ARTICLE

$LPdCl_2$(amine) Complexes Supported by Terphenyl Phosphanes: Applications in Aryl Amination Reactions†

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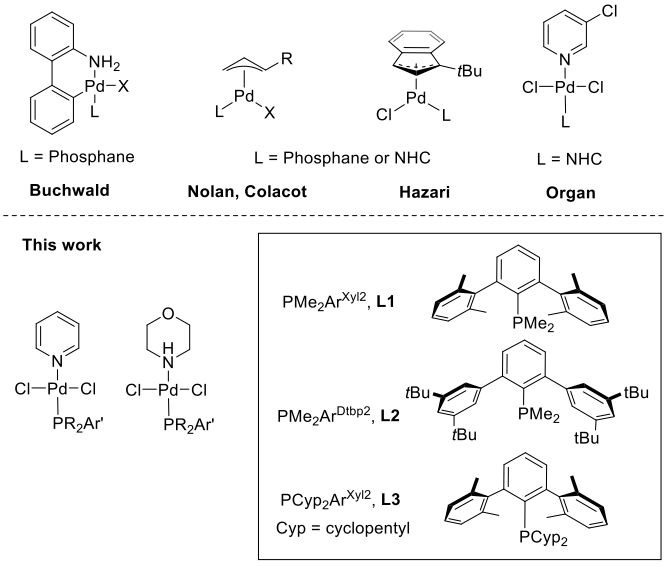
Despite the excellent catalytic properties display by NHC-Pd-PEPPSI complexes in cross-coupling, phosphane analogs have been barely screened. In this work, we report the synthesis and characterization of a series of $LPdCl_2$(amine) complexes bearing dialkylterphenyl phosphanes (PR_2Ar') and pyridine or morpholine ligands. The novel compounds have been tested as precatalysts in aryl amination reactions. The complex [$(PCyp_2Ar^{Xyl2})PdCl_2$(morpholine)] shows the best catalytic activity allowing the room-temperature coupling of aryl bromides and chlorides with aniline.

Introduction

The use of well-defined precatalysts is becoming a more common practice in palladium-catalyzed cross-coupling reactions.[1] Preformed Pd precatalysts offer substantial benefits over the in situ generation protocols, particularly a much more efficient activation to the catalytically active species[2] and a better control of the Pd to ligand ratio. For bulky monodentate ligands, an optimal 1:1 ratio is often found,[3] with a monoligated 12-electron LPd(0) species being proposed as the active catalyst.[4] Accordingly, the development of palladium precatalysts with the adequate 1:1 Pd to ligand ratio has received considerable research attention over the last two decades[5] Among the Pd precatalysts described, those based on Pd(II) are the most popular due to their better air-and moisture-stability that facilitates their handling and storing. However, their catalyst efficiency is highly dependent on the ease with which they are reduced to the active LPd(0) under catalytic conditions.[5c]

Prominent families of Pd(II) precatalysts (Scheme 1) include palladacycles derived from 2-aminobiphenyl scaffold,[6] η^3-allyl-[2b,7] and η^3-indenyl-type[8] precatalysts and PEPPSI-precatalysts[9] (PEPPSI = Pyridine-Enhanced Precatalyst Preparation, Stabilization and Initiation). The PEPPSI precatalysts has been extensively screened with N-heterocyclic carbenes (NHCs) as supporting ligands. With the combination of the PEPPSI platform and NHCs, the group of Organ has described remarkable results in Negishi couplings of secondary alkylzinc halides[10] and in C-N[11] and C-S[11a,12] bond formation reactions under very mild conditions. These major developments have made possible thanks to the versatility of the PEPPSI platform to accommodate the steric demand of bulky NHC ligands.

Considering the excellent performance of the PEPPSI-precatalysts in a wide range of cross-coupling reactions, it is somewhat surprising that the PEPPSI platform has scarcely been tested with tertiary phosphanes, typically the ligand of choice in Pd catalysis. In a recent report, Shaughnessy and co-workers[13] have compared the catalytic activity of two Pd-PEPPSI complexes supported by neopentylsubstituted phosphane with those of the halide-bridged phosphane palladium derivatives $[(PR_3)PdCl_2]_2$ in C-N cross-coupling reactions. Moreover, the group of Nolan have described the preparations of PR_3-Pd-PEPPSI with PPh_3,[14a] SPhos[14a] and 1,4,7-triaza-9-phosphatricyclo[5.3.2.1]tridecane (CAP).[14b] The precatalyst with PPh_3 promotes the Suzuki coupling between 4-bromoanisol and phenylboronic acid whereas the CAP derivative shows poor catalytic activity in the amination of 4-chloroanisol with morpholine at 80 °C.



