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Neutral palladium(II) complexes with P,N Schiff-base ligands: Synthesis, characterization and application as Suzuki–Miyaura coupling catalysts

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ABSTRACT

Palladium(II) complexes of the general formulae $[PdCl_2(P^{\wedge}N)]$ and $[Pd(Me)Cl(P^{\wedge}N)]$ were obtained from bidentate ligands bearing phosphine and imine donor groups. The complexes were shown to be highly active catalysts for the Suzuki–Miyaura cross-coupling reaction. The complexes are tolerant of a wide variety of reaction conditions such as solvent, choice of base as well as substituents on both arylboronic acids and aryl halides.

1. Introduction

Transition metal-catalyzed C–C and C–X (X = heteroatom) bond forming reactions are a powerful synthetic tool in organic chemistry. In this regard, palladium complexes form some of the most versatile and useful catalysts in these organic transformations. The facile interchange between the two stable oxidation states, Pd(II) and Pd(0), and the compatibility of many palladium compounds with most functional groups, are mainly responsible for the rich chemistry enjoyed by palladium compounds [1]. This facile interchange between the Pd(II)/Pd(0) oxidation states is what most palladium-catalyzed C–C bond forming reactions such as ethylene oligo/polymerization reactions, Suzuki–Miyaura, Heck and Negishi coupling reactions rely on.

The most common Suzuki–Miyaura catalysts currently in use are phosphine complexes with strong P-donors, owing to the stability displayed by these complexes as well as the comparative ease with which their properties can be modified. The coupling pathway requires a sequential oxidative addition at an active Pd(0) by an aryl halide, activation and transmetallation with the organoborate substrate, and finally, reductive elimination to give the target product and regeneration of the active species [2]. As such, a pre-catalyst such as $Pd(PPh_3)_4$ would need to enter the catalytic cycle through two successive ligand dissociations to give the 14-electron catalytically active complex $Pd^0(PPh_3)_2$. Such low-valent, low-coordinate palladium complexes are known to be extremely unstable and their formation is energetically unfavourable. One of the main challenges facing these catalyst systems is therefore the facile decomposition and deactivation of such complexes, which can lead to poor catalyst performance [2] thereby making the use of high Pd loading (2–12 mol%) necessary [3–9]. It is therefore desirable to design catalysts that are both chemically stable and catalytically active. One way of achieving this is through the use of hemilabile supporting ligands.

The concept of hemilability was introduced in the 1970's by Rauchfuss [10,11] to describe multidentate ligands that 'would bind well enough to the metal centre to allow isolation of the complex, but would readily dissociate the hard end component thus generating a vacant site for substrate binding' [12]. This is a particularly desirable characteristic for complexes which might have application in catalysis, and since the majority of metals used in such systems are middle or late transition metals, it is usually the soft donor atom which is continually bound to the metal centre [13]. An important property of these ligands is that they can stabilize metal

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ions in a variety of oxidation states and geometries, which normally form during the catalytic cycle [10]. In addition, the hard donor sites are weakly coordinated to the soft metal centre, and can be easily dissociated in solution, affording a vacant site whenever demanded, whereas the chelate effect confers stability to the catalyst precursor in the absence of substrate [10] thereby preventing catalyst decomposition/deactivation.

Over the past few decades, interest in metal complexes of this type of ligands, which are essentially functionalized phosphine ligands, and their role in catalysis has been steadily growing as the different features associated with each donor atom confer unique properties to their metal complexes [13–16]. Unlike homo-donor chelate ligands, hetero-donor ligands have a distinct *trans* effect which can play a role in controlling the selectivity/activity, especially in co- and/or homo-polymerization processes [17]. The syntheses and reactivity/catalytic activity of complexes bearing hemilabile ligands of the type P^N [10,18] and P^O [19] have been widely reported.

Of these heterodentate ligands, those bearing phosphorus and nitrogen as their donor atoms have emerged as an important class of ligands [18]. The π-acceptor ability of the phosphine can stabilize a metal centre in a low oxidation state, while the nitrogen σ-donor ability makes the metal centre more susceptible to oxidative addition reactions. This electronic asymmetry can also be used to optimize a ligand for a particular reaction by appropriate choice of the nature of the donor atoms. For example, binding the phosphorus atom directly to a more electronegative atom such as oxygen or nitrogen [18,20] will reduce its electron donating capability while also enhancing its π-acceptor capacity. On the other hand, the presence of an imino rather than amino group will result in a nitrogen donor atom of greater δ-donating capabilities [18,21]. Moreover, these types of ligand allow modulation of the steric crowding around the metal centre through the simple variation of the substituents on the imine and phosphine groups [22]. Recent years have seen an increase in the amount of research on the synthesis and application of iminophosphine complexes as catalysts for coupling reactions and it has been found that these complexes show great promise [9,23–28].

We recently reported the use of well-defined neutral iminophosphine Pd(II) complexes in ethylene oligomerization reactions [29]. We, herein, report the use of these complexes with hemilabile iminophosphine ligands as pre-catalysts in Suzuki–Miyaura coupling reactions using low catalyst loadings under relatively mild reaction conditions. The tested complexes show tolerance of a wide variety of conditions, including different solvents, bases, substituents on both the phenylboronic acid and the aryl halides used.

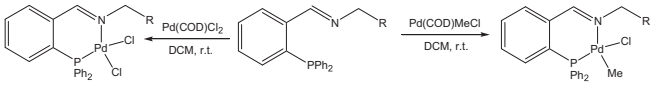
2. Results and discussion

2.1. Preparation of the iminophosphine ligands *1a–1e* and complexes *2a–2e*

We recently reported the preparation and characterization of the iminophosphine ligands **1a–1e** as well as their palladium dichloride complexes **2a–2e** and the activity of these complexes as pre-catalysts in ethylene oligomerisation reactions [29]. In this report, we present the preparation and characterization of analogous palladium chloromethyl complexes (**3a–3e**) based on the same ligands and investigate the application of both types of complexes in the Suzuki–Miyaura reaction (Scheme 1).

