Mechanistic study on the coupling reaction of aryl bromides with arylboronic acids catalyzed by (iminophosphine)palladium(0) complexes. Detection of a palladium(II) intermediate with a coordinated boron anion

Bruno Crociani, Simonetta Antonaroli, Alessia Marini, Ugo Matteoli and Alberto Scrivanti

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The complexes [Pd(η1-dmfu)(P–N)] [P–N = 2-(PPh2)C6H4-1-CH=NR, R = C6H4OMe-4; CHMe2; C6H4Me2-2,6; C6H4(CHMe2)-2,6] react with an excess of BrC6H4R1-4 (R1 = CHMe2, R = CHMe2, R1 = CF3, Me) yielding the oxidative addition products [PdBr(C6H4R1-4)(P–N)] at different rates depending on R [C6H4OMe-4 > C6H4Me2(CHMe2)-2,6 > CHMe2 ≈ C6H4Me2-2,6] and R1 (CF3, ≫ Me). In the presence of K2CO3 and activated olefins (ol = dmfu, fn), the latter compounds react with an excess of 4-R2C6H4B(OH)2, (R2 = H, Me, OMe, Cl) to give [Pd(η1-ol)(P–N)] and the corresponding biaryl through transmetallation and fast reductive elimination. The transmetallation proceeds via a palladium(II) intermediate with an O-bonded boron anion, the formation of which is markedly retarded by increasing the bulkiness of R. The intermediate was isolated for R = CHMe2, R1 = CF3 and R2 = H. The boron anion is formulated as a diphenylborinate anion associated with phenylboronic acid and/or as a phenylboronate anion associated with diphenylboronic acid. In general, the oxidative addition proceeds at a lower rate than transmetallation and represents the rate-determining-step in the coupling reaction of aryl bromides with arylboronic acids catalyzed by [Pd(η1-dmfu)(P–N)].

Introduction

The palladium-catalyzed cross-coupling between organic electrophiles and organoboron compounds (Suzuki–Miyaura reaction) is a very efficient and widely used method for the formation of carbon–carbon bonds. In particular, when aryl halides and arylboronic acids are used, the reaction yields biaryls, which are important intermediates for the synthesis of more complex molecules widely used as pharmaceuticals, agrochemicals or advanced materials.

The commonly accepted mechanism of this reaction involves an initial oxidative addition of the aryl halide to a palladium(0) species, followed by transfer of the aryl group from the boronic acid to the palladium(II) centre (transmetallation) and eventually by reductive elimination to give the biaryl product and regenerate the catalytically active palladium(0) species (Scheme 1). An alternative mechanism involves the reaction of the arylboronic acid with the complex [Pd(OR)(Ar)(L)2] in situ formed by ligand exchange between [PdX(Ar)(L)2] and the base RO− (alkoxide, hydroxide or carboxylate anion).

Following our studies on the catalytic activity of the zerovalent complexes [Pd(η1-dmfu)(P–N)] [dmfu = dimethyl fumarate; P–N = 2-(PPh2)C6H4-1-CH=NR, R = alkyl or aryl group], we have recently reported that these complexes are quite efficient catalysts (or catalyst precursors) in the coupling of arylboronic acids with aryl bromides (turnover numbers of up to 105 h−1 in anhydrous toluene at 110 °C, in the presence of K2CO3). With a suitable choice of the reaction conditions, an almost complete conversion of the substrates to biaryls can be obtained also when deactivating groups are present on the aryl bromide. These results prompted us to carry out a mechanistic investigation of the fundamental steps of the catalytic cycle of Scheme 1 in order to achieve a better understanding of (i) the factors which affect the
reaction rates and (ii) the mechanism of the transmetallation step, because the formation of the anion Ar$^+$Br(OH)$^-$ or the complex [Pd(OR)(Ar)(L)$_2$] can hardly occur under the catalysis conditions used.