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† Electronic Supplementary Information (ESI) available: detailed experimental procedures, spectroscopic and analytical data, and X-ray crystallographic data. CCDC 2158769 (**1b**), 2158767 (**2a**), 2158768 (**3a**) and 2158770 (**5**). See DOI: 10.1039/x0xx00000x

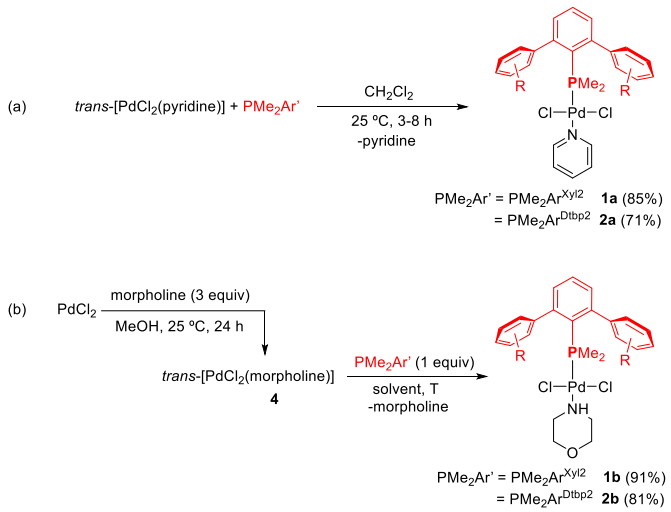
Scheme 1 Examples of Pd(II) precatalysts

A family of sterically demanding, electron-rich dialkylterphenyl phosphane ligands have been developed in our research group.[15] We have focused in applying these phosphane ligands in cross-coupling chemistry using preformed precatalysts. In this vein, we have recently shown that [Pd(2-aminobiphenyl)L](OMs)[16a,b] (OMs = mesylate) and [LNi(allyl)Cl][16c] precatalysts, both supported by terphenyl phosphanes, exhibit excellent activities in C-N and C-S bond formation reactions, respectively. With the aim of broadening the array of precatalysts compatible with terphenyl phosphane ancillary ligands we turned our attention to the Pd-PEPPSI type precatalysts, largely used with NHC ligands. This type of precatalysts in combination with bulky phosphane ligands have been barely studied. Herein, we report the preparation of a series of terphenyl phosphane-supported $LPdCl_2$(amine) complexes (amine = pyridine and morpholine) as well as their catalytic activity in the Buchwald-Hartwig amination reaction,[17] highlighting the importance of the amine ligand in the reactivity of the best performing catalyst system.

Results and discussion

Synthesis and characterization of complexes.

The synthesis of Pd-PEPPSI-PMe_2Ar' complexes [$(PMe_2Ar')PdCl_2$(pyridine)] **1a, 2a** was accomplished by a slight modification of the procedure recently developed by the Nolan group for the preparation of NHC analogues.[14a] The palladium precursor *trans*-[$PdCl_2$(pyridine)$_2$] was reacted with equimolar amounts of the dimethylsubstituted phosphanes **L1** and **L2** in CH_2Cl_2 at room temperature (Scheme 2a). The substitution reaction took approximately 8 h to reach completion with PMe_2Ar^{Xyl2}, **L1**, while for the ligand PMe_2Ar^{Dtbp2}, **L2**, the reaction was completed almost in 3 h. It seems that the increased steric demand for ligand **L1**, due to the presence of *ortho* substituents on the side phenyl rings of the terphenyl moiety slows down the substitution of the pyridine ligand. Both complexes **1a** and **2a** were obtained, as microcrystalline yellow solids, in high yields.



Scheme 2 Preparation of Pd-PEPPSI-PMe_2Ar' complexes **1**-**2**.

Organ has shown that the replacement of the pyridine ligand by morpholine in the PEPPSI precatalysts facilitates their activation to the active monoligated Pd(0) species.[18] On this basis, the preparation of the *trans*-ligated morpholine derivatives [$(PMe_2Ar')PdCl_2$(morpholine)], **1b**, **2b**, was carried out. The synthesis of complexes **1b** and **2b**, required the use of *trans*-[$PdCl_2$(morpholine)$_2$] adduct, **4**. This precursor was easily obtained following the method reported for the pyridine analog[14a], consisting in the reaction of $PdCl_2$ with 3 equiv of morpholine in MeOH at room temperature for 24 h (Scheme 2b). The insolubility of bis(morpholine) adduct **4** in all common NMR solvents hampered its NMR characterization, but its purity was confirmed by elemental analysis (see ESI for details).