2.2. Preparation of the Pd(P^N)MeCl complexes *3a–3e*

The reaction of Pd(COD)MeCl with the appropriate iminophosphine ligands gave the desired palladium methylchloride



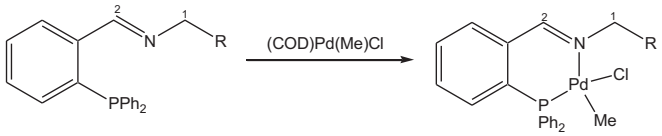
	2	1	3
R	Compound	Compound	Compound
Phenyl	**2a**	**1a**	**3a**
4-Tolyl	**2b**	**1b**	**3b**
3-Pyridyl	**2c**	**1c**	**3c**
2-Thionyl	**2d**	**1d**	**3d**
2-Furyl	**2e**	**1e**	**3e**

Scheme 1. Preparation of iminophosphine palladium dichloride (**2a–2e**) [29] and chloromethyl complexes (**3a–3e**).

complexes as air and moisture-stable crystalline solids in moderate to good yields (65–79%). Similar trends are observed in the characterization data of both the reported palladium dichloride [29] and palladium chloromethyl complexes (Table 1). In the ^{1}H NMR spectra of the chloromethyl complexes, the signals for the imine protons appear as singlets in the region δ 8.16–8.80 ppm (Table 1). Upon ligand coordination there is an upfield shift from δ 8.98–9.05 ppm (observed in the free ligand) and this upfield shift has been attributed to the conformational change that occurs in the ligand upon chelation [15,19,21d]. A similar trend was observed for the dichloride complexes, where an upfield shift of the signals for the imine protons to δ 8.52–8.84 ppm was observed [29]. As in the dichloride complexes, a downfield shift to δ 5.09–5.49 ppm is observed for the methylene protons (N-C***H***$_2$–R) upon chelation. A slightly bigger downfield shift (to δ 5.47–5.69 ppm) was observed for the same protons in the palladium dichloride complexes due to the deshielding that occurs for these protons when the adjacent imine group coordinates to the metal centre. The deshielding is, therefore, more significant for the palladium dichloride complexes as there is less electron density on the metal centre in the dichloride complexes due to the electronegative chlorido-ligands than there is in analogous palladium chloromethyl complexes. For both the dichloride and chloromethyl complexes, there is only a slight effect on the signals for the thiophenyl and furfuryl protons, indicating that these groups do not participate in coordinating to the metal centre. The signals for the methyl protons in Pd-Me appear as doublets in the region δ 0.21–0.61 ppm, with coupling constants of $^3J_{HP} = 2.4–3.2$ Hz. As a result of the different *trans* influence of the two donor atoms in the ligands, the phosphine is expected to coordinate trans to the chloride. This coordination mode is demonstrated by the small coupling constants between the phosphorus and the Pd-Me protons [15,30–32].

In the ^{13}C NMR spectrum of the methylchloride complexes, the signals for the imine carbons are found in the region 162.4–164.7 ppm (Table 1). This is a downfield shift from 160.6 to 161.4 ppm observed for the free ligands, further confirming the coordination of the imine group to the metal centre [21d]. On the contrary, there is an upfield shift of 1.5–3.2 ppm with respect to the free ligand in the signals for the methylene carbons upon coordination to the metal centre [33]. The signals for the Pd-Me occur as a singlet at δ 0.62–2.9 ppm, which is comparable to similar complexes [30]. The downfield shift of the phosphine signals from −13.4 to −14.5 ppm in the free ligands to 37.4–38.3 ppm in the ^{31}P NMR spectra of the complexes reflects the coordination of the phosphine to the palladium [15,34–36]. This downfield shift is slightly more significant for the

Table 1
Characterization data for the iminophosphine palladium chloromethyl complexes **3a**–**3e**.[a]



Entry	Complex	R	Yield (%)	$\nu_{C=N}$ (cm^{-1})	δ_H(Pd–C***H***$_3$) (ppm)	δ_H (H1) (ppm)	δ_H(H2) (ppm)	δ_C(Pd–***C***H$_3$) (ppm)	δ_C(C1) (ppm)	δ_C(C2) (ppm)	δ_P (ppm)
1	**3a**	Phenyl	65	1638 (1636)	0.21 (d, ^3J = 3.2 Hz)	5.09 (s) (4.70)	8.80 (s) (9.05)	0.62 (s)	62.5 (65.2)	164.7 (d, ^3J = 5.0 Hz) (160.6)	38.3 (s) (−13.8)
2	**3b**	4-Tolyl	79	1638 (1635)	0.56 (d, ^3J = 3.0 Hz)	5.40 (s) (4.64)	8.16 (s) (9.00)	2.3 (s)	66.6 (64.8)	162.4 (d, ^3J = 4.9 Hz) (160.3)	37.4 (s) (−13.6)
3	**3c**	3-Pyridyl	72	1635 (1634)	0.61 (d, ^3J = 3.0 Hz)	5.49 (s) (4.63)	8.40 (s) (8.98)	2.6 (s)	64.4 (62.4)	163.7 (d, ^3J = 5.1 Hz) (161.3)	37.6 (s) (−13.4)
4	**3d**	2-Thionyl	73	1637 (1634)	0.55 (d, ^3J = 2.9 Hz)	5.48 (s) (4.87)	8.24 (s) (9.01)	2.3 (s)	61.5 (60.0)	163.4 (d, ^3J = 5.1 Hz) (160.8)	37.5 (s) (−14.5)
5	**3e**	2-Furyl	71	1637 (1635)	0.56 (d, ^3J = 2.4 Hz)	5.47 (s) (4.64)	8.24 (s) (8.98)	2.9 (s)	59.1 (57.1)	163.7 (d, ^3J = 5.1 Hz) (161.4)	37.4 (s) (−14.5)

[a] Corresponding ligand data in parentheses.

chloromethyl complexes (51.0–52.1 ppm) than it is for the dichloride complexes (44.2–49.7 ppm). In both cases, the presence of only one signal in the ^{31}P NMR spectra indicates the formation of only one product.

In the IR spectra of the complexes, the peaks for the imine bond occur in the region 1635–1638 cm^{-1}, which is a slight hypsochrombic shift with respect to the free ligands (1634–1636 cm^{-1}). In contrast, the palladium dichloride complexes showed a distinct bathochromic shift of between 8 and 11 cm^{-1} with respect to the free ligands, which is typical for coordinated imines of this type [30,37,38].

2.3. X-ray structure of *3b*

The solid-state structure of complex **3b** (Fig. 1) was determined by X-ray diffraction analysis in order to complete the characterization of the complex and to gain further insight into the coordination mode of these types of ligands. Selected structural data are listed in Table 2.

The X-ray crystal structure confirms the *cis* orientation of the phosphine and the methyl groups around the metal centre. The complex displays a distorted square planar arrangement around the metal centre. Further, as expected, the iminophosphine ligand coordinates in a bidentate fashion to the palladium centre, with the phosphine end of the ligand coordinated *trans* to the chloride ligand. The ligand forms a puckered chelate ring with the palladium centre, in which the =CHC$_6$H$_4$ unit lies above the Pd(P,N)MeCl plane with the torsion angle Pd(1)–P(1)–C(16)–C(11) being 38.89 (17)°. The bite angle N(1)–Pd(1)–P1 of 87.45 (5)° deviates slightly from the expected 90° angle, which can be attributed to the steric strain imposed by the 6-membered chelate ring N(1)–Pd(1)–P(1)–C(16)–C(11)–C(10) that is formed upon coordination to the palladium centre. This reduction in the bite angle of N(1)–Pd(1)–P(1) as well as the compensatory increase in the N(1)–Pd(1)–Cl(1) angle has been observed in other palladium methylhalide complexes of iminophosphines [15,21,33,39–41]. The remaining two angles around the palladium centre are close to the expected 90°, i.e 89.79 (6)° and 89.18 (6) for C(1)–Pd(1)–P(1) and C(1)–Pd(1)–Cl(1) respectively. These values are in good agreement with those obtained for similar complexes [31,42,43].