**Results and discussion**

The model reaction chosen for the mechanistic study is reported in eqn (1):

$$\text{R}^1=\text{CF}_3, \text{Me}$$  
$$\text{R}^2=\text{Cl}, \text{H}, \text{Me}, \text{OMe}$$

$$\begin{align*}
\text{R}^-\text{Br} &+ \text{R}^1\text{Ar}^-\text{OH}\xrightarrow{\text{Cat}} \text{R}^-\text{Ar}^-\text{O} \\
\text{toluene, K}_2\text{CO}_3 &
\end{align*}$$

(1)

The zerovalent complexes [Pd($\eta^2$-ol)(P–N)] [ol = dimethyl fumarate (dmfu) or fumaronitrile (fn); P–N = iminophosphine] used as catalysts are shown in Scheme 2. Where possible, the reactions of the single steps of the cycle in Scheme 1 have been carried out in dry toluene (or toluene-d$_8$) at 90 °C in a N$_2$ atmosphere under pseudo-first-order conditions, generally using a palladium complex/reactant molar ratio of 1:10 with an initial palladium complex concentration of 1 × 10$^{-2}$ mol dm$^{-3}$. The progress of the reactions was monitored by IR spectroscopy in the range 2400–1500 cm$^{-1}$ and by $^{31}$P NMR spectroscopy.

**Step (a): oxidative addition**

The reactions studied are summarized in Scheme 3.

With a ten-fold excess of BrC$_6$H$_4$R$^1$-4, the completion times of Table 1 were evaluated by IR and $^{31}$P NMR spectra at different times.

For the dmfu complexes 1a–4a, the progress of the reaction was indicated by the increasing intensity of the ν(C=O) band of free dmfu at 1725 cm$^{-1}$ and the concomitant decreasing intensity of the ν(C≡N) band of the $\eta^2$-bound olefin at 2203 cm$^{-1}$. For the fn complex 5a, the decreasing intensity of the ν(C≡N) band of the $\eta^2$-bound olefin at 2203 cm$^{-1}$ was monitored. In the $^{31}$P NMR spectra, the δ($^{31}$P) singlet of the starting complexes 1a–4a (in the range 19.3–23.2 ppm) progressively disappears with concomitant formation of the δ($^{31}$P) singlet of the products 1b–5b in the range 20.7–28.0 ppm. Even though the reactions are accompanied by a slight decomposition to palladium metal, the completion times evaluated from IR data are very close to those obtained from $^{31}$P NMR spectra.

As expected, in the reactions of 2a with BrC$_6$H$_4$R$^1$-4 the rate decreases considerably on going from R$^1$ = CF$_3$ to R$^1$ = Me in agreement with a lower electrophilic character of the C–Br carbon atom. The rate of the oxidative addition of BrC$_6$H$_4$CF$_3$-4 to complexes 1a–5a depends essentially on the electronic and steric properties of the imino nitrogen substituent R and on the π-accepting properties of the olefin as it decreases in the order 1a > 4a > 2a ≈ 3a ≫ 5a. This trend closely parallels that found for the analogous oxidative additions of IC$_6$H$_4$CF$_3$-4: 1a > 2a ≫ 5a.$^7$ From a kinetic study of the latter reactions,$^7$ this trend was rationalized in terms of electronic effects which reduce the electron density on the central metal and increase the strength of the Pd–olefin and Pd–N bonds, on the basis of the following Table 1 Completion times for reaction (2) of Scheme 3$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>Aryl bromide</th>
<th>Product</th>
<th>Completion time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>BrC$_6$H$_4$CF$_3$-4</td>
<td>1b</td>
<td>ca. 15 min</td>
</tr>
<tr>
<td>2a</td>
<td>BrC$_6$H$_4$CF$_3$-4</td>
<td>2b</td>
<td>ca. 55 min</td>
</tr>
<tr>
<td>2a</td>
<td>BrC$_6$H$_4$Me-4</td>
<td>5b</td>
<td>ca. 7 h</td>
</tr>
<tr>
<td>3a</td>
<td>BrC$_6$H$_4$CF$_3$-4</td>
<td>3b</td>
<td>ca. 60 min</td>
</tr>
<tr>
<td>4a</td>
<td>BrC$_6$H$_4$CF$_3$-4</td>
<td>4b</td>
<td>ca. 35 min</td>
</tr>
<tr>
<td>5a</td>
<td>BrC$_6$H$_4$CF$_3$-4</td>
<td>1b</td>
<td>ca. 20 h</td>
</tr>
</tbody>
</table>

$^a$ For a molar ratio 1a–5a/aryl bromide of 1:10 in toluene at 90 °C.