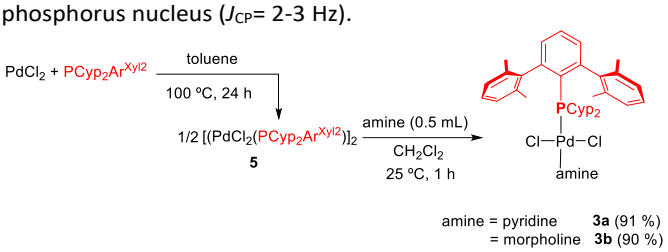
The substitution reaction of one of the morpholine ligands in **4** by PMe_2Ar^{Xyl2}, **L2**, proved more difficult than that of pyridine and prolonged heating (72 h) at 60 °C in 1,2-dichloroethane was necessary to achieve full conversion. However, with the less steric encumbered ligand PMe_2Ar^{Dtbp2}, **L2**, the reaction proceeded cleanly in CH_2Cl_2 at room temperature in only 3 hours. Compounds **1b**, **2b** were isolated in high yields as yellow solids.

Since the steric bulk of the phosphane appeared to be crucial for the success of amine substitution reactions shown in Scheme 2, it was not unexpected that no reaction occurred when bis(amine) adducts were combined with the largest phosphane ligand $PCyp_2Ar^{Xyl2}$, **L3**, even on prolonged heating time. Thus, the $PCyp_2Ar^{Xyl2}$ derivatives **3a** and **3b** were prepared using the palladium dimer [$PdCl_2(PCyp_2Ar^{Xyl2})]_2$, **5**, as the metal precursor.[18,19] The latter was obtained from the thermal reaction of equimolar amounts of $PdCl_2$ and the ligand $PCyp_2Ar^{Xyl2}$ in toluene at 100 °C. Compound **5** is a dimer in the solid state but, in polar solvents (CH_2Cl_2 or $CHCl_3$) displays a monomeric structure in which the phosphane ligand adopts a bidentate κ^1-P,η^1-C coordination mode involving one of the side aryl ring of the terphenyl moiety.[15a-b,16a-b,20] NMR spectra and structural data for complex **5** are found in Electronic Supplementary Information (Figure S4, Table S3).

The reaction of the palladium dimer [$(PCyp_2Ar^{Xyl2})PdCl_2]_2$, **5**, with an excess of amine in CH_2Cl_2 at room temperature for 1 h yielded complexes [$(PCyp_2Ar^{Xyl2})PdCl_2$(amine)], **3a** (amine = pyridine) and **3b** (amine = morpholine) in very good yields as orange solids (Scheme 3).

All [$(PR_2Ar')PdCl_2$(amine)] complexes prepared in this study exhibit excellent air and moisture stability and can be handled under ambient conditions without decomposition. They were fully characterized by elemental analysis and multinuclear NMR spectroscopy. ^{1}H and $^{13}C\{^1H\}$ NMR spectra of these molecules are consistent with the expected *trans* arrangement of the phosphane and amine ligands. Thus, for all these compounds the four substituents on the flanking rings of the terphenyl fragments (i.e., methyl or *tert*-butyl groups) originate a singlet resonance, and for complexes **1** and **2**, the two methyl groups bound to the P atom give rise to a doublet. Furthermore, ^{13}C resonances due to *ortho*-CH groups of the coordinated pyridine ligand as well as those of *ortho*-CH_2 groups of morpholine

appear as doublets due to the coupling with the *trans*-phosphorus nucleus (J_{CP}= 2-3 Hz).



Scheme 3 Preparation of Pd-PEPPSI-PCyp$_2$Ar^{Xyl2} complexes **3**.

The molecular structures of complexes **1**-**3** in the solid state were confirmed by X-ray diffraction studies. Single crystals of **1b**, **2a** and **3b** were obtained by slow recrystallization from petroleum ether/CH_2Cl_2 mixtures at -20 °C. As anticipated, the three complexes adopt slightly distorted square-planar geometries, with the phosphane and the amine ligands arranged *trans* to each other (Figures 1-3). The Pd-N bond lengths (2.133(2) Å for **1b**, 2.1243(16) Å for **2a** and 2.1199(18) Å for **3a**) are well within the range of 2.109-2.137 Å found for *trans*-(NHC)PdCl$_2$(amine) complexes with pyridine[9a,21] and morpholine[18] ligands, and are also comparable to those reported for the few Pd-PEPPSI-PR$_3$ derivatives described so far, that is 2.24 Å for [(PPh$_3$)PdCl$_2$(pyridine)],[14a] 2.135 Å for [(TNpP)PdCl$_2$(3-Cl-pyridine)][13] (TNpP = trisneopentyl phosphane) and 2.168 Å for [(CAP)PdCl$_2$(pyridine)].[14b] Moreover, the Pd-P bond in complex **3a** (2.261(6) Å is somewhat longer than in complexes **1b** and **2a** (*ca.* 2.24 Å), likely as a consequence of the larger steric demand of the PCyp$_2$Ar^{Xyl2} ligand. Interestingly, in the structures of **1b** and **3a** one of the xylyl ring of the terphenyl moiety is situated almost parallel to the coordination plane, with the shortest Pd-C separation being *ca*. 3.3 Å, well about the 2.12 Å value of the sum of the covalent radii of C_{sp^2} (0.73 Å) and Pd (1.39 Å)[22] (Figure 1 and 3).

