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Catalytic reactivity of the complexes $[Pd\{(Ph_2P)_2N(^tBu)\text{-}P,P'\}X_2]$, X = Cl, Br, I, in the Suzuki-Miyaura C–C coupling reaction: Probing effects of the halogeno ligand X^- and the ligand's ^tBu group

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ABSTRACT

The synthesis, as well as the spectroscopic and structural characterization of three analogous palladium(II) complexes, $[Pd\{(Ph_2P)_2N(^tBu)\text{-}\kappa^2P,P'\}X_2]$, X = Cl, Br, I, is presented. X-ray crystallography studies revealed a similar square planar PdP_2X_2 first coordination sphere among the three complexes. The catalytic reactivity of these complexes was tested in the Suzuki-Miyaura coupling reaction, showing that the X = Cl, Br, complexes are more active than the X = I analogue. The differences in the catalytic reactivity within this series of complexes, as well as comparisons with similar palladium(II) catalysts reported in the literature, are discussed with respect to the different electronegativity of the three halogens and the strong +I inductive effect of the ligand's ^tBu group.

1. Introduction

The bis(phosphino)amine type of ligands, $(R_2P)_2N(R')$, constitute a distinct sub-family of chelating diphosphine ligands coordinating to various transition metals in bidentate fashion [1,2]. The large number of complexes $[M\{(R_2P)_2N(R')\text{-}\kappa^2P,P'\}X_2]$, M = Ni, Pd, Pt; X = Cl, Br, I, bearing this type of ligands, has been recently reviewed [2]. A search in the Cambridge Structural Database (CSD) [3] revealed a host of structurally characterized complexes containing X = Cl, i.e. $[Pd\{(R_2P)_2N(R')\text{-}\kappa^2P,P'\}Cl_2]$ [4]. On the other hand, the analogous complexes containing X = Br, I, are rather scarce (*vide infra*), despite the fact that the complex $[Pd\{Ph_2PN(^iPr)P(Ph)(Me)\text{-}\kappa^2P,P'\}I_2]$ was reported more than 20 years ago [5].

Complexes of the $[Pd\{(R_2P)_2N(R')\text{-}\kappa^2P,P'\}Cl_2]$ type have been employed as catalysts in the Suzuki-Miyaura or Heck C–C coupling reaction [4e,j,x,y,z]. In recent work reported by some of us, the complexes $[Pd\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3\text{-}\kappa^2P,P'\}X_2]$, X = Cl, Br [6], I [7], have been immobilized onto STx-1 montmorillonite clay and the free and anchored complexes investigated as homogeneous and heterogenized catalysts, in the Suzuki-Miyaura coupling reaction. The catalytic reactivity of the latter three complexes has also been explored in the hydroalkoxycarbonylation reaction [7]. Very recently, Balakrishna and co-workers reported the immobilization of $[Pd\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3\text{-}\kappa^2P,P'\}Cl_2]$ onto graphene oxide, and the investigation of the catalytic reactivity of both free and anchored complexes in Suzuki–Miyaura, Ullmann coupling and cyanation reactions [8].

Furthermore, the analogous nickel(II) complex, $[Ni\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3\text{-}\kappa^2P,P'\}Cl_2]$, was immobilized onto SBA-15 mesoporous molecular sieves by some of us, thus affording an heterogenized Kumada coupling catalyst [9]. The catalytic reactivity in the same reaction was earlier also reported for the complexes $[Ni\{(Ph_2P)_2N(S\text{-}CHMePh)\text{-}\kappa^2P,P'\}X_2]$, X = Cl, Br [10]. In addition, other nickel(II) complexes of the type $[Ni\{(R_2P)_2N(R')\}$-

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$\kappa^2P,P'\}X_2]$, X = Cl, Br, have been shown to catalyse the polymerization [11] or oligomerization [12–15] of ethene, as well as the vinyl type polymerization of norbornene [16,17]. Along these lines, chromium complexes bearing $(R_2P)_2N(R')$ ligands are also known to be active catalysts in the oligomerization of olefins [18].