Scheme 2

Scheme 3
mechanism:

\[
[Pd(n^2-dmfu)(P–N)] + S \rightarrow [Pd(n^2-dmfu)(S)(\kappa^1-P-N)] + \text{dmfu}
\]

where S is a solvent molecule and \([Pd(n^2-dmfu)(S)(\kappa^1-P-N)]\) is an intermediate containing a P-monodentate iminophosphine. From the data presented it can be seen that steric effects are also important, but a clear trend cannot be recognized. As a matter of fact, for the complexes 1a, 3a and 4a, containing N–aryl substituents, the rate decreases on going from 1a (\(R = C_6H_4OMe-4\)) to 3a (\(R = C_6H_4Me_2-2,6\), i.e. with increasing the steric bulk of the N–aryl group, and this effect can be understood on the basis of the proposed mechanism which involves a solvent assisted rupture of the Pd–olefin and Pd–N bonds. By contrast, an increased rate is observed on going from 3a to 4a [\(R = C_6H_4(CHMe_2)_2-2,6\)] where the steric requirements of the N–aryl group are further increased. In a possible rationalization, this may be attributed to an intramolecular steric clash between the isopropyl groups and dmfu which would favour the olefin dissociation and/or the Pd–N bond breaking. However, this explanation needs to be confirmed by further kinetic measurements.

All the complexes 1b–5b have been isolated and characterized (see Experimental). These palladium(II) derivatives may exist as supported by the low-frequency values of the \(3c\) phosphorus atom of the iminophosphine.

Table 2 Completion times for reaction (3)*

<table>
<thead>
<tr>
<th>Complex</th>
<th>R</th>
<th>R¹</th>
<th>R²</th>
<th>ol</th>
<th>T/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1b</td>
<td>C₆H₄OMe-4</td>
<td>CF₃</td>
<td>H</td>
<td>fn</td>
<td>ca. 5</td>
</tr>
<tr>
<td>2b</td>
<td>CHMe₂</td>
<td>CF₃</td>
<td>H</td>
<td>dmfu</td>
<td>ca. 20</td>
</tr>
<tr>
<td>2b</td>
<td>CHMe₂</td>
<td>CF₃</td>
<td>Me</td>
<td>fn</td>
<td>ca. 7</td>
</tr>
<tr>
<td>2b</td>
<td>CHMe₂</td>
<td>CF₃</td>
<td>OMe</td>
<td>fn</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>2b</td>
<td>CHMe₂</td>
<td>CF₃</td>
<td>Cl</td>
<td>fn</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>3b</td>
<td>C₆H₄Me₂-2,6</td>
<td>CF₃</td>
<td>H</td>
<td>fn</td>
<td>ca. 35</td>
</tr>
<tr>
<td>4b</td>
<td>C₆H₄(CHMe₂)$_2$-2,6</td>
<td>CF₃</td>
<td>H</td>
<td>fn</td>
<td>ca. 30</td>
</tr>
<tr>
<td>5b</td>
<td>CHMe₂</td>
<td>Me</td>
<td>H</td>
<td>fn</td>
<td>ca. 40</td>
</tr>
</tbody>
</table>

*For initial mixtures 1b–5b/4-R$^\prime$C₆H₄B(OH)$_2$/K$_2$CO$_3$/ol in a 1 : 10 : 20 : 1.5 molar ratio at 90 °C in toluene.

As commonly accepted, the formation of the biaryl and the complex [Pd(η$^2$-ol)(P–N)] occurs through aryl transfer from the boronic acid to the palladium(II) centre of 1b–5b (transmetallation) to give a labile intermediate [Pd(C₆H₄R$^1$-4)(C₆H₄R$^2$-4)(P–N)]. The subsequent reductive elimination of the biaryl generates a coordinatively unsaturated Pd(P–N) fragment which is stabilized by η$^1$-coordination of the olefin. During our experiments, however, signals stemming from an intermediate of the type [Pd(C₆H₄R$^1$-4)(C₆H₄R$^2$-4)(P–N)] were never detected in the $^{31}$P NMR spectra of the reaction mixtures. This implies that reductive elimination and olefin coordination are much faster than transmetallation. By contrast, the $^{31}$P NMR spectra shows the initial formation of a palladium(II) intermediate containing a coordinated boron anion which undergoes the transmetallation step (see later). Thus, the overall reaction (3) consists of at least three consecutive steps as shown in Scheme 4.