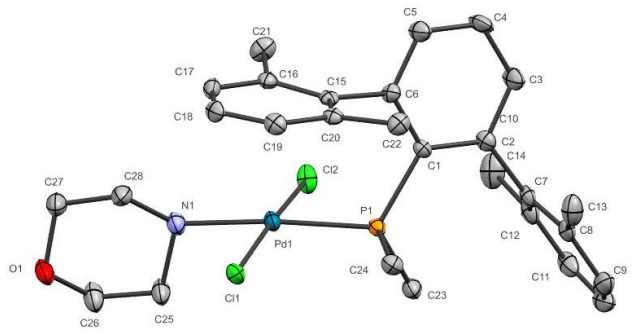


Figure 1 Molecular structure of **1b**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Pd1-P1 2.2439(8), Pd1-Cl1 2.3070(8), Pd1-Cl2 2.3244(8), Pd1-N1 2.133(2), P1-Pd1-Cl1 92.01(3), P1-Pd1-Cl2 89.60(3), Cl1-Pd1-Cl2 173.57(3), N1-Pd-P1 172.43(7), N1-Pd1-Cl1 91.26(7), N1-Pd1-Cl2 86.42(7).

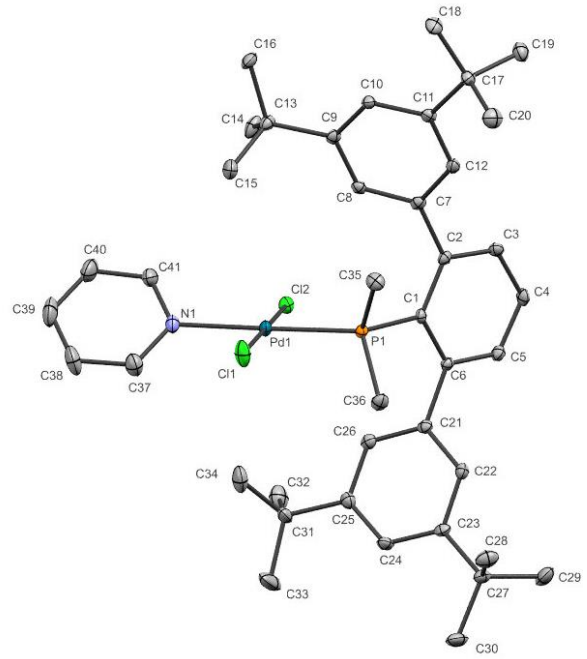


Figure 2 Molecular structure of **2a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Pd1-P1 2.2434(5), Pd1-Cl1 2.3016(5), Pd1-Cl2 2.3087(5), Pd1-N1 2.1243(16), P1-Pd1-Cl1 86.148(19), P1-Pd1-Cl2 94.852(18), Cl1-Pd1-Cl2 178.53(2), N1-Pd1-P1 175.36 (5), N1-Pd1-Cl1 89.69(5), N1-Pd1-Cl2 89.35(5).