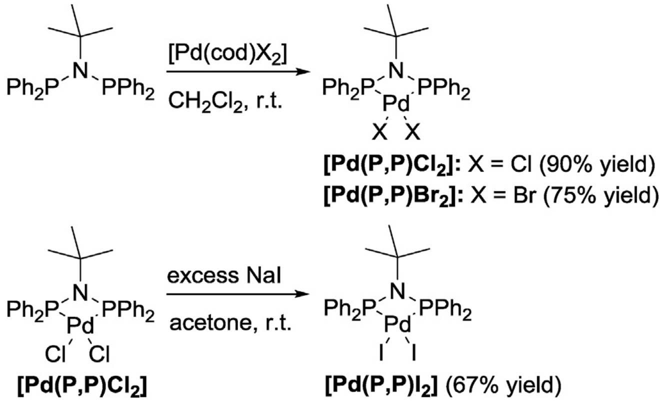
Based on the above, it is of importance to investigate the structural or electronic factors affecting the catalytic reactivity of complexes $[Pd\{(R_2P)_2N(R')\text{-}\kappa^2P,P'\}X_2]$. For instance, possible effects of the identity of the halogeno X^- ligands need to be explored. For that purpose, in this work, the three analogous complexes $[Pd\{(Ph_2P)_2N(^tBu)\text{-}\kappa^2P,P\}X_2]$, X = Cl, Br, I, which, in the following, are referred to as **[Pd(P,P)X$_2$]**, were synthesized and comparatively investigated by X-ray crystallography and spectroscopic methods. Despite the large number of structurally characterized complexes $[M\{(R_2P)_2N(R')\text{-}\kappa^2P,P'\}X_2]$, M = Ni [4x,z,9-17,19], Pd [4–8], Pt [4a,b,c,d,e,f,g,h,k,s,u,w,aa,20], reported in the literature, a search in the CSD [3] confirmed that structurally characterized complexes of this type, bearing the $(R_2P)_2N(^tBu)$ ligand, have not yet been reported. This ligand [21] has been employed, along with other similar ligands, for the synthesis of chromium(I) complexes of the type $[Cr(CO)_4\{(R_2P)_2N(R')\text{-}\kappa^2P,P\}]^+$, which were used as pre-catalysts for the selective oligomerization of ethylene [22]. The same ligand has also been used for the investigation of ruthenium-catalyzed aromatic amine alkylation of anilines [23]. Moreover, recently, the complex $[Fe\{(Ph_2P)_2N(^tBu)\text{-}\kappa^2P,P\}(Cp)(H)]$ has been employed to investigate hydride transfer reactions [24].

As a continuation of our research activities regarding the evaluation of P,N-containing ligands towards Pd-catalyzed coupling reactions [6,7,25], the complexes **[Pd(P,P)X$_2$]**, X = Cl, Br, I, exhibiting a similar PdP_2X_2 first coordination, were investigated as catalysts in the Suzuki-Miyaura C–C coupling reaction. Our previous work has shown that the identity of X^- affects the catalytic reactivity of the complexes, since complexes bearing X = Cl, Br, are more active than the corresponding complex with X = I [6,7]. Therefore, we sought to confirm this effect, but, in addition, to assess the importance of the R′ group's nature, which is expected to affect the electronic and, possibly, catalytic properties of such complexes. For this purpose, comparisons are made with other $[Pd\{(R_2P)_2N(R')\}\text{-}\kappa^2P,P'\}X_2]$ complexes, in order to assess whether the ^tBu group, which exhibits a strong +I inductive effect, may confer an increased catalytic reactivity.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization of palladium(II) complexes