The formation of an intermediate of the type 6 is particularly evident in the reaction of 2b with PhB(OH)$_2$. At 25 °C and with a 2b/PhB(OH)$_2$ molar ratio increasing from 1 : 3 to 1 : 10, the $^{31}$P NMR spectra at different times show the progressive decrease of the δ($^{31}$P) siglet of 2b at 27.7 ppm and the simultaneous increase of the δ($^{31}$P) siglet of 6 at 33.2 ppm [spectrum (a) of Fig. 1].

The rate of step (i) in Scheme 4 increases with increasing concentration of the arylboronic acid and is also influenced by the steric requirements of the imino group R and by the electronic properties of the para substituent R$^1$ on the aryl ligand. The latter effect is observed in the spectrum (b) of Fig. 1. Under the same experimental conditions, in the reaction 5b/PhB(OH)$_2$/K$_2$CO$_3$/dmfu (1 : 5 : 10 : 1.5 molar ratio) the intermediate of type 6 is formed more slowly (ca. 50% after 30 min from mixing of the reactants). Thus, the rate of step (i) decreases on going from 2b (R$^1$ = CF$_3$) to 5b (R$^1$ = Me), i.e. when the electron-withdrawing CF$_3$ substituent on the aryl ligand is replaced by the
**Scheme 4**  
(i) + K₂CO₃ → KBr, nucleophilic substitution; (ii) transmetallation; (iii) reductive elimination and olefin coordination; Y = boron anion (see further).

**Fig. 1**  
(a) ³¹P NMR spectrum of the reaction mixture 2b/PhB(OH)₂/K₂CO₃/dmfu (1 : 5 : 10 : 1.5 molar ratio) in toluene-d₈ at 25 °C after 25 min from mixing of the reactants: ⬤ signal of the intermediate 6, □ signal of the starting complex 2b.  
(b) ³¹P NMR spectrum of the reaction mixture 5b/PhB(OH)₂/K₂CO₃/dmfu (1 : 5 : 10 : 1.5 molar ratio) in toluene-d₈ at 25 °C after 25 min from mixing of the reactants: ⬤ signal of the intermediate 6, □ signal of the starting complex 5b.

Electron-donating Me group. At 90 °C and with a complex/aryl boronic acid molar ratio of 1 : 10, the formation of 6 is relatively fast in the reaction of 1b (R = C₆H₄OMe-4) with PhB(OH)₂, and in the reactions of 2b (R = CHMe₂) with 4-R₂C₆H₄B(OH)₂ (R₂ = H, Me, OMe, Cl). As can be seen in the spectra (a) and (b) of Fig. 2, the starting complex 2b has completely disappeared after 8 min from the mixing of the reactants.

In the reactions of 3b (R = C₆H₃Me₂-2,6) and 4b [R = C₆H₅(CHMe₂)₂-2,6] with PhB(OH)₂, the intermediate of the type 6 is not observed during the course of reaction (3). In the ³¹P NMR spectra of the reaction mixture at different times (Fig. 3), the decreasing δ(³¹P) singlet of the starting complex and the increasing δ(³¹P) singlet of the zerovalent product [Pd(η²-fn)(P–N)] are the only observed signals throughout. This can be ascribed to a marked rate decrease of step (i) relative to the subsequent step (ii) brought about by the greater steric hindrance towards nucleophilic substitution of the bromide ligand exerted by the bulkier N–aryl groups. From the present data it appears that formation of the intermediate 6 [step (i)] is rate-determining in reaction (3) of 3b or 4b with PhB(OH)₂, whereas transmetallation [step (ii)] is rate-determining in reaction (3) of...
Fig. 3  (a) $^{31}$P NMR spectrum of complex 3b in toluene-$d_8$ at 90 °C. (b) and (c) $^{31}$P NMR spectra of the reaction mixture 3b/PhB(OH)$_2$/K$_2$CO$_3$/fn (1 : 10 : 15 : 1.5 molar ratio) in toluene-$d_8$ at 90 °C after 12 and 35 min, respectively, from the mixing of the reactants: □ signal of the starting complex 3b, ■ signal of the product [Pd($\mu^3$-fn)(P–N)].