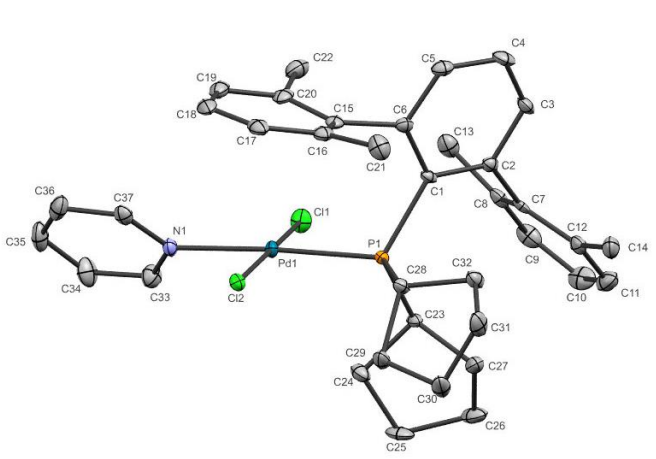


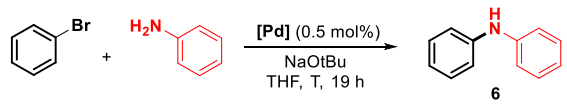
Figure 3 Molecular structure of **3a**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Pd1-P1 2.2610(6), Pd1-Cl1 2.3101(6), Pd1-Cl2 2.3034(5), Pd1-N1 2.1199(18), P1-Pd1-Cl1 87.99(2), P1-Pd1-Cl2 88.74(5), Cl1-Pd1-Cl2 176.30(2), N1-Pd1-P1 174.42(5), N1-Pd1-Cl1 88.47(5), N1-Pd1-Cl2 88.74(5).

Catalytic results

The performance of new [(PR$_2$Ar')PdCl$_2$(amine)] complexes **1**-**3** as precatalysts was tested in the Buchwald-Hartwig cross-coupling of aniline with bromobenzene. The model C-N coupling reaction was conducted in THF at room temperature, using NaO*t*Bu as the base and 0.5 mol% Pd loading. The PMe$_2$Ar' precatalysts **1**-**2** proved they were completely inactive, even when the couplings were carried out by heating up to 80 °C (Table 1, entries 1-4; see also Table S1 in the ESI). However, 84%

conversion to the coupling product (Table 1, entry 5) was obtained at room temperature when the pyridine adduct with the larger phosphane ($PCyp_2Ar^{Xyl2}$) **3a** was applied. Full conversion was attained when the C-N coupling was carried out at 50 °C (Table 1, entry 6). Recently, Shaughnessy and co-workers have described that enolizable ketones are valuable reducing additives for Pd(II) precatalysts in aryl amination reactions.[13] Accordingly, the catalytic activity of **3a** was examined, at room temperature, in the presence of 8 mol% of two different enolizable ketones, acetone and 2-butanone. Gratifyingly, both additives facilitated the activation of **3a** at room temperature and complete conversions were observed to the coupling product (Table 1, entries 7 and 8). It is worth noting that no competing α-arylation products were detected by GC in the crude reaction mixtures. Even though no influence of the nature of "throw-away"[23] amine ligand was noted in the outcome of reactions catalyzed by **1** and **2**, there was a clear difference in performance between precatalysts **3**. At room temperature, and in the absence of any activators, **3b** gave quantitative conversion to diphenylamine product (Table 1, entry 9). Consequently, **3b** displayed the best catalytic performance of the series of $[(PR_2Ar')PdCl_2(amine)]$ complexes. To complete this survey, the catalytic activity of the chloride-bridged dimer **5** was also tested in the model reaction, as upon reduction, this compound should provide the same active $[(PCyp_2Ar^{Xyl2})$-Pd(0)] species. However, **5** resulted to be totally unproductive at room temperature (Table 1, entry 10), which underlines the importance of the amine ligand during precatalyst activation. Although we did not observe palladium black formation in any experiments, mercury drop test were carried out with reactions displayed in entries 7-9. No effect on the rate or product yield was detected, suggestive evidence for homogenous catalysis.

Table 1. Catalytic activity of complexes **1**-**3** in the N-arylation of aniline.[a]



Entry	Precatalyst	Temperature (°C)	Conversion (%)[b]
1	**1a**	80	0
2	**2a**	80	0
3	**1b**	80	0
4	**2b**	80	0
5	**3a**	25	84
6	**3a**	50	>99
7[c]	**3a**	25	>99
8[d]	**3a**	25	>99
9	**3b**	25	>99
10[e]	**5**	25	0

[a] Reaction conditions: bromobenzene (1 mmol), aniline (1.2 mmol), NaO*t*Bu (1.2 mmol), precatalyst (0.005 mmol), reaction time 19 h (unoptimized).[b] Conversions were determined by GC analysis of the reaction mixtures using dodecane as internal standard (average of two runs) [c] Reaction performed in the presence of acetone (8 mol%). [d] Reaction performed in the presence of 2-butanone (8 mol%). [e] 0.25 mol% **5** (0.5 mol% Pd)