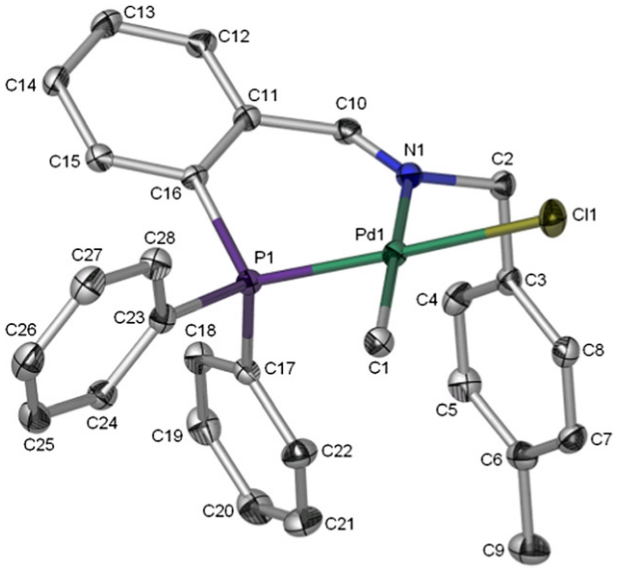


Fig. 1. Molecular structure of **3b** showing the atomic numbering scheme.

Table 2
Selected bond ligands (Å) and angles (°) for **3b**.

Bond lengths	
Pd(1)–Cl(1)	2.3985(6)
Pd(1)–P(1)	2.1846(5)
Pd(1)–N(1)	2.1595(16)
Pd(1)–C(1)	2.0586(19)
P(1)–C(16)	1.8255(19)
P(4)–C(11)	1.824(3)
N(1)–C(10)	1.278(2)
N(1)–C(2)	1.484(2)
Bond angles	
P(1)–Pd(1)–Cl(1)	177.15(2)
N(1)–Pd(1)–(Cl(1)	93.85(5)
C(1)–Pd(1)–Cl(1)	89.18(6)
N(1)–Pd(1)–P(1)	87.45(5)
C(1)–Pd(1)–P(1)	89.79(6)
C(1)–Pd(1)–N(1)	173.39(7)

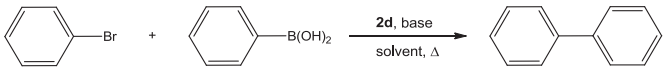
2.4. Suzuki–Miyaura coupling reactions

Complex **2d** was used in preliminary testing in order to optimize reaction conditions (temperature, nature of base, solvent, catalyst loading). The coupling of bromobenzene and phenylboronic acid was chosen as the model reaction and all reactions were carried out under aerobic conditions. Secondly, complexes **2b**, **2d**, **2e** and **3b** were evaluated for activity in Suzuki–Miyaura coupling reactions to test the effect of palladium precursor (**2b** and **3b**) and substituents (**2b**, **2d** and **2e**) that may influence the second coordination sphere of the metal centre.

The data in Table 3 show the results obtained from the coupling of bromobenzene with phenylboronic acid under different reaction conditions when complex **2d** was used as the pre-catalyst. The complex is active even at temperatures as low as 85 °C (entry 1, Table 3), with almost complete conversion (94%) being obtained in 3 h. Increasing the temperature to 100 °C (entry 2, Table 3) results in an increase in reaction rate, and 92% conversion is reached in 1 h (compared to 77% obtained after 1 h at 85 °C) and 97% conversion at the end of 3 h. Increasing the temperature beyond 100 °C (entries 3 and 4, Table 3) does not have a significant beneficial effect on catalyst performance, although complete conversion is reached within 2.5 h at 140 °C. At 110 °C, 90% and 98% conversion were reached within 1 h and 3 h respectively. In all cases, most conversion occurs in the first hour of the reaction, with ≥90% conversion being reached within an hour at 100 °C and 110 °C. Based on the reactions obtained from the temperature study, all subsequent reactions were carried out at 100 °C.

Entries 1, 5 and 6 show the effect of catalyst loading on the performance of complex **2d**. The best performance is obtained when 0.1 mol% Pd is used. Increasing catalyst loading to 1.0 and 5.0 mol% Pd (entries 5 and 6) results in catalyst decomposition (shown by formation of palladium black) within the first 5 min and 1 min, respectively. This observation is in agreement with those by de Vries [44] Rothenberg [45,46] and others [47,48], that only homeopathic amounts of palladium (typically 0.01–0.1 mol%) are needed for cross-coupling reactions. This is attributed to the fact that once palladium has been reduced to Pd(0), it forms nanoclusters that have low stability. These clusters eventually aggregate to form palladium black. Therefore, lowering palladium concentration in the reaction mixture favours oxidative addition of the aryl bromide to the Pd(0) species over cluster formation and subsequent catalyst deactivation [44a]. This result is of particular importance because the use of low catalyst loading is beneficial only when high reaction rates accompanied by almost complete conversions are observed. Otherwise expensive and time-consuming procedures for product separation and purification would be necessary, negating the beneficial effects of using low catalyst loading.

Table 3
Influence of temperature, base, solvent and catalyst loading on the activity of **2d**.[a]



Entry	Mol% Pd	Conditions	Time (h)	Solvent	Base	Conversion %[b]
1	0.1	85 °C	3	Toluene	K_2CO_3	94
2	0.1	100 °C	3	Toluene	K_2CO_3	97
3	0.1	110 °C	3	Toluene	K_2CO_3	98
4[e]	0.1	140 °C	2.5	Toluene	K_2CO_3	100
5	1.0	100 °C	3	Toluene	K_2CO_3	91
6	5.0	100 °C	3	Toluene	K_2CO_3	72
7	0.1	100 °C	1.5	Toluene	KOH	98
8	0.1	100 °C	24	Toluene	NaOAc	42
9	0.1	100 °C	24	Toluene	Na_2CO_3	29
10	0.1	100 °C	1.5	Toluene	Cs_2CO_3	98
11	0.1	100 °C	1.5	Toluene	NaOH	95
12	0.1	100 °C	3	1,4-Dioxane	K_2CO_3	97
13	0.1	100 °C	24	DMF	K_2CO_3	95[c]
14	0.1	100 °C	24	Acetonitrile	K_2CO_3	52
15[d]	0.1	100 °C	24	Toluene	K_2CO_3	4

[a] Conditions: Solvent (15 ml), aryl halide (5.0 mmol), phenylboronic acid (7.5 mmol), base (10.0 mmol).
[b] Determined by GC with n-decane as internal standard.
[c] 38% conversion observed after 3 h.
[d] 0.1 mol% Hg with respect to bromobenzene.
[e] Reaction done in a sealed tube.