The $(Ph_2P)_2N(^tBu)$ ligand [21] was reacted, in a 1:1 stoichiometry, with a dichloromethane solution of $[Pd(cod)X_2]$ (cod = 1,5-cyclooctadiene), X = Cl, Br, affording the complexes **[Pd(P,P)X$_2$]**, X = Cl, Br (Scheme 1). Complex **[Pd(P,P)I$_2$]** was prepared by adding an excess of NaI to complex **[Pd(P,P)Cl$_2$]**, in acetone, in order for the Cl^- ligand of the latter complex to be substituted by I^- (Scheme 1). All complexes were characterized by IR and ^1H and ^{31}P NMR spectroscopies (see spectra in Supporting Information). Based on comparisons with similar palladium(II) complexes reported in the literature [4a,c,d,h,u,x,y,z], the IR peaks of **[Pd(P,P)X$_2$]**, X = Cl, Br, I, at 870, 872, 867 cm^{-1}, respectively, are assigned to ν(P-N-P), and those at 1437, 1434, 1434 cm^{-1}, respectively, to the ν(P-Ph). These data provide evidence that the conformation of the P-N-P backbone in the three complexes is similar, which is also supported by X-ray crystallography studies (*vide infra*). The presence of a lone singlet in the ^{31}P NMR spectra of **[Pd(P,P)X$_2$]**, X = Cl, Br, I, at δ 33.12, 30.96 and 25.09 ppm, respectively, as well as the absence of the signal at δ 57.8 ppm corresponding to the $(Ph_2P)_2N(^tBu)$ ligand [21], provides a clear evidence that, in all complexes, the ligand coordinates to palladium(II) *via* both P atoms, which are equivalent to each other, confirming similar observations recently reported for the analogous three complexes $[Pd\{(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3\text{-}\kappa^2P,P\}X_2]$, X = Cl, Br [6], I [7]. Positive ESI-MS spectra of complexes showed bands corresponding exactly to $[M-X]^+$ and $[M+Na]^+$ (see experimental section and also in SI).



Scheme 1. Synthesis of complexes **[Pd(P,P)X$_2$]**, X = Cl, Br, I.

2.2. Crystal structures

Suitable crystals suitable for X-ray crystallographic studies of all complexes were obtained by the layering method, employing a solvent mixture of dichloromethane/n-hexane (1:3 by volume). The structure of complexes **[Pd(P,P)X$_2$]** (X = Cl, Br, I) (Fig. 1) contains discrete molecules (except for the X = Cl complex which, in addition, contains two CH_2Cl_2 lattice molecules per formula unit) exhibiting a distorted square planar PdP_2X_2 core. Palladium(II) is coordinated to the (P,P) chelating ligand, forming a four-membered Pd–P–N–P ring. In all cases, the PdP_2X_2 core is planar, showing small mean deviation from the best plane defined by the Pd, P1, P2, X1 and X2 atoms (0.056 for Cl, 0.081 for Br and 0.034 for I), with the P1 atom exhibiting the largest deviation (0.08 and 0.11 Å for X = Cl, Br, respectively) and P2 atom (0.05 Å) for X = I. The four-membered Pd–P1–N–P2 ring is planar, with the mean deviation from the best plane defined by these four atoms being 0.016, 0.023 and 0.056 Å for X = Cl, Br, I, respectively.

The Pd–P and Pd–X bond lengths, listed in Table 1, are typical of similar complexes reported in the literature [4–8]. As expected, the Pd–X bond lengths follow the trend Pd–I > Pd–Br > Pd–Cl, with average values 2.64, 2.48 and 2.36 Å, respectively. The Pd–P bond lengths are shorter than the Pd–X ones, with average values 2.205, 2.214 and 2.232 Å for X = Cl, Br, I, respectively. The P-Pd-P endocyclic angle of the three complexes is rather conserved at *ca.* 71°, confirming earlier observations on similar literature complexes [4–8]. Furthermore, the P1-N-P2 angles of the three complexes are also similar (Table 1), in agreement with their similar ν(P-N-P) IR transitions (*vide supra*).

2.3. Catalytic activity in Suzuki-Miyaura cross-coupling

Proper base selection and optimization of palladium(II) complex efficiency were performed in the Suzuki-Miyaura coupling of the deactivated 4-bromoanisole with phenylboronic acid in DMF as a solvent at 80 °C for 2 h, using a relatively low palladium loading (0.1 mol%) (Table 2). Complexes **[Pd(P,P)Cl$_2$]** and **[Pd(P,P)Br$_2$]** afforded a higher conversion to 4-methoxybiphenyl compared to **[Pd(P,P)I$_2$]** by using K_3PO_4 as a base (compare entries 1–3). These