1b with PhB(OH)$_2$, or of 2b with 4-R$^2$C$_6$H$_4$B(OH)$_2$ (R$^2$ = H, Me, OMe, Cl). In the latter cases, the completion times of Table 2 give a measure of the reaction rates for the transmetallation step (ii). It is interesting to note that under comparable steric requirements the rate increases with increasing electron-withdrawing properties of the imino substituent R [1b (R = C$_6$H$_4$OMe-4) > 2b (R = CHMe$_2$)] and with increasing electron-donating properties of the 4-R$^2$ group on the arylboronic acid.

Characterization of the intermediate 6b

The intermediate 6b was isolated as an off-white microcrystalline solid from the reaction of 2b with PhB(OH)$_2$, in the presence of K$_2$CO$_3$ (see Experimental). Unfortunately, the crystals proved unsuitable for X-ray analysis. Therefore, the characterization is essentially based on elemental analysis, IR and multinuclear ($^1$H, $^{31}$P, $^{11}$B, $^{19}$F) NMR spectra along with FAB mass spectra. The available data suggest a structure containing an O-bonded boron anion formed by a diphenylborinate anion associated with a molecule of phenylboronic acid (structure I of Fig. 4) or by a phenylboronate anion associated with a molecule of diphenylborinic acid (structure II of Fig. 4).

The IR spectrum in the solid and in CHCl$_3$ solution show the presence of different OH groups. In the solid, the ν(OH) vibrations are detected as a rather sharp band at 3627 cm$^{-1}$ and as a much broader band at 3430 cm$^{-1}$, while a sharp band at 3596 cm$^{-1}$ and a broader band at 3410 cm$^{-1}$ are observed in solution. This pattern clearly indicates the presence of OH groups with the H atom involved in hydrogen-bonding (higher frequency band) and OH groups with the H atom involved in hydrogen-bonding (lower frequency band). The integration of the $^1$H NMR spectrum (CDCl$_3$) in the range 8.2–6.8 ppm gives a value of 35 in good agreement with the number of the phenyl and N=CH protons (34) resonating in that range. Significant structural information is afforded by the MS spectrum where the peaks at $m/z$ 105 and 165 are assigned to the ions [PhBOH]$^+$ and [Ph$_3$B]$^+$, respectively, and the cluster of peaks centered at $m/z$ 688 is assigned to the ion [Pd(OBPh)(C$_6$H$_4$CF$_3$-4)(P–N)]$^+$ [P–N = 2-(PPh$_2$)C$_6$H$_4$-1-CH=NCHMe$_2$]. Furthermore, clusters of peaks centered at $m/z$ 436, 582 and 598 are also observed and assigned to the ions [Pd(P–N)]$^+$, [Pd(C$_6$H$_4$CF$_3$-4)(P–N)]$^+$ and [Pd(OH)(C$_6$H$_4$CF$_3$-4)(P–N)]$^+$, respectively.

In the temperature range $-35 \div +25$ °C, the $^{19}$F and $^{31}$P NMR spectra show the presence of a sharp singlet only, while the $^1$H NMR spectra are characterized by a single set of resonances. Accordingly, the intermediate 6b may exist in solution either with a single structure or with both structures I and II in a fast interconversion (on the NMR timescale). Furthermore, in the $^1$H NMR spectra the methyl protons of the N–CHMe$_2$ group appear as a single doublet indicating that the coordination plane around the palladium centre acts as a time-averaged symmetry plane for the whole molecule, in accord with the proposed structures. The $^{11}$B NMR spectrum of 6b in Fig. 5 shows two broad signals at 31.8 and 7.4 ppm, which become somewhat sharper at higher temperatures.

Fig. 4  Proposed structures for the intermediate 6b.

Fig. 5  $^{11}$B NMR spectrum of 6b in CDCl$_3$ at $-10$ °C.

Fig. 5
From chemical shift considerations, the signal at 31.8 ppm is assigned to a three-coordinate $^{11}$B centre whereas that at 7.4 ppm is assigned to a four-coordinate $^{11}$B centre.\textsuperscript{11}

If our formulation is correct, the presence of the Ph$_2$BO unit in the structures of the intermediate 6b implies that a Ph/OH exchange has occurred between two PhBO$_2$ moieties in the course of the reaction [step (i) of Scheme 4]. We have therefore studied the interaction of PhB(OH)$_2$ with anhydrous K$_2$CO$_3$ in toluene-$d_8$ [spectra (a) and (b) of Fig. 6].