Entries 2 and 7–11 in Table 3 highlight the effect of various bases on the catalytic performance of complex **2d**. K_2CO_3, the relatively cheap and easy to handle base chosen for the preliminary investigations, turned out to be one of the most efficient, along with KOH (entry 7), Cs_2CO_3 (entry 10) and NaOH (entry 11), which gave conversions in excess of 96% in 3 h or less. When these bases were used, conversions in excess of 80% were obtained as early in the reaction as 40 min, with 91% conversion being reached in this time when Cs_2CO_3 was used as base. In contrast, the organic base, NaOAc (entry 8) as well as Na_2CO_3 (entry 9) performed poorly, with only 42% and 29% conversion, respectively, obtained after 24 h of reaction. Interestingly, comparing entries 2 and 9, but also 7 and 11, a 'potassium effect' [25] becomes evident. It seems that the cation plays an important role in determining the efficiency of the base to activate the boronic acid as previously reported [25,49–51].

Polar aprotic solvents like THF, DMF and dioxane are often used for coupling reactions as they allow for the best solubility of both the substrates and the catalysts. As a result, high conversions with high selectivities (depending on the choice of ligand) can be obtained under mild conditions. A study of solvent effects on the activity of complex **2d** revealed that while the reaction proceeds well in toluene (entry 2) and 1,4-dioxane (entry 12), catalytic performance is greatly affected in DMF and even more so in acetonitrile (entries 13 and 14). Scrivanti and co-workers [25] reported that no catalytic activity was observed when they used the hetero-donor P^O complex [$PdCl_2${8-(di-tertbutylphosphinooxy) quinoline)}] as a pre-catalyst for Suzuki- Miyaura coupling in DMF. They attributed the lack of catalytic activity in this solvent to a possible mechanism whereby these solvents could activate a process such as ligand hydrolysis leading to catalyst decomposition. Since in our case catalytic activity is just slowed down and not completely suppressed, this mode of catalyst deactivation is not operative. A possible explanation could be that, since both acetonitrile and DMF are basic solvents with N-donor atoms, they could compete with the imine moiety of the ligand in coordinating to the palladium centre and the resultant complexes could be less active than the iminophosphine complex. This possibility is further supported by the fact that in DMF, which is less basic than acetonitrile due to conjugation, and therefore less available for coordination, the reaction proceeds to almost complete conversion (94% after 24 h), whereas in acetonitrile only 52% conversion is obtained in the same period. The reaction in 1,4-dioxane proceeds at a much higher rate than it does in DMF and the same logic can be applied to explain this. Since the oxygen donor atoms in dioxane are a harder base than the nitrogen donor atom in DMF, this solvent is less likely to coordinate to the palladium centre and therefore it is less likely to interfere with catalyst performance.

Nobre and Monteiro [23] reported the use of $Pd(OAc)_2$ in combination with iminophosphine ligands (2-diphenylphosphinobenzylidene)-2-methylpropan-2-amine or (2-diphenylphosphinobenzylidene)-2,6-diisopropylaniline as catalysts for the coupling of phenylboronic acid and 4-bromotoluene. They also observed that for this catalyst system, dioxane and toluene were the best solvents (with 72% conversion being obtained for both solvents at 50 °C and

1 mol% Pd). Poor results were obtained when acetonitrile was used [23]. The activity of complex **2d** compares generally favourably with other hetero-donor palladium complexes reported for Suzuki–Miyaura coupling [9,23,25,26] with lower catalyst loading and shorter reaction times required, while high reaction rates are maintained. It is important to note that the majority of iminiphosphine palladium(II) complexes reported for Suzuki–Miyaura coupling reactions bear ligands with aryl groups on the imine nitrogen [23–25] while the complexes in this report bear ligands with benzyl, fyrfuryl and thiophenyl groups on the imine nitrogen. The presence of the methylene group seems to enhance the catalytic activity of these complexes, possibly due to the reduced steric crowding in these complexes. Improved conversions and activities are achieved while milder reactions conditions are employed compared to the previously reported complexes.

Finally, to determine whether the catalytic species is the molecular iminophosphine palladium complex or nanoparticles (colloids or nanoclusters), a mercury poisoning test was carried out by adding mercury to the reaction mixture before the catalytic test was performed. Mercury is known to form an amalgam with Pd(0) species, blocking active sites on catalytically active nanoparticles. The results from the mercury test (entry 15) show an almost complete suppression of catalytic activity in the presence of mercury, indicating that the probability of the actual active species in these reactions being a form of nanoparticles (colloids, nanoclusters, etc) can not be excluded. It should be noted, however, that not only colloidal Pd(0) but also molecular Pd(0) complexes have been reported to be destroyed by elemental mercury [52,53]. It is clear that our iminophosphine ligands are capable of stabilizing the active catalyst.

Next we set out to investigate different aryl halides and substituted phenylboronic acids as substrates under the optimized conditions determined in the preliminary study for **2d** (0.1 mol% Pd, K_2CO_3, toluene, 100 °C; see Table 4). In palladium-catalyzed coupling reactions, oxidative addition to a Pd(0) species is often the rate-determining step in the catalytic cycle [54], and the relative reactivity typically decreases in the order of I > OTf > Br >> Cl because of the different C-X dissociation energies, (e.g. C–I 240 kJ/mol to C–Cl 339 kJ/mol). However, for some catalyst systems, a reversal of reactivity between aryl bromides and aryl halides has been reported, as in these cases, transmetalation of the Pd(II)-X species is the rate-determining step. Smith and co-workers [55] carried out mechanistic studies of the Suzuki coupling in the production of the drug trityl losartan, an angiotensin II receptor antagonist used for the treatment of high blood pressure, in which they determined that the rate-determining step depends on the identity of the aryl halide. They found that when using aryl bromide, oxidative addition was rate-determining since the coupling rate was strongly dependant on the concentrations of the catalyst and the aryl bromide but independent of the aryl boronic acid. In contrast, when aryl iodide was used as substrate, the coupling rate was found to be proportional to the concentrations of the catalyst and the aryl boronic acid but independent of the concentration of iodotoluene, i.e., the transmetalation was rate-determining. This observation has been attributed to the strength of the Pd(II)-X bond in the products of the oxidative addition step [56–58], and was supported by density functional theory calculations for the Stille cross-coupling reaction, which showed that the overall activation barriers for the transmetalation process increase in the order: X = Cl < Br < I [56]. Comparing the efficiency of the different aryl halides as substrates in this reaction reveals that the best results are obtained when bromobenzene is used (entry 3) and the poorest results are obtained when chlorobenzene is used as substrate (entry 2). Although a slower reaction rate (compared to bromobenzene) is observed when iodobenzene is used as the substrate (entry 1), the reaction proceeds almost to completion after 24 h (97%).

Complex **2d** is tolerant of both electron-withdrawing and electron-donating groups on the aryl bromide. The best results were obtained when highly electron-deficient aryl bromides such as 2-bromobenzonitrile (entry 6) and 4-bromobenzaldehyde (entry 4) were used. 100% conversion was reached within 50 min for both substrates. Using relatively electron-rich aryl bromides slows down the rate of reaction (entries 5 and 7), with the poorest results (80% conversion after 24 h) obtained when 4-bromobenzyl bromide was used as substrate (entry 5). The complex also shows tolerance for electron withdrawing and electron donating substituents on phenylboronic acid. Good conversions were obtained in cases where 3-chloro- and 3-methoxy-substituted phenylboronic acids were used. In the case of 2-methoxyphenylboronic acid, only moderate conversion was obtained, and this could be due to steric effects resulting from the close proximity of the methoxy group to the boronic acid moiety. Very little conversion was obtained when 3,4-(methylenedioxy)phenylboronic acid was used with only 15% conversion being observed after 24 h with 3-thiopheneboronic acid as substrate resulting in only 6% of the desired product, possibly due to poisoning of the active catalytic species by substrates with donor sites.