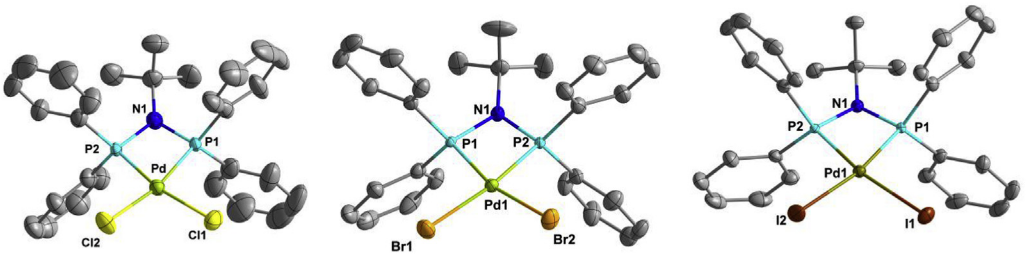


Fig. 1. Partially labeled ORTEP plots for the molecular structure of the complexes **[Pd(P,P)X$_2$]**, X = Cl, Br, I (from left to right). Color code: Pd olive green, Cl yellow, Br orange, I brown, N blue, P cyan, C grey. The thermal ellipsoids are plotted at a probability level of 50%. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Selected bond angles and lengths of complexes **[Pd(P,P)X$_2$]**, X = Cl, Br, I.

X	Bond angles (°)						
	X1–Pd–X2	X1–Pd–P1	X2–Pd–P2	P1–Pd–P2	Pd–P1–N	Pd–P2–N	P1–N–P2
Cl	95.63(4)	95.14(3)	97.99(3)	71.34(3)	95.31(9)	95.46(9)	97.82(14)
Br	94.66(1)	97.39(2)	96.90(2)	71.36(3)	95.04(9)	95.30(8)	98.16(13)
I	95.22(1)	96.06(1)	97.53(1)	71.23(2)	95.02(6)	94.58(6)	98.36(8)
Bond lengths (Å)							
	Pd–X1	Pd–X2	Pd–P1	Pd–P2	P1–N	P2–N	
Cl	2.3569(8)	2.3654(9)	2.2055(8)	2.2048(8)	1.708(3)	1.704(3)	
Br	2.4754(4)	2.4802(4)	2.2181(7)	2.2105(8)	1.709(2)	1.709(3)	
I	2.6408(2)	2.6482(2)	2.2294(5)	2.2342(5)	1.713(2)	1.722(2)	

Table 2
Optimization of palladium(II) catalyst and base selection for the Suzuki-Miyaura coupling of 4-bromoanisole with phenylboronic acid.[a]

Entry	Complex	Base	Time (h)	Conversion (%)[b]	
				ArPh[c]	PhPh[d]
1	**[Pd(P,P)Cl$_2$]**	K_3PO_4	2	81	1
2	**[Pd(P,P)Br$_2$]**	K_3PO_4	2	85	1
3	**[Pd(P,P)I$_2$]**	K_3PO_4	2	76	1
4	**[Pd(P,P)Cl$_2$]**	K_2CO_3	2	90	<1
5	**[Pd(P,P)Cl$_2$]**	Cs_2CO_3	2	94	1
6	**[Pd(P,P)Br$_2$]**	K_2CO_3	2	91	<1
7	**[Pd(P,P)Br$_2$]**	Cs_2CO_3	2	95	1
8	**[Pd(P,P)Br$_2$]**	Cs_2CO_3	1	89	<1

[a] Reaction conditions: 4-MeO-C_6H_4-Br (125 μL, 1.0 mmol), $PhB(OH)_2$ (183 mg, 1.5 mmol), base (2.0 mmol), dodecane (70 μL, 0.3 mmol), 0.5 mM solution of catalyst in DMF (2 mL, 1.0 μmol), 80 °C, argon.
[b] Determined by GC (dodecane as internal standard).
[c] Coupling product.
[d] Homo-coupling by-product.

$$\mathrm{ArBr} + \mathrm{PhB(OH)_2} \xrightarrow[\substack{\mathrm{DMF/Cs_2CO_3} \\ 80\ ^\circ\mathrm{C,\ 1h}}]{\mathbf{[Pd(P,P)Br_2]}\ (0.1\ \mathrm{mol\%})} \mathrm{ArPh}$$

Scheme 2. Suzuki-Miyaura cross-coupling.