To explain the differences in reactivity between precatalysts **3a** and **3b**, reaction rate experiments on the formation of **6** were performed at 25 °C (Figure 4). Precatalysts **3b** initiated the reaction with the faster rate reaching full conversion in 80 min. Instead, **3a** showed an induction period of about 15 min leading to lower conversion after 5 h. However, in the presence of the activator (2-butanone), such an induction period disappeared and precatalyst **3a** displayed a similar reaction profile to that of **3b**. It appears that morpholine allows for a faster reduction of the Pd(II) precatalyst[18,21a] and/or stabilizes $(PCyp_2Ar^{Xyl2})$-Pd(0) species in solution in a more efficient way than pyridine does, preventing its deactivation.[19a,c]

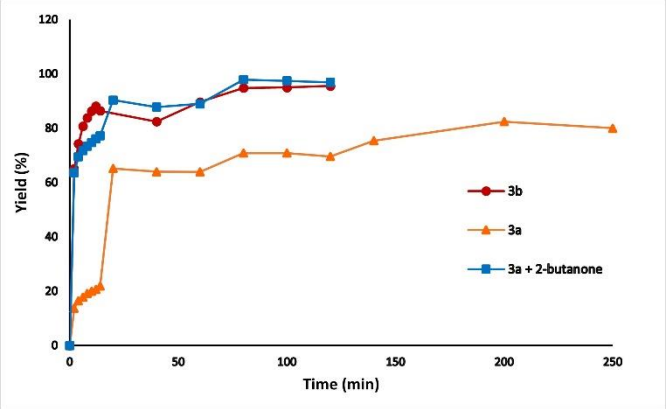


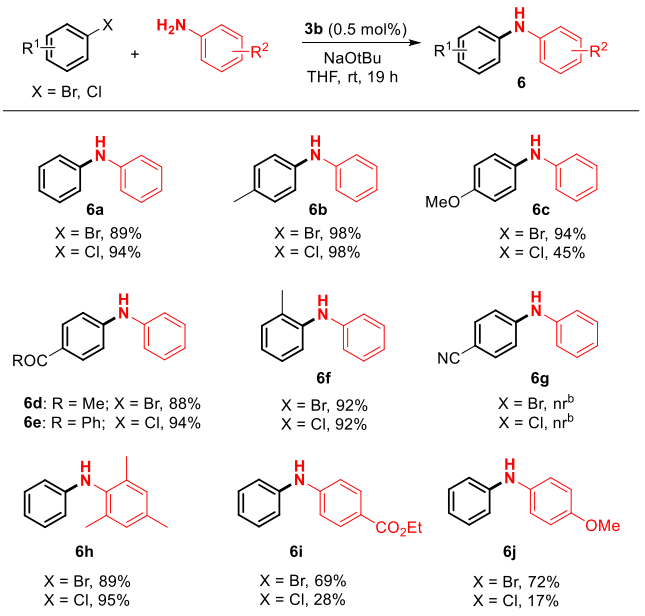
Figure 4. Reaction rate experiments for the coupling reaction between bromobenzene and aniline. Reaction conditions: bromobenzene (1 mmol), aniline (1.2 mmol), NaO*t*Bu (1.2 mmol), precatalyst (0.5 mol%), THF (1 mL), additive (8 mol%). Conversions were determined by GC against a calibrated internal standard (dodecane). Reactions were performed in duplicate.

Chloroarenes are usually more challenging electrophiles in cross-coupling reactions due to their lower reactivity.[24] Considered the good performance displayed by **3b** in the previous coupling, we decided to examine its activity in the reaction of aniline with chlorobenzene, using the conditions outlined in Table 1 (entry 9). Pleasingly, the C-N coupling proceeded with full conversion to the expected product at room temperature. Interestingly, the difference in catalytic performance between complexes **3a** and **3b** becomes more accentuated with the less reactive electrophile. Thus, under the same conditions, the pyridine adduct **3a** gave only 10% conversion, being necessary to run the reaction at 50 °C in the presence of a reducing agent (acetone or 2-butanone) to achieve complete conversions (see Table S2 in the ESI).

Finally, applying **3b** as precatalyst, the arylation of aniline with a short range of aryl bromides and chlorides was conducted at room temperature (Table 2). Excellent yields of coupling products were obtained with electron neutral (Table 2, **6a**), electron-rich (Table 2, **6b**) and electron-deficient (Table 2 **6d** and **6e**) chlorides and bromides. While the strong deactivated 4-bromoanisol was successfully coupled with aniline, the corresponding chloride provided only modest yield (Table 2, **6c**). *Ortho*-substitution was also well tolerated (Table 2, **6f**). However, with 4-bromo- and chlorobenzonitrile coupling reactions did not proceed probably due to coordination of the

nitrile moiety to the metal center. Regarding the aniline scope, the sterically hindered 2,4,6-trimethylaniline could be coupled effectively with both bromo and chlorobenzene (Table 2, **6g**). However, the couplings with anilines bearing either electron-withdrawing or electron donating *p*-substituents worked better with bromobenzene than with chlorobenzene (Table 2, **6h-i**).