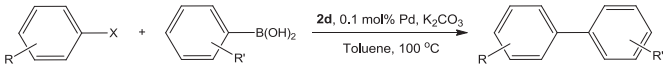
2.5. Catalytic activity of complexes *2b*, *2d*, *2e* and *3d*

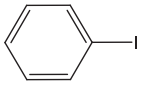
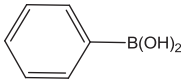
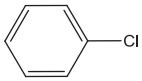
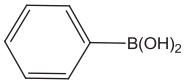
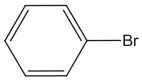
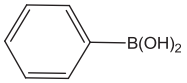
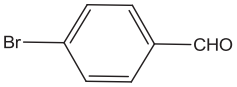
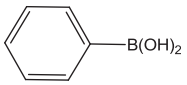
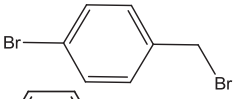
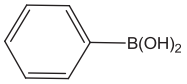
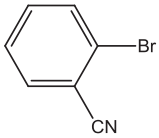
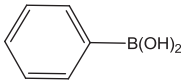
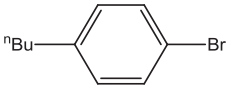
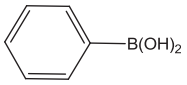
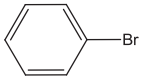
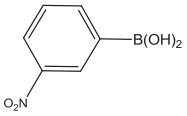
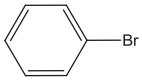
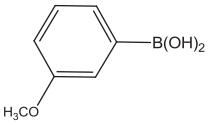
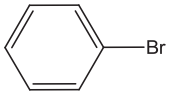
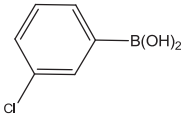
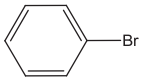
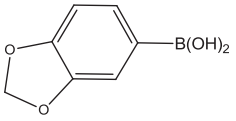
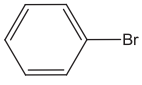
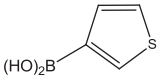
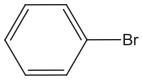
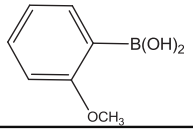
A comparative study of catalytic activity involving complexes **2b**, **2d**, **2e** and **3d** was carried out to determine the effects of palladium precursor as well as ligand substituents using conditions optimized for **2d** (see Table 5). Comparing the results obtained for **2d** and **3d** (entries 2 and 4) indicates that the methyl chloride complex is slightly more active than its dichloride counterpart. Under the same reaction conditions 100% conversion is reached within 90 min with the methyl chloride complex (**3d**) while only 96% conversion (same time) is achieved with the dichloride complex (**2d**) in 90 min and 97% after 3 h. Furthermore, comparing the results obtained for **2b**, **2d** and **2e** (entries 1–3) shows that having a ligand bearing a donor atom in the second coordination sphere of the metal centre has a beneficial influence on the catalytic activity of the complex. Of the three complexes, complex **2e**, bearing the furyl substituent gave the best results, with 100% conversion being obtained in 30 min while **2b** and **2d** gave 96% conversion over the same period. In all cases, good turnover numbers (>960 mol/mol Pd) and turnover frequencies (>1920 mol/mol Pd/h) were observed.

3. Conclusions

In conclusion, several new chloromethyl palladium complexes based on iminophosphine ligands recently reported by us were prepared and characterized. A selection of these complexes as well as the dichloride complexes was tested for activity in Suzuki–Miyaura coupling reactions. An extensive study on the scope of these complexes was performed. They were found to be compatible with a wide range of reaction conditions as well as functional groups on both the aryl halides and the arylboronic acids. The results show that for these iminophosphine complexes, low catalyst loadings are required while high conversions and short reaction times are maintained. In addition, having a substituent bearing a donor atom on the imine moiety was found to enhance catalytic activity. Palladium methyl chloride complexes were found to be more active than their palladium dichloride counterparts. A distinct halide effect was observed, as well as a reversal in reactivity pattern between bromobenzene and iodobenzene.

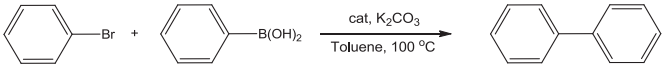
Table 4
Suzuki–Miyaura coupling of various aryl halides with phenylboronic acids using complex **2d**.[a]



Entry	Ar-X	Ar′-B(OH)$_2$	Mol% Pd	Time	%Conv.[b]	%Yield[c]
1			0.1	3 h	66[d]	54
2			0.1	24 h	27	16
3			0.1	3 h	97	90
4			0.1	50 min	100	95
5			0.1	24 h	80	73
6			0.1	50 min	100	96
7			0.1	2 h	100	93
8			0.1	24 h	19	ND[e]
9			0.1	2 h	92	87
10			0.1	1.5 h	100	96
11			0.1	24 h	15	ND[e]
12			0.1	24 h	6	ND[e]
13			0.1	24 h	63	51

[a] Conditions: Solvent (15 ml), aryl halide (5.0 mmol), phenylboronic acid (7.5 mmol), base (10.0 mmol).
[b] Determined by GC with n-decane as internal standard.
[c] Isolated yields. Products were characterized by mass spectrometry and for entry 5, the product was also characterized by ^{1}H NMR spectroscopy.
[d] 97% conversion observed after 24 h.
[e] Product was not isolated.

Table 5
Catalytic activity of complexes **2b**, **2d**, **2e** and **3d** for the coupling of bromobenzene and phenylboronic acid.[a]



Entry	Catalyst	Mol% Pd	Conversion %[b]	TON[f,h]	TOF[g,h]
1	**2b**	0.1	98[c]	980	1960
2	**2d**	0.1	96[d]	960	1920
3	**2e**	0.1	100	1000	2000
4	**3b**	0.1	96[e]	960	1920

[a] Conditions: Solvent (10 ml), aryl halide (5.0 mmol), phenylboronic acid (7.5 mmol), base (10.0 mmol), 0.1 mol% Pd, time (30 min).
[b] Determined by GC with n-decane as internal standard.
[c] 100% conversion obtained after 40 min.
[d] 97% conversion obtained after 3 h.
[e] 100% conversion obtained after 1.5 h.
[f] TON: mol of aryl bromide converted/mol catalyst.
[g] TOF: mol of aryl bromide converted/mol catalyst per hour.
[h] TON and TOF values at 30 min of reaction.