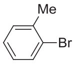
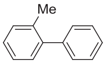
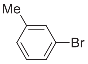
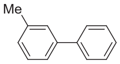
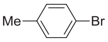
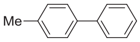
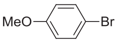
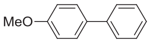
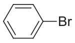
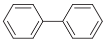
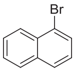
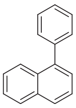
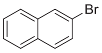
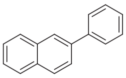
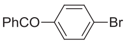
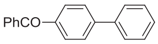
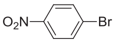
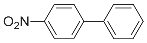
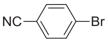
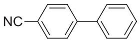
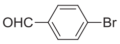
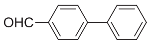
two more active catalysts were further evaluated using K_2CO_3 or Cs_2CO_3 as a base, showing that the conversion rate decreases in the order $Cs_2CO_3 > K_2CO_3 > K_3PO_4$ (compare entries 1, 4, 5 for **[Pd(P,P)Cl$_2$]**, and entries 2, 6, 7 for **[Pd(P,P)Br$_2$]**, but also that **[Pd(P,P)Br$_2$]** is only very slightly more active than **[Pd(P,P)Cl$_2$]** (compare entries 4 vs 6 and 5 vs 7). Thus, the most efficient combination of catalyst/base was found to be **[Pd(P,P)Br$_2$]**/Cs_2CO_3 affording 95% conversion into the biaryl (entry 7). The conversion was also high (89%) just after 1 h of reaction time (entry 8).

Catalysis by complex **[Pd(P,P)Br$_2$]** (0.1 mol%) was then performed for a variety of electron-rich and electron-poor aryl bromides in DMF/Cs_2CO_3 at 80 °C for 1 h, affording conversions to biaryls in the range 75–89% with TOFs 750–890 h^{-1} (Scheme 2, Table 3). Conversion to unsubstituted biphenyl as homo-coupling by-product was usually less than 1%. Purification of the products was achieved by column chromatography affording isolated yields up to 80%.

The observed effect of the catalytic reactivity clearly exerted by the halogeno ligand X^- (significantly higher reactivity for X = Cl, Br complexes over the X = I analogue), is in agreement with similar observations concerning the analogous complexes [Pd{$(Ph_2P)_2N(CH_2)_3Si(OCH_3)_3$-$\kappa^2 P,P$}$X_2$], X = Cl, Br [6], I [7]. As already stated for these complexes [7], the different electronegativity of the corresponding halogen could have a significant effect on catalytic reactivity, since the larger electron density of palladium(II) in the X = Cl, Br, complexes, due to the higher electronegativity of chlorine and bromine compared to that of iodine, is expected to facilitate reduction to palladium(0), to which oxidative addition of the aryl bromide takes place, further promoting, this way, the catalytic cycle.

The reaction conditions employed in the catalytic experiments presented in Tables 2 and 3 (catalyst loading 0.1 mol% Pd, 80 °C) can be considered to be relatively mild compared to similar palladium(II) catalysts containing R′ moieties with aromatic groups, using more drastic conditions (1.0 mol% Pd loading, 80 °C) [4e,x,y,z]. Furthermore, it should be noted that temperatures between 90 and 110 °C were used for a similar catalyst at 0.1 mol% Pd loading bearing R′ = ^{i}Pr, [4j]. Although direct comparisons between the above catalytic systems cannot be made because of the different reaction conditions, the observed reactivity of our catalysts bearing R′ = ^{t}Bu, combined with the reported one for the catalyst containing R′ = ^{i}Pr [4j], provides evidence that the strong +I inductive effect exerted by the ^{i}Pr and ^{t}Bu groups is favorable. The latter may enhance the catalytic reactivity of the corresponding palladium(II) complexes, possibly due to the fact that the $(Ph_2P)_2N(R')$, R′ = ^{i}Pr,

Table 3
Suzuki-Miyaura coupling of aryl bromides with phenylboronic acid catalyzed by **[Pd(P,P)Br$_2$]**.[a]

Entry	ArBr	Coupling product	Conversion (%)[b]	TOF (h^{-1})[c]	Yield (%)[d]
1			75	750	66
2			82	820	72
3			76	760	65
4[e]			89	890	78
5			89	890	79
6			79	790	70
7			89	890	78
8			88	880	80
9			88	880	79
10			87	870	78
11			89	890	80

[a] Reaction conditions: ArBr (1.0 mmol), PhB(OH)$_2$ (183 mg, 1.5 mmol), Cs$_2$CO$_3$ (652 mg, 2.0 mmol), dodecane (70 μL, 0.3 mmol), 0.5 mM solution of **[Pd(P,P)Br$_2$]** in DMF (2 mL, 1.0 μmol), 80 °C, 1 h, argon.