Table 2. Scope of the arylation of aniline catalyzed by **3b** at room temperature.[a]



[a] Reaction conditions: aryl halide (1 mmol), aniline (1.2 mmol), NaO*t*Bu (1.2 mmol), precatalyst (0.005 mmol), room temperature, reaction time 19 h (unoptimized). Isolated yields of products (average of two runs). [b] No reaction.

The catalytic activity displays by precatalysts **3b** under such mild reaction conditions (room temperature, low catalyst loading) compares well to those reported for profitable palladium precatalysts, such as [(NHC)Pd(cynnamyl)Cl][7a,25] or PEPPSI-IPr[26] under similar catalytic conditions.

Experimental

General considerations.

All preparations and manipulations were carried out under oxygen-free nitrogen, using conventional Schlenk techniques. Solvents were dried with a MBraun SPS 800 solvent purification system, degassed, and stored over molecular sieves, or dried and degassed using literature procedures. Dialkylterphenyl phosphanes PMe_2Ar^{Xyl2},[15a] PMe_2Ar^{Dtbp2},[15b] $PCyp_2Ar^{Xyl2}$,[15b] and the palladium precursor *trans*-$[PdCl_2(py)_2]$[14a] were synthesized following described procedures. All other reagents were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on a Bruker Avance DPX-300 and Avance 400 Ascend/R. The ^1H and ^{13}C resonances of the solvent were used as the internal standard and the chemical shifts are reported relative to tetramethylsilane (TMS), while ^{31}P was referenced to external H_3PO_4. All GC analyses were performed on Agilent 7820A Gas Chromatographer with a FID detector. Elemental analyses were performed by the Servicio de Microanálisis of the Instituto de Investigaciones Químicas (IIQ). X-ray diffraction studies and high resolution mass spectra were accomplished at Centro de Investigación, Tecnología e Innovación de la Universidad de Sevilla (CITIUS)

Synthesis of $[(PMe_2Ar^{Xyl2})PdCl_2(pyridine)]$, 1a.

To a suspension of trans-$PdCl_2(pyridine)_2$ (97 mg, 0.29 mmol) in CH_2Cl_2 (10 mL) a solution of PMe_2Ar^{Xyl2} (100 mg, 0.29 mmol) in CH_2Cl_2 (5 mL) was added. The reaction mixture was stirred at room temperature for 8 h. Volatiles were removed under vacuum and the resulting solid was purified by recrystallization from petroleum ether/CH_2Cl_2 (2:1) mixtures at -20 °C, rendering the title compound as a yellow solid. Yield: 149 mg (85 %).^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.74 (m, 2H, *o*-py), 7.71 (t, 1H, $^3J_{HH}$= 7.2 Hz, p-py), 7.55 (t, 1H, $^3J_{HH}$= 7.2 Hz, *p*-C_6H_3), 7.30-7.23 (m, 4H, *p*-Xyl, *m*-py), 7.14-7.07 (m, 6H, *m*-C_6H_3, *m*-Xyl), 2.21 (s, 12H, CH_3), 1.36 (d, 6H, $^2J_{HP}$= 13.3 Hz, P-CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): δ 151.2 (d, $^4J_{CP}$ = 2 Hz, *o*-py), 146.0 (d, $^2J_{CP}$ = 12 Hz, *o*-C_6H_3), 141.2 (d, $^3J_{CP}$ = 3 Hz, *ipso*-Xyl), 137.8 (*p*-py), 136.8 (*o*-Xyl), 131.2 (d, $^4J_{CP}$ = 2 Hz, *o*-C_6H_3), 130.9 (d, $^1J_{CP}$ = 11 Hz, *ipso*-C_6H_3) 128.4 (*p*-C_6H_3), 127.9 (*m*-py), 124.2 (*p*-Xyl), 124.2 (*m*-Xyl), 22.1 (CH_3), 17.5 (d, $^1J_{CP}$ = 37 Hz, P-CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 298 K): δ 2.4. Anal. Calcd for $C_{29}H_{32}Cl_2NPPd$: C, 57.78; H, 5.35; N, 2.32. Found: C, 57.50; H, 5.59; N, 2.64.

Synthesis of $[(PCyp_2Ar^{Dtbp2})PdCl_2(pyridine)]$, 3a.