4. Experimental

4.1. General remarks

All reactions were carried out under nitrogen or argon atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques unless otherwise stated. Solvents were dried and purified by refluxing under argon in the presence of a suitable drying agent. After purification, the solvents were transferred under vacuum into a Teflon-valve storage vessel. All commercially available chemicals were purchased from either Sigma–Aldrich or Merck and used without further purification. $PdCl_2$ was obtained from Johnson Matthey. 2-Diphenylphosphinobenzaldehyde [59], Pd(COD)Cl_2 [60], Pd(COD)MeCl [61], ligands **1a**–**1e** [29] and complexes **2a**–**2e** [29] were all prepared using literature procedures. NMR spectra were recorded on a Varian Mercury-300 MHz (^{1}H: 300 MHz; ^{13}C: 75.5 MHz; ^{31}P: 121 MHz) or Varian Unity-400 MHz (^{1}H: 400 MHz; ^{13}C: 100.6 MHz; ^{31}P: 161.9 MHz) spectrometer. ^{1}H NMR spectra were referenced internally using the residual protons in deuterated solvents ($CDCl_3$: δ 7.27; DMSO: δ 2.50) and values reported relative to the internal standard tetramethylsilane (δ 0.00). ^{13}C NMR spectra were referenced internally to the deuterated solvent resonance ($CDCl_3$: δ 77.0; DMSO: δ 39.4) and the values are reported relative to tetramethylsilane (δ 0.00). All chemical shifts are quoted in δ (ppm) and coupling constants, *J*, in Hertz (Hz). Melting points were determined on a Reichert-Jung Thermovar hotstage microscope and are uncorrected. Infrared spectra were recorded on a Thermo Nicolet. FT-IR instrument in the 4000–300 cm^{-1} range using KBr discs. Microanalyses were determined using a Fisons EA 1108 CHNO-S instrument. Mass spectra were recorded on a Waters API Q-TOF Ultima (ESI, 70 eV). GC analyses were performed using a Varian 3900 gas chromatograph equipped with an FID and a 50 m × 0.20 mm HP-PONA column (0.50 μm film thickness).

4.2. General procedure for the preparation of palladium chloromethyl complexes *3a*–*3e*

To a solution of the appropriate ligand in CH_2Cl_2 (15 ml) was added an equimolar amount of a Pd(COD)(Me)Cl solution in CH_2Cl_2 (15 ml). The reaction was stirred at room temperature for 15 h, after which the solvent was reduced *in vacuo* and hexane was added to precipitate the product. The resultant solid was washed with hexane and then dried. The desired products were obtained as pale yellow or off-white solids in moderate to good yields.

4.2.1. Preparation of [Pd($C_{26}H_{22}$NP)(Me)Cl (*3a*)

Complex **3a** was prepared by the reaction of Pd(COD)(Me)Cl (0.30 g, 1.13 mmol) with **1a** (0.42 g, 1.13 mmol) and the product was obtained as a pale yellow powder (0.39 g, 65%). M.p. 169–171 °C. IR (KBr): 1638 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (400 MHz, $CDCl_3$): 0.21 (d, $^3J_{HP}$ = 3.2 Hz, 3H; Pd-C***H***$_3$), 5.09 (s, 2H; N-C***H***$_2$–R), 7.13 (dd, $^3J_{HH}$ = 7.7, 10.5 Hz, 1H; Ar-***H***), 7.18–7.23 (m, 8H; Ar-***H***), 7.34 (m, 1H; Ar-***H***), 7.46 (dt, $^3J_{HH}$ = 2.3, 7.6 Hz, 4H; Ar-***H***), 7.53 (m, 2H; Ar-***H***), 7.71 (br t, $^3J_{HH}$ = 7.5 Hz, 1H; Ar-***H***), 7.82 (br t, $^3J_{HH}$ = 7.5 Hz, 1H; Ar-***H***), 7.94 (dd, $^3J_{HH}$ = 4.3, 6.3 Hz, 1H; Ar-***H***), 8.80 (s, 1H; ***H***-imine). ^{13}C NMR (100.6 MHz, $CDCl_3$): 0.62 (s; Pd-***C***H$_3$), 62.5 (s; N-***C***H$_2$–R), 124.4 (s; Ar-***C***), 124.7 (d, J_{CP} = 7.6 Hz; Ar-***C***), 127.8 (s; Ar-***C***), 128.3 (s; Ar-***C***), 129.5 (d, J_{CP} = 8.8 Hz; Ar-***C***), 130.1 (d, J_{CP} = 11.9 Hz; Ar-***C***), 132.4 (s; Ar-***C***), 134.3 (s; Ar-***C***), 134.8 (d, J_{CP} = 12.1 Hz; Ar-***C***), 135.5 (s; Ar-***C***), 136.0 (d, J_{CP} = 13.6 Hz; Ar-***C***), 137.4 (s; Ar-***C***), 138.0 (s; Ar-***C***), 138.5 (d, J_{CP} = 8.3 Hz; Ar-***C***), 164.7 (d, $^3J_{CP}$ = 5.0 Hz; ***C***-imine). ^{31}P NMR (161.9 MHz, $CDCl_3$): 38.3 (s). EI-MS: *m/z* 501.10 $[M - Cl]^+$. Anal. Calc. for $C_{27}H_{25}ClNOPPd$ (536.34): C, 60.46; H, 4.70; N, 2.61. Found: C, 60.91; H, 4.43; N, 2.87.