[b] Conversion to coupling product as determined by GC (dodecane as internal standard).

[c] TOF = Turnover Frequency (moles of aryl bromide transformed to biphenyl per mole of Pd per hour).

[d] Isolated yield by column chromatography.

[e] Entry 8 in Table 1.

^{t}Bu, ligands increase the electron density of palladium(II) and, hence, favour its reduction to palladium(0) (*vide supra*).

3. Conclusions

Three analogous palladium(II) complexes, namely [Pd{(Ph$_2$P)$_2$N(^{t}Bu)-κ^2*P,P*}X$_2$], X = Cl, Br, I, were structurally and spectroscopically characterized. The fact that these complexes contain a similar square planar PdP$_2$X$_2$ first coordination sphere allows the assessment of the effects on their catalytic reactivity of the halogeno X$^-$ within a series of structurally similar catalysts. The complexes containing X = Cl, Br, are more active catalysts in the Suzuki-Miyaura coupling reaction, confirming recent observations on the catalytic reactivity within the series [Pd{(Ph$_2$P)$_2$N(CH$_2$)$_3$Si(OCH$_3$)$_3$-κ^2*P,P*}X$_2$], X = Cl, Br [6], I [7]. The different electronegativity of the three halogens may be the critical factor for the observed differences. In addition, comparisons concerning the catalytic reactivity of similar palladium(II) complexes provide some evidence of increased reactivity when R′ = ^{t}Bu, possibly due to its strong +I inductive effect.

4. Experimental section

4.1. General

The synthetic work was carried out under inert conditions, using Schlenk techniques. The solvents were dried and distilled according to procedures reported in the literature [26]. The (Ph$_2$P)$_2$N(^{t}Bu) ligand [21] and the [Pd(cod)X$_2$] complexes, X = Cl, Br, (cod = 1,5-cyclooctadiene) [27] were synthesized according to literature procedures. All other chemicals were commercially available. FT-IR spectra (average of 50 scans) were recorded at room temperature on a Shimadzu IR Affinity-1 spectrophotometer. Pellets of the specimens were prepared after mixing with dry KBr. ^{1}H and ^{31}P NMR solution spectra (CDCl$_3$) were acquired on a Varian 300 or 600 MHz spectrometer. Chemical shift values in ^{1}H NMR spectra were referenced internally to the residual solvent resonance, and the ^{31}P spectra were referenced to external 85% H$_3$PO$_4$ in H$_2$O. Gas chromatography was undertaken using a Hewlett-Packard (HP) Model GC-6890 equipped with FID with a HP-5 capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness). Inlets and Detector temperature was kept constant at 260 and 300 °C, respectively. The oven temperature was held at 60 °C for 3 min and then raised with a rate of 10 °C/min to 260 °C, under constant flow (0.6 mL/min). Spectra analysis was done using HP ChemStation. HRMS were obtained by using a Thermo Scientific LTQ Orbitrap Velos (ESI) spectrometer.

4.2. *Palladium dichloro{N,N-bis(diphenylphosphanyl)tert-butylamine}, **[Pd(P,P)Cl$_2$]***

[Pd(cod)Cl$_2$] (0.097 g, 0.340 mmol) was dissolved in dichloromethane (10 mL) at room temperature. Addition of the (Ph$_2$P)$_2$N(^{t}Bu) ligand (0.150 g, 0.340 mmol) afforded a yellow solution, which was stirred at room temperature for 24 h and subsequently concentrated to 2 mL. Addition of 5 mL n-hexane afforded 0.190 g of a yellow powder, which was filtrated and dried under vacuum (90% yield), m.p. (dec.) 164–170 °C. IR (KBr, cm^{-1}): 509 (s), 521 (s), 567 (s), 596 (m), 693 (s), 711 (m),748 (s), 870 (s) ν(P-N-P), 1008 (s), 1100 (s), 1176 (s), 1222 (s), 1248 (s), 1311 (s), 1372 (s), 1402 (s), 1437 (s) ν(P-Ph), 1481 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23–8.19 (m, 8H, Ar), 7.66–7.65 (m, 4H, Ar), 7.61–7.59 (m, 8H, Ar), 0.99 (s, 9H, ^{t}Bu). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 33.12. HRMS (positive ESI-MS): calcd for $C_{28}H_{29}ClNP_2Pd$ $[M-Cl]^+$ 582.0493, found 582.0504; calcd for $C_{28}H_{29}Cl_2NNaP_2Pd$ $[M+Na]^+$ 640.0079, found 640.0083.