![Fig. 6 $^{11}$B NMR spectra of PhB(OH)$_2$ at 25 °C: (a) in toluene-$d_8$; (b) in toluene-$d_8$ saturated with anhydrous K$_2$CO$_3$; (c) in CDCl$_3$.](image)

As can be seen, in the presence of K$_2$CO$_3$ the signal of the phenylboronic acid at 32.0 ppm considerably broadens and a new broad resonance appears at 7.4 ppm suggesting that a four-coordinate boron anion is formed. From the close similarity in the $^{11}$B chemical shifts, it is likely that such an anion is also present in the structure of 6b.

In the intermediate, the boron anion is weakly bound to the metal centre as it can be completely displaced by chloride anions [reaction (1) of scheme 5].

The intermediacy of 6b in the catalytic cycle is confirmed by the reaction (2) of Scheme 5, which occurs in ca. 20 min when the complex is heated at 90 °C in toluene in the presence of fumaronitrile and PhB(OH)$_2$ with a 6b/PhB(OH)$_2$/fn molar ratio of 1 : 7 : 1.5 [cf. the completion time of ca. 20 min for the reaction (3) of 2b, under comparable experimental conditions].

**Conclusion**

From the present mechanistic study it appears that in the cross-coupling of arylboronic acids with aryl bromides catalyzed by [Pd($\eta^1$-ol)(P–N)] the oxidative addition of the aryl bromide is generally the rate-determining step of the catalytic cycle. Thus, the greater catalytic activity displayed by the zerovalent complexes with ol = dmfu and with an imino N–aryl group of low steric requirements, such as Ph and C$_6$H$_4$OMe-4,* can be related to the higher rates of their reactions with ArBr. The oxidative addition products [PdBr(Ar)(P–N)] react with arylboronic acids in the presence of K$_2$CO$_3$ and of an activated olefin yielding the corresponding biaryls and regenerating the starting complexes [Pd($\eta^1$-ol)(P–N)] by transmetallation followed by fast reductive elimination and $\eta^1$-coordination of the olefin. The transmetallation step proceeds through the intermediacy of a complex containing an O-bonded boron anion which is formulated as an arylboronate anion associated with a molecule of diarylborinic acid and/or a diarylborinate anion associated with a molecule of arylboronic acid.

**Experimental**

$^1$H, $^{31}$P and $^{19}$F NMR spectra were recorded on a Bruker AM400 spectrometer operating at 400.13, 161.98 and 376.50 MHz, respectively. The $^{11}$B NMR spectra were recorded on a Bruker AMX300 spectrometer operating at 96.25 MHz. Chemical shifts are reported in ppm downfield from SiMe$_4$ for $^1$H, from H$_3$PO$_4$ as external standard for $^{31}$P, from CFCl$_3$ as external standard for $^{19}$F and from BF$_3$·Et$_2$O as external standard for $^{11}$B. The spectra were run at 25 °C except when noted. IR spectra were recorded on a Perkin–Elmer 983G spectrophotometer. The FAB mass spectra in a matrix of 3-nitrobenzyl alcohol were obtained with a VG Quattro Micromass spectrometer. All the

![Scheme 5](image)
reactions were carried out under N2. Toluene was distilled from sodium/benzophenone and methanol was dried over magnesium turnings.12 The aryl bromides BrC6H4R-4 (R1 = CF3, Me), the arylboronic acids 4-R2C6H4B(OH)2 (R2 = H, Me, OMe, Cl), the olefins dfmuf and fn, and the anhydrous potassium carbonate were commercially available and were used without further purification. The complexes [Pd(?-ol)(P–N)] (1a–5a) were prepared as reported in the literature.5,13

Synthesis of [PdBr(C6H4R1-4)(P–N)] (1b–5b)

The complex [Pd(η2-dmfu)(P–N)] (1a) and the aryl bromide BrC6H4CF3-4 (1.13 g, 5 mmol) were dissolved in toluene (50 cm3). After addition of activated charcoal and filtration, the solution was evaporated to about 3 cm3. Upon addition of Et2O, the product precipitated as a pale-yellow solid. The complex 2b was prepared in a similar manner starting from 2a (0.58 g, 0.5 mmol) and BrC6H4Me-4 (1.71 g, 10 mmol) and heating the mixture at 110 °C for 20 min. All the compounds were further purified by recrystallization from CH2Cl2/Et2O.