4.2.2. Preparation of [Pd($C_{27}H_{24}$NP)(Me)Cl (*3b*)

Complex **3b** was prepared by the reaction of **1b** (0.42 g, 1.07 mmol) and Pd(COD)(Me)Cl (0.28 g, 1.07 mmol) and the product was obtained as a pale yellow solid (0.47 g, 79%). M.p. 122–124 °C (decomp.). IR (KBr): 1638 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (400 MHz, $CDCl_3$): 0.56 (d, $^3J_{HP}$ = 2.9 Hz, 3H; Pd-C***H***$_3$), 2.36 (s, 3H; Ar-C***H***$_3$), 5.40 (s, 2H; N-C***H***$_2$–R), 6.91 (d, $^3J_{HH}$ = 7.7 Hz, 2H; Ar-***H***), 7.02 (m, 1H; Ar-***H***), 7.08 (br s, 1H; Ar-***H***), 7.10 (d, $^4J_{HH}$ = 5.9 Hz, 2H; Ar-***H***), 7.14 (d, $^4J_{HH}$ = 5.1 Hz, 3H; Ar-***H***), 7.26 (t, $^3J_{HH}$ = 7.2 Hz, 4H; Ar-***H***), 7.40 (t, $^3J_{HH}$ = 7.2 Hz, 3H; Ar-***H***), 7.47 (dd, $^3J_{HH}$ = 4.1 Hz, 7.5 Hz, 1H; Ar-***H***), 7.55 (t, $^3J_{HH}$ = 7.4 Hz, 1H; Ar-***H***), 8.16 (s, 1H; ***H***-imine). ^{13}C NMR (100.6 MHz, $CDCl_3$): 2.3 (s; Pd-***C***H$_3$), 21.2 (s; Ar-***C***H$_3$), 66.6 (s; N-***C***H$_2$–R), 126.8 (s; Ar-***C***), 127.2 (s; Ar-***C***), 127.3 (s; Ar-***C***), 127.5 (s; Ar-***C***), 127.8 (d, J_{CP} = 5.9 Hz; Ar-***C***), 128.0 (s; Ar-***C***), 128.1 (s; Ar-***C***), 128.2 (s; Ar-***C***), 128.6 (d, J_{CP} = 11.1, Ar-***C***), 128.8 (s; Ar-***C***), 129.4 (d, J_{CP} = 13.6 Hz; Ar-***C***), 129.7 (s; Ar-***C***), 129.9 (s; Ar-***C***), 130.7 (s; Ar-***C***), 130.8 (d, J_{CP} = 2.0 Hz; Ar-***C***), 131.3 (d, J_{CP} = 1.3 Hz; Ar-***C***), 131.8 (s; Ar-***C***), 131.9 (d, J_{CP} = 6.8 Hz; Ar-***C***), 132.2 (s; Ar-***C***), 132.3 (s; Ar-***C***), 133.6 (d, J_{CP} = 5.5 Hz; Ar-***C***), 133.9 (d, J_{CP} = 12.4 Hz; Ar-***C***), 137.0 (s; Ar-***C***), 137.4 (d, J_{CP} = 14.3 Hz; Ar-***C***), 162.4 (d, $^3J_{CP}$ = 4.9 Hz; ***C***-imine). ^{31}P NMR (161.9 MHz, $CDCl_3$): 37.4 (s). EI-MS: *m/z* 514.10 $[M - Cl]^+$. Anal. Calc. for $C_{28}H_{27}ClNPPd$ (536.34): C, 61.10; H, 4.94; N, 2.54. Found: C, 61.54; H, 4.61; N, 2.49.

4.2.3. Preparation of [Pd($C_{25}H_{21}N_2$P)(Me)Cl (*3c*)

Compound **3c** was prepared by the reaction of Pd(COD)MeCl (0.13 g, 0.50 mmol) and **1c** (0.19 g, 0.5 mmol product was obtained as a pale yellow powder (0.19 g, 72%). M.p. 180–182 °C. IR (KBr): 1635 cm^{-1} ($\nu_{C=N}$, imine). ^{1}H NMR (400 MHz, $CDCl_3$): 0.61 (d, $^3J_{HP}$ = 3.0 Hz, 3H; Pd-C***H***$_3$), 5.49 (s, 2H; N-C***H***$_2$–R), 7.09 (dd, $^3J_{HH}$ = 7.4 Hz, 9.8 Hz, 1H; Ar-***H***), 7.14–7.17 (m, 5H; Ar-***H***), 7.39–7.41 (m, 4H; Ar-***H***), 7.46–7.49 (m, 3H; Ar-***H***), 7.60–7.62 (m, 1H, Ar-***H***), 7.65–7.66 (m, 1H; Ar-***H***), 8.00 (td, $^3J_{HH}$ = 1.8 Hz, 7.8 Hz, 1H; Ar-***H***), 8.32 (d, $^4J_{HH}$ = 2.2, Hz, 1H; Ar-***H***), 8.40 (s, 1H, ***H***-imine), 8.51 (dd, $^3J_{HH}$ = 1.6 Hz, 4.8 Hz, 1H; Ar-***H***). ^{13}C NMR (100.6 MHz, $CDCl_3$): 2.6 (s; Pd-***C***H$_3$), 64.4 (s; N-***C***H$_2$–R), 123.3 (s; Ar-***C***), 126.5 (s; Ar-***C***), 128.7 (d, J_{CP} = 11.2 Hz; Ar-***C***), 130.4 (d, J_{CP} = 1.7 Hz; Ar-***C***), 131.1 (d, J_{CP} = 2.3 Hz; Ar-***C***), 132.3 (d, J_{CP} = 6.7 Hz; Ar-***C***), 132.5 (s; Ar-***C***), 133.1 (d, J_{CP} = 12.4 Hz; Ar-***C***), 133.8 (s; Ar-***C***), 133.9 (s; Ar-***C***), 134.1 (s; Ar-***C***), 136.1 (d, J_{CP} = 8.7 Hz; Ar-***C***), 137.4 (s; Ar-***C***), 149.0 (s; Ar-***C***), 150.4 (s; Ar-***C***), 163.6 (d, $^3J_{CP}$ = 4.8 Hz; ***C***-imine). ^{31}P NMR (161.9 MHz, $CDCl_3$): 37.6 (s). EI-MS: *m/z* 501.11 $[M - Cl]^+$. Anal. Calc. for $C_{26}H_{24}ClN_2PPd$ (537.33): C, 58.12; H, 4.50; N, 5.21. Found: C, 58.52; H, 4.56; N, 5.13.

4.2.4. Preparation of [Pd($C_{24}H_{20}$NPS)(Me)Cl (*3d*)

Complex **3d** was prepared by the reaction of **1d** (0.41 g, 1.07 mmol) and Pd(COD)(Me)Cl (0.28 g, 1.07 mmol) and the product

was obtained as a pale yellow solid (0.42 g, 73%). M.p. 188–190 °C. IR (KBr): 1637 cm^{-1} ($\nu_{C=N}$). ^1H NMR (400 MHz, $CDCl_3$): 0.56 (d, 3H, $^3J_{HP}$ = 2.9 Hz, 3H; Pd-C***H***$_3$), 5.48 (s, 2H; N-C***H***$_2$–R), 6.36 (br s, 1H; ***H***-thiophene), 6.73 (d, $^3J_{HH}$ = 2.6 Hz, 1H; ***H***-thiophene), 7.10 (br s, 1H; ***H***-thiopehene), 7.16 (t, $^3J_{HH}$ = 8.8 Hz, 1H; Ar-***H***), 7.29 (t, J_{HH} = 5.8 Hz, 4H; Ar-***H***), 7.39 (t, $^3J_{HH}$ = 7.6 Hz, 4H; Ar-***H***), 7.48 (t, $^3J_{HH}$ = 7.5 Hz, 3H; Ar-***H***), 7.54–7.55 (m, 1H; Ar-***H***), 7.64 (t, $^3J_{HH}$ = 7.3 Hz, 1H; Ar-***H***), 8.24 (br s, 1H; ***H***-imine). ^{13}C NMR (100.6 MHz, $CDCl_3$): 2.3 (s; Pd-***C***H_3), 61.5 (s; N-***C***H_2–R), 123.9 (***C***-thiophene), 127.0 (***C***-thiophene), 127.7 (d, J_{CP} = 42.0 Hz; Ar-***C***), 128.3 (s; ***C***-thiophene), 128.8 (s; Ar-***C***), 130.0 (d, J_{CP} = 11.3 Hz; Ar-***C***), 130.9 (d, J_{CP} = 2.1 Hz; Ar-***C***), 131.2 (d, J_{CP} = 1.5 Hz; Ar-***C***), 132.4 (d, J_{CP} = 6.8 Hz; Ar-***C***), 133.7 (s; Ar-***C***), 134.2 (d, J_{CP} = 12.4 Hz; Ar-***C***), 135.9 (d, J_{CP} = 8.5 Hz; Ar-***C***), 137.3 (d, J_{CP} = 14.4 Hz; Ar-***C***), 138.6 (s; ***C***-thiopehene), 163.4 (d, $^3J_{CP}$ = 5.1 Hz; ***C***-imine). ^{31}P NMR (161.9 MHz, $CDCl_3$): 37.5 (s). EI-MS: *m/z* 506.83 $[M - Cl]^+$. Anal. Calc. For $C_{25}H_{23}ClNPPdS$ (542.37): C, 55.36; H, 4.27; N, 2.58; S, 5.91. Found: C, 55.42; H, 4.25; N, 2.31; S, 5.87.