To a solution of $[(PCyp_2Ar^{Xyl2})]PdCl_2]_2$ (140 mg, 0.11 mmol) in CH_2Cl_2 (10 mL), pyridine (0.5 mL) was added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h. The resulting orange solution was taken to dryness and the solid residue was purified by recrystallization from petroleum ether:diethyl ether (2:1) mixtures at -20 °C. The title compound was obtained as an orange crystalline solid. Yield: 143 mg, (91 %). ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.70 (m, 2H, *o*-py), 7.60 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-py), 7.39 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-C_6H_3), 7.21-7.16 (m, 4H, *p*-Xyl, *m*-py), 7.04 (d, 4H, ^{3}JHH = 7.4 Hz, *m*-Xyl),6.95 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HP}$ = 4.7 Hz, *m*-C_6H_3), 2.73-2.67 (m, 4H, Cyp), 2.20 (s, 12H, CH_3), 2.05-1.95 (m, 2H, Cyp), 1.30-0.77 (m, 12H, Cyp). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K): δ 150.2 (*o*-py), 141.9 (o-C_6H_3), 136.5 (*p*-py), 132.2 (*ipso*-Xyl), 131.7 (*o*-Xyl), 131.4 (d, $^3J_{CP}$ = 9 Hz, *m*-C_6H_3), 128.9 (d, $^4J_{CP}$= 2 Hz, *p*-C_6H_3), 127.0 (*m*-Xyl), 123.0 (*m*-py), 122.9 (*p*-Xyl), 38.8 (d, $^2J_{CP}$ = 27 Hz, *C*H-Cyp), 29.5 (CH_2-Cyp), 26.0 (d, J_{CP} = 6 Hz, CH_2-Cyp), 23.8 (d, J_{CP} = 13 Hz, CH_2-Cyp), 21.6 (CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 298 K): δ 32.6. Anal. Calcd for $C_{37}H_{44}Cl_2NPPd$: C, 62.50; H, 6.24; N, 1.97. Found: C, 62.86; H, 6.40, N, 2.03.

General procedure for the aryl amination of aniline.

NaO*t*Bu (1.2 mmol) was placed into a vial equipped with a J Young tap containing a magnetic bar. The aryl halide (1.0 mmol), the precatalyst **3b** (1.0 mL, 0.005 M in THF) and aniline (1.2 mmol) were added in turn under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 19 h. The solution was evaporated to dryness and the residue was purified by flash chromatography on silica gel.

X-ray structural characterization

Single crystals of compounds **1b**, **2a**, **3a** and **5** suitable for X-ray diffraction analyses were grown by slow evaporation of solution of the complexes in petroleum ether:CH_2Cl_2 (2:1) mixtures cooled to -20 °C. Crystals of suitable size were mounted in a loop fibre covered with perfluoropolyether oil (FOMBLIN®, Aldrich). Data collections were performed on a Bruker-AXSX8Kappa diffractometer equipped with an Apex-II CCD area detector, using a graphite monochromator Ag Kα1 (λ=0.56086 Å) and a Bruker Cryo-Flex low-temperature device.[27] Data collections were processed with APEX-W2D-NT (Bruker, 2004), cell refinement and data reduction with SAINT-Plus (Bruker, 2004) and the absorption was corrected by multiscan method applied by SADABS.[28] The structures were solved by SHELXT and the starting models were refined by full-matrix least-squares procedures with SHELXL, using the software package Olex2 suite.[29] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. Weighted R factors (*wR*) and all goodness-of-fit (S) are based on F^2, conventional *R* factors (*R*) are based on *F*. A summary of the fundamental crystal and refinement data are provided in Table S2 (ESI). Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in cif files. A summary of cell parameters, data collection, structures solution, and the refinement of crystal structures are provided below. The corresponding crystallographic data were deposited with the Cambridge Crystallographic Data Centre as supplementary publications. CCDC 2158769 (**1b**), 2158767 (**2a**), 2158768 (**3a**) and 2158770 (**5**).

Conclusions

In summary, we reported the preparation and characterization of a series of novel $LPdCl_2$(pyridine) and $LPdCl_2$(morpholine) complexes supported by terphenyl phosphanes. We have applied these complexes as precatalysts for the Buchwald-Hartwig amination reaction and the complex [($PCyp_2Ar^{Xyl2}$)$PdCl_2$(morpholine)] was identified as the most readily activated at room temperature, providing the efficient coupling of aryl bromides and chlorides with aniline under the conditions developed. This study clearly demonstrates the compatibility of bulky phosphanes with the Pd-PEPPSI type precatalysts platform and underlines the impact of the "throw-away" ligand in modulating the reactivity of PEPPSI-type Pd precatalysts.

Conflicts of interest

There are no conflicts to declare.

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