Complex 1b. (0.24 g, 66%) (Found C 54.18, H 3.40, N 1.94%; C33H26BrF3NOPPd requires C 54.53, H 3.61, N 1.93%;) νmax/cm–1 (O–H) 3627 m, 3430 m (br), (B–O) 1557 vs, (C–H) 3056 s, (P–C) 1511 m (Nujol); δν (CDCl3) 28.3 (s).

Complex 2b. (0.24 g, 66%) (Found C 54.18, H 3.40, N 1.94%; C33H26BrF3NOPPd requires C 54.53, H 3.61, N 1.93%;) νmax/cm–1 (O–H) 3627 m, 3430 m (br), (B–O) 1557 vs, (C–H) 3056 s, (P–C) 1511 m (Nujol); δν (CDCl3) 28.7 (s).

Complex 3b. (0.27 g, 75%) (Found C 56.14, H 3.80, N 1.95%; C33H26ClF3NOPPd requires C 56.33, H 3.91, N 1.93%;) νmax/cm–1 (O–H) 3627 m, 3430 m (br), (B–O) 1557 vs, (C–H) 3056 s, (P–C) 1511 m (Nujol); δν (CDCl3) 28.7 (s);

Complex 4b. (0.22 g, 56%) (Found C 58.31, H 4.39, N 1.80%; C33H26BrF3NOPPd requires C 58.44, H 4.65, N 1.79%;) νmax/cm–1 (O–H) 3627 m, 3430 m (br), (B–O) 1557 vs, (C–H) 3056 s, (P–C) 1511 m (Nujol); δν (CDCl3) 28.7 (s);

Complex 5b. (0.21 g, 70%) (Found C 56.81, H 4.60, N 2.33%; C33H26BrF3NOPPd requires C 57.21, H 4.80, N 2.30%;) νmax/cm–1 (O–H) 3627 m, 3430 m (br), (B–O) 1557 vs, (C–H) 3056 s, (P–C) 1511 m (Nujol); δν (CDCl3) 8.13 (1 H, s, N=CH), 7.8–7.0 (16 H, m, aryl protons), 6.35–6.49 (2 H, m, m-H of C6H4Me-4), 5.47 (1 H, spt, J(1/J2) = 6.4 Hz, CHMe2), 2.06 (3 H, s, CH3), 1.21 (6 H, d, J(1/J2) = 6.4 Hz, CH2); δν (CDCl3) 26.8 (s).

Preparation of the intermediate 6b

A mixture of complex 2b (0.33 g, 0.5 mmol), PhB(OH)2 (0.31 g, 2.5 mmol), anhydrous K2CO3 (0.69 g, 5 mmol) and dmfu (0.07 g, 0.5 mmol) in dry toluene (50 cm3) was stirred at room temperature for 45 min. The insoluble material was filtered off and the solution was evaporated to dryness at 20 °C under reduced pressure. The solid residue was dissolved in anhydrous methanol (ca. 6 cm3). After stirring for a few minutes an off-white product precipitated. The product was purified by recrystallization from toluene/n-hexane (1 : 1.5 v/v) at −20 °C. The compound must be stored at −20 °C because it decomposes slowly at room temperature. Freshly recrystallized samples were used for each measurement. A certain amount of dfmuf in the reaction mixture is required in order to prevent the formation of metallic palladium from further reactions of the intermediate. The presence of Br ions in the insoluble material resulting from the initial filtration of the reaction mixture in toluene was ascertained by qualitative analysis with AgNO3.

Any attempt to isolate intermediates of type 6 from analogous reactions of 2b with 4-R2C6H4Br(OH)2 (R2 = Me, OMe, Cl) or of 5b with PhB(OH)2 failed because of the greater solubility of the intermediates in methanol.

Intermediate 6b. (0.20 g, 45%) (Found C 63.28, H 4.86, N 1.45%; C29H29BrNPPd requires C 57.21, H 4.80, N 2.30%;) νmax/cm–1 (O–H) 3627 m, 3430 m (br), (B–O) 1557 vs, (C–H) 3056 s, (P–C) 1511 m (Nujol); δν (CDCl3) 8.1–6.8 (35 H, m, aryl protons and N=CH), 5.20 (1 H, spt, J(1/J2) = 6.4 Hz, CHMe2), 2.20 (0.8 H, s, OH), 1.17 (6 H, d, J(1/J2) = 6.4 Hz, CH2); δν (CDCl3) 32.8 (s); δν (toluene-d5) –62.01 (s). Selected MS peaks: m/z 105 (21%), 165 (18), 436 (12), 582 (70), 598 (38), 688 (20).