4.2.5. Preparation of [Pd($C_{24}H_{20}$NOP)(Me)Cl (**3e**)

Complex **3e** was prepared by the reaction of **1e** (0.39 g, 1.07 mmol) and Pd(COD)(Me)Cl (0.28 g, 1.07 mmol) and the product was obtained as a pale yellow solid (0.40 g, 71%). M.p. 193–195 °C. IR (KBr): 1637 cm^{-1} ($\nu_{C=N}$). ^1H NMR (400 MHz, $CDCl_3$): 0.56 (d, $^3J_{HP}$ = 2.4 Hz, 3H; Pd-C***H***$_3$), 5.47 (s, 2H; N-C***H***$_2$–R), 6.35 (br s, 1H; ***H***-furan), 6.72 (d, $^3J_{HH}$ = 2.6 Hz, 1H; ***H***-furan), 7.06 (1H, br s, ***H***-furan), 7.15 (t, $^3J_{HH}$ = 8.7 Hz, 1H; Ar-***H***), 7.26–7.29 (m, 4H; Ar-***H***), 7.38 (t, $^3J_{HH}$ = 7.3 Hz, 4H; Ar-***H***), 7.48 (t, $^3J_{HH}$ = 7.5 Hz, 3H; Ar-***H***), 7.56–7.58 (m, 1H; Ar-***H***), 7.62 (t, $^3J_{HH}$ = 7.3 Hz, 1H; Ar-***H***), 8.24 (br s, 1H; ***H***-imine). ^{13}C NMR (100.6 MHz, $CDCl_3$): 2.9 (s; Pd-***C***H_3), 59.1 (s; N-***C***H_2–R), 110.6 (s; ***C***-furan), 111.3 (s; ***C***-furan), 126.9 (d, J_{CP} = 57.5 Hz; Ar-***C***), 128.2 (s; ***C***-furan), 128.7 (d, J_{CP} = 11.2 Hz; Ar-***C***), 130.9 (d, J_{CP} = 2.0 Hz; Ar-***C***), 131.4 (d, J_{CP} = 1.7 Hz; Ar-***C***), 132.2 (d, J_{CP} = 6.8 Hz; Ar-***C***), 133.5 (s; Ar-***C***), 134.1 (d, J_{CP} = 12.6 Hz; Ar-***C***), 135.9 (d, J_{CP} = 8.7 Hz; Ar-***C***), 136.0 (s; Ar-***C***), 142.8 (s; ***C***-furan), 149.5 (s; Ar-***C***), 163.7 (d, $^3J_{CP}$ = 5.1 Hz; ***C***-imine). ^{31}P NMR (161.9 MHz, $CDCl_3$): 37.4 (s). EI-MS: *m/z* 490.21 $[M - Cl]^+$. Anal. Calc. For $C_{25}H_{23}ClNOPPd$ (526.30): C, 57.05; H, 4.40; N, 2.66. Found: C, 57.56; H, 4.39; N, 2.98.

4.3. Suzuki–Miyaura coupling reactions

A 100 ml round bottom flask was fitted with a reflux condenser and a magnetic stirrer bar. The flask was charged with toluene (15 ml) and the appropriate amount of catalyst reagents and the internal standard (n-Decane: 2.59 mmol). The contents were thoroughly mixed and an initial sample (t_0) was then taken. The reaction flask was placed in an oil bath at the desired temperature and the reaction mixture allowed to heat/reflux with stirring. A sample was taken and analyzed every 10 min for the first hour and every 30 min thereafter until t_{3h}. In cases where conversion was not complete after 3 h, the reaction mixture was then allowed to stir for a total of 24 h. The reaction at 140 °C was performed in a sealed tube. All catalytic reactions were done under aerobic conditions. Percentage conversions were determined by GC with n-decane as the internal standard and the coupling products were characterized by mass spectrometry (Table 4) as well as ^1H NMR spectroscopy (Entry 5, Table 4 only).

4.4. X-ray data collection and structure refinement of [Pd($C_{27}H_{24}$NP)(Me)Cl (**3b**)

Single-crystal X-ray diffraction data for **3b** were collected on a Bruker KAPPA APEX II DUO diffractometer using graphite-monochromated Mo-Kα radiation (χ = 0.71073 Å). Data collection was carried out at 173(2) K. Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Cell refinement and data reduction were performed using the program SAINT [62]. The data were scaled and absorption corrections were performed using SADABS [63]. The structure was solved by direct methods using SHELXS-97 [63] and refined by full-matrix least-squares methods based on F^2 using SHELXL-97 [63] and using the graphics interface program X-Seed [64]. The programs X-Seed and POV-Ray [65] were both used to prepare molecular graphic images. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically with C-H distances ranging from 0.95 Å to 0.98 Å and refined as riding on their parent atoms, with U_{iso} (H) = 1.2–1.5 U_{eq} (C). The structure was successfully refined to the R factor 0.0238. The parameters for crystal data collection and structure refinements are in Table 6.

Table 6
Crystal and refinement data for **3b**.

Empirical formula	$C_{28}H_{27}ClNPPd$
Formula weight	550.33
T, K	173(2)
λ, Å	0.71073
Crystal system	Monoclinic
Space group	P21/*n*
a, Å	10.0673(8)
b, Å	21.8872(18)
c, Å	11.0593(9)
α, deg	90
β, deg	92.3710(10)
γ, deg	90
V, Å^3	2434.8(3)
Z	4
$Density_{calc}$, mg/mL	1.501
Absorption coefficient, mm^{-1}	0.954
F(000)	1120
Crystal size, mm	0.24 × 0.23 × 0.12
θ range for data collection, deg	1.86 to 27.14
Limiting indices	$-12 \le h \le 12, -28 \le k \le 28, -14 \le l \le 14$
Reflections collected/unique	38460/5380 [*R*(int) = 0.0444]
Completeness to θ	27.14 (99.9%)
Max. and min. transmission	0.8941 and 0.8034
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5380/0/291
Goodness-of-fit on F^2	1.025
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0238, w*R*2 = 0.0546
R indices (all data)	*R*1 = 0.0321, w*R*2 = 0.0584
Largest diff. peak and hole	0.370 and −0.405 e A^{-3}

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Appendix A. Supplementary material

CCDC 819785 contains the supplementary crystallographic data for complex **3b** for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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