4.3. *Palladium dibromo{N,N-bis(diphenylphosphanyl)tert-butylamine}, **[Pd(P,P)Br$_2$]***

By reacting [Pd(cod)Br_2] (0.042 g, 0.132 mmol) with the $(Ph_2P)_2N(^tBu)$ ligand (0.050 g, 0.132 mmol), employing the procedure described above, ***[Pd(P,P)Br$_2$]*** was afforded as 0.060 g of a yellow powder (76% yield), m.p. (dec.) > 200 °C. IR (KBr, cm^{-1}): 506 (s), 523 (m), 565 (s), 595 (m), 691 (s), 709 (m),744 (s), 872 (s) ν(P-N-P), 997 (s), 1092 (s), 1176 (m), 1225 (s), 1247 (s), 1308 (s), 1375 (m), 1434 (s) ν(P-Ph), 1457 (s), 1478 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23 (m, 8H, Ar), 7.68–7.65 (m, 4H, Ar), 7.61–7.59 (m, 8H, Ar), 0.99 (s, 9H, ^{t}Bu). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 30.96. HRMS (positive ESI-MS): calcd for $C_{28}H_{29}BrNP_2Pd$ $[M-Br]^+$ 625.9988, found 625.9997; calcd for $C_{28}H_{29}Br_2NNaP_2Pd$ $[M+Na]^+$ 727.9069, found 727.9077.

4.4. *Palladium diiodo{N,N-bis(diphenylphosphanyl)tert-butylamine}, **[Pd(P,P)I$_2$]***

Complex **[Pd(P,P)Cl$_2$]** (0.070 g, 0.113 mmol) was dissolved at room temperature in aceton (10 mL), followed by the addition of NaI in stoichiometric excess (0.070 g, 0.452 mmol), affording a dark yellow solution, which was stirred at room temperature for 24 h. The reaction mixture was then concentrated to dryness and the solid residue was re-dissolved in dichloromethane (10 mL). This solution was filtrated through celite in order to remove the remaining NaI or NaCl formed during the reaction. The filtrate was concentrated to 4 mL, n-hexane (10 mL) were then added to allow precipitation of the expected product, that was collected by filtration, and dried under vacuum to afford 0.060 g (67% yield) of a dark yellow powder, m.p. (dec.) > 200 °C. IR (KBr, cm^{-1}): 506 (s), 528 (m), 562 (s), 591 (m), 692 (s), 748 (s), 867 (s) ν(P-N-P), 995 (m), 1101 (s), 1097 (s), 1176 (s), 1224 (s), 1245 (s), 1307 (w), 1375 (m), 1434 (s) ν(P-Ph), 1457 (s), 1480 (s). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.23 (m, 8H, Ar), 7.68–7.65 (m, 4H, Ar), 7.61–7.59 (m, 8H, Ar), 0.96 (s, 9H, ^{t}Bu). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 25.09. HRMS (positive ESI-MS): calcd for $C_{28}H_{29}INP_2Pd$ $[M-I]^+$ 673.9849, found 673.9877; calcd for $C_{28}H_{29}I_2NNaP_2Pd$ $[M+Na]^+$ 823.8792, found 823.8830.

4.5. *General experimental procedure for the Suzuki-Miyaura coupling*

Aryl bromide (1.0 mmol), phenylboronic acid (183 mg, 1.5 mmol), Cs_2CO_3 (652 mg, 2.0 mmol), palladium(II) complex **[Pd(P,P)Br$_2$]** in DMF (0.5 mM, 2 mL, 1.0 μmol) and dodecane (70 μL, 0.3 mmol) as internal standard were stirred over a preheating oil bath at 80 °C under argon for 1 h. After cooling to room temperature, addition of water (5 mL) and extraction with dichloromethane (2 × 10 mL), the organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, passed through celite and analyzed by GC. GC retention times were compared with those of authentic samples. After evaporation of the any volatile residue, isolation of the pure biaryl was achieved by column chromatography on silica gel using a mixture of hexane/AcOEt as eluent. All biaryls are known compounds [25c], and were characterized by ^{1}H and ^{13}C NMR spectra.