Reaction of 6b with aqueous NaCl

A saturated solution of NaCl in water (10 cm3) was added to a solution of 6b (60 mg, 0.068 mmol) in CH2Cl2 (10 cm3). The mixture was vigorously stirred for 30 min at room temperature. The organic layer was separated, dried over anhydrous Na2SO4 and concentrated to a small volume (ca. 3 cm3) at reduced pressure. Addition of Et2O caused the precipitation of the off-white product 2e which was reprecipitated from a CH2Cl2/Et2O mixture.

Complex 2c. (34 mg, 82%) (Found C 58.54, H 3.95, N 2.25%; C22H22Cl2NPPd requires C 51.94, H 4.36, N 1.58%;) νmax/cm–1 (O–H) 3627 m, 3430 m (br), (B–O) 1322 vs, (C–H) 3039 s, (P–C) 1511 m (Nujol); δν (CDCl3) 8.15 (1 H, s, N=CH), 7.8–7.1 (16 H, m, aryl protons), 6.8–6.84 (2 H, m, m-H of C6H4CF3–4), 5.48 (1 H, spt, J(1/J2) = 6.4 Hz, CHMe2), 1.25 (6 H, d, J(1/J2) = 6.4 Hz, CH2); δν (CDCl3) 28.7 (s); δν (toluene-d5) –61.54 (s).

Synthesis of [PdCl2(2-(PPh2)C6H4-1-CH=NCHMe2)]

The iminophosphine 2-(PPh2)C6H4-1-CH=NCHMe28 (0.17 g, 0.5 mmol) was added to a stirred solution of [PdCl2(N=CMe2)]4 (0.13 g, 0.5 mmol) in CH2Cl2 (25 cm3). After 30 min the solution was evaporated to ca. 3 cm3 and diluted with Et2O to precipitate the product as a yellow microcrystalline solid. The compound was reprecipitated from CH2Cl2/Et2O (0.22 g, 86.5%) (Found C 51.75, H 4.21, N 2.65%; C47H43B2F3NO3PPd requires C 63.72, H 4.89, N 1.58%;) νmax/cm–1 (O–H) 3627 m, 3430 m (br), (B–O) 1322 vs, (C–H) 3039 s, (P–C) 1511 m (Nujol); δν (CDCl3) 26.8 (s).
5.6 Hz, CHMe), 1.14 (6 H, d, J(HH) = 6.4 Hz, CHMe); 1J(HH) = 6.4 Hz, CHMe). 1J(HH) = 6.4 Hz, CHMe); δp (CDCl3) 32.5 (s).

Synthesis of [PdCl(C6H4Me-4)(2-(PPh2)C6H4-1-CH≡NCHMe2)] (5c)
A mixture of [PdCl2(2-(PPh2)C6H4-1-CH≡NCHMe2)] (0.51 g, 1 mmol), 4-MeC6H4B(OH)2 (0.41 g, 3 mmol), anhydrous K2CO3 (1.38 g, 10 mmol) and dmf (0.14 g, 1 mmol) in dry toluene (50 cm3) was stirred at room temperature for 30 min. The insoluble material was filtered off and the solution was evaporated to dryness at reduced pressure. The solid residue was dissolved in CH2Cl2 (20 cm3) and the solution was filtered over Celite. Upon addition of methanol (30 cm3) the solution was concentrated to a small volume (ca. 5 cm3) and stored at −20 °C for 2 h. The resulting yellowish precipitate was filtered, washed with cold methanol and recrystallized from CH2Cl2/Et2O to give the off-white microcrystalline product 5c.

Complex 5c. (0.21, 37%) (Found C 61.72, H 5.18, N 2.48%; C29H29ClNPPd requires C 61.31, H 4.86, N 2.49%; m

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References
14 The complex [PdCl(N≡CMe2)]2 was prepared from reaction of PdCl2 with boiling acetonitrile in the same way as described for the analogue [PdCl(N≡CPH2)]2; see: F. R. Hartley, Organomet. Chem. Rev., Sect. A, 1970, 6, 119–137.