), 6.28 (d, $^3J_{H-H}$ = 8.5 Hz, 2H, Ar CH), 6.53 (s, 2H, H^4, H^5), 7.04–7.09 (m, 2H, Ar CH), 7.20–7.34 (m, 8H, Ar CH), 9.00 (m, 1H, Ar CH). $^{13}C-\{^1H\}$ NMR (C_6D_6, 100.6 MHz, 298 K) δ (ppm) = 24.0 (s, CH–CH_3), 25.3 (s, CH–CH_3), 26.7 (Cy CH_2), 27.4 (d, J_{C-P} = 5.7 Hz, Cy CH_2), 27.6 (d, J_{C-P} = 3.8 Hz, Cy-CH_2), 29.0 (s, *C*H–CH_3), 31.8 (d, J_{C-P} = 12.2 Hz, Cy CH_2), 32.7 (d, J_{C-P} = 13.1 Hz, Cy CH_2), 36.1 (d, $^1J_{C-P}$ = 15 Hz, Cy CH), 55.1 (s, O–CH_3), 103.6 (s, Ar CH), 120.7 (s, Ar CH), 121.7 (s, C^{IV}), 123.3 (s, CH), 125.1 (d, J_{C-P} = 17.2 Hz, C^4, C^5), 128.7 (s, Ar CH), 129.0 (s, Ar CH), 132.3 (s, Ar CH), 137.7 (d, J_{C-P} = 2.9 Hz, C^{IV}), 138.0 (d, J_{C-P} = 15.0 Hz, C^{IV}), 138.2 (s, C^{IV}), 146.4 (s, C^{IV}), 146.4 (d, J_{C-P} = 43.0 Hz, Ar CH), 158.6 (s, C^{IV}), 199.5 (d, $^2J_{C-P}$ = 84.5 Hz, C^2). $^{31}P-\{^1H\}$ NMR (C_6D_6, 121 MHz, 298 K) δ (ppm) = 66.9.

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Notes and references

1 The announcement can be found on the Nobel Prize official website: http://nobelprize.org/nobel_prizes/chemistry/laureates/2010/

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