4.6. *X-ray crystallography*

A crystal of **[Pd(P,P)Cl$_2$]·2CH$_2$Cl$_2$** (0.14 × 0.21 × 0.45 mm) was mounted in air; crystals of **[Pd(P,P)Br$_2$]** (0.11 × 0.11 × 0.25 mm) and **[Pd(P,P)I$_2$]** (0.06 × 0.08 × 0.23 mm) were taken from the mother liquor and immediately cooled to −113 °C. Diffraction measurements were made on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite monochromated Mo Kα radiation. Data collection (ω-scans) and processing (cell refinement, data reduction and Empirical absorption correction) were performed using the CrystalClear program package [28]. Important crystallographic data are listed in Table 4. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on F^2 with SHELXL ver.2014/6 [29]. Further experimental crystallographic details for **[Pd(P,P)Cl$_2$]·2CH$_2$Cl$_2$**: $2\theta_{max} = 54°$; reflections collected/unique/used, 41955/7524 [$R_{int} = 0.0241$]/7524;

Table 4
Crystallographic data for complexes **[Pd(P,P)X$_2$]**, X = Cl, Br, I.

	[Pd(P,P)Cl_2]·2CH_2Cl_2	[Pd(P,P)Br_2]	[Pd(P,P)I_2]
Formula	$C_{30}H_{33}Cl_6NP_2Pd$	$C_{28}H_{29}Br_2NP_2Pd$	$C_{28}H_{29}I_2NP_2Pd$
Fw	788.61	707.68	801.66
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$
a (Å)	10.7148(12)	10.0400(2)	10.6143(2)
b (Å)	15.2050(16)	14.6240(3)	15.1406(3)
c (Å)	21.201(3)	19.1974(4)	17.8385(3)
α (°)	90.0	90.0	90.0
β (°)	90.0	96.444(1)	90.121(1)
γ (°)	90.0	90.0	90.0
V (Å^3)	3454.0(7)	2800.85(10)	2866.76(9)
Z	4	4	4
T (°C)	24	−113	−113
Radiation	Mo Kα	Mo Kα	Mo Kα
ρ_{calcd} (g cm^{-3})	1.517	1.678	1.857
μ (mm^{-1})	1.116	3.647	2.930
Reflections with $I > 2\sigma(I)$	7325	5252	5823
R_1[a]	0.0238	0.0307	0.0188
wR_2[a]	0.0640	0.0738	0.0415

[a] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$ and $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(\alpha P)^2+bP]$ and $P = [\max(F_o^2, 0)+2F_c^2]/3$. $A = 0.0409$, b = 0.99 for X = Cl; $\alpha = 0.0375$, b = 3.12 for X = Br; $\alpha = 0.0149$, b = 2.83 for X = I.

405 parameters refined; $(\Delta/\sigma)_{max} = 0.001$; $(\Delta\rho)_{max}/(\Delta\rho)_{min} = 0.526/\text{-}0.458$ e/Å^3; $R1/wR2$ (for all data), 0.0246/0.0645 and the Flack parameter takes the value 0.01(3). Further experimental crystallographic details for **[Pd(P,P)Br$_2$]**: $2\theta_{max} = 54°$; reflections collected/unique/used, 29061/6109 [$R_{int} = 0.0418$]/6109; 387 parameters refined; $(\Delta/\sigma)_{max} = 0.001$; $(\Delta\rho)_{max}/(\Delta\rho)_{min} = 0.564/\text{-}0.902$ e/Å^3; $R1/wR2$ (for all data), 0.0389/0.0775. Further experimental crystallographic details for **[Pd(P,P)I$_2$]**: $2\theta_{max} = 54°$; reflections collected/unique/used, 39517/6247 [$R_{int} = 0.0261$]/6247; 423 parameters refined; $(\Delta/\sigma)_{max} = 0.003$; $(\Delta\rho)_{max}/(\Delta\rho)_{min} = 1.190/\text{-}0.886$ e/Å^3; $R1/wR2$ (for all data), 0.0211/0.0424. Hydrogen atoms were located by difference maps and were refined isotropically or were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically. The plots of the structures shown in Fig. 1 were drawn using the Diamond 3 program package [30].

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Appendix A. Supplementary data

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