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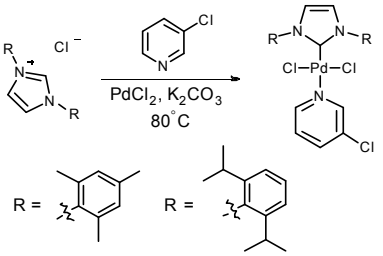
A family of electronically diverse pyridyl- and picolyl-substituted imidazolium salts have been prepared and coordinated to palladium in a single step, to deliver a variety of palladium(II)-N-heterocyclic carbene (NHC) complexes. Neutral $Pd(NHC)X_2$, cationic $[Pd(NHC)_2X]X$ and dicationic $[Pd(NHC)_2]X_2$-type complexes have been isolated and fully characterised, with single-crystal X-ray analysis revealing a variety of coordination environments around the palladium centres. The pre-formed complexes have been employed in a model Suzuki-Miyaura cross-coupling reaction to yield a sterically congested tetra-*ortho*-substituted biaryl product, showcasing turnover numbers comparable to Pd-PEPPSI-IPr catalyst.

Introduction

Introduced by Hine[1] and Doering[2] into organic chemistry in the 1950s, and by Fischer[3] into the organometallic domain ten years later, carbenes originated as intriguing chemical phenomena which have since played important roles as both ephemeral and structurally defined compounds. N-heterocyclic carbenes (NHCs) have emerged as a highly versatile and efficient class of ancillary ligand for a variety of catalytic processes, such as metathesis, C–H activation and asymmetric hydrogenation reactions, often showcasing higher efficacy than their widely-used phosphine counterparts.[4-10] Palladium represents one of the most versatile transition metals utilised for catalysing a multitude of transformations, being applied in the synthesis of polymers,[11] nano-complexes,[12] liquid crystals[13] and, most commonly, natural products.[14-16] Numerous Pd-NHC complexes have been reported, including homoleptic Pd^0 *bis*-carbene,[17,18] chelating/macrocyclic Pd^{II} carbene[19,20] and mixed carbene-phosphine Pd complexes.[21,22] Well-defined Pd-NHCs bearing ancillary nitrogen donor ligands have demonstrated significant activities in both carbon-carbon and carbon-heteroatom cross-coupling reactions. Examples include C,N–palladacycles,[23-25] $[Pd(NHC)(Et_3N)Cl_2]$ described by Navarro[26] and $[Pd(NHC)(Im)Cl_2]$ (Im = imidazole) developed by Shao.[27] Arguably at the forefront of such catalysts are Pd-PEPPSI complexes pioneered by Organ, which are readily prepared *via* their corresponding imidazolium salt precursors (Scheme 1).[28,29]



Scheme 1 Synthetic route to Pd-PEPPSI catalysts.[28,29]

From a catalytic view-point, the displaceable pyridine ligand of the PEPPSI pre-catalysts plays a pivotal role in the formation of the active species by both stabilising the complex and dissociating upon activation. Furthermore, the steric topography around the Pd is crucial, with bulkier NHC *N*-substituents generally leading to higher catalytic activity.[28] Pd complexes in which a pyridyl donor is tethered to the NHC ligand have previously been reported[30-34] and, in some cases, the steric effects of the ligand have been examined in catalysis.[35] Following our recent findings regarding the electronic effects of hemilabile NHC-appended pyridyl donors on Cu,[36] it was decided to prepare a family of related complexes with Pd. Altering the electronic properties of the pyridyl donor, in addition to the ligand rigidity/flexibility, was found to have a notable effect on the structural chemistry of the complexes and their catalytic activities in Suzuki-Miyaura cross-coupling reactions. Such complexes were found to perform similarly to Pd-PEPPSI-IPr (IPr = 1,3-*bis*(2,6-diisopropylphenyl)imidazole-2-ylidene) in a cross-coupling reaction to produce sterically congested tetra-*ortho*-substituted biaryl compounds.

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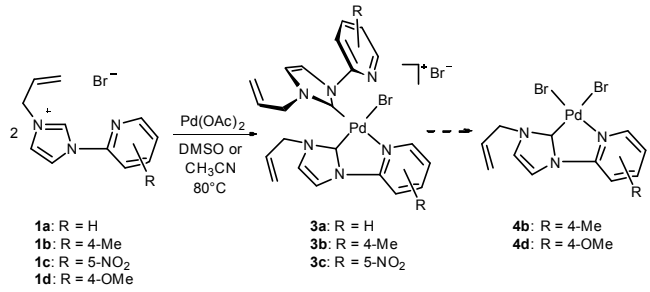
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Results and discussion

Imidazolium bromides **1a–1d** were synthesised and treated with 0.5 equivalents $Pd(OAc)_2$ under anhydrous conditions. Pd^{II}-*bis*-NHC complexes **3a–3c** were formed from imidazolium precursors **1a**-**1c** (Scheme 2), and were fully characterised using ^{1}H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry and microanalysis.



Scheme 2 Preparation of Pd^{II}-*bis*-NHC dibromide complexes **3a–3c** and Pd^{II}-*mono*-NHC dibromide complexes **4b** and **4d**.

Crystals of complex **3a** suitable for X-ray diffraction analysis were grown. The coordination environment around the metal centre can be described as distorted square planar, with the smallest angle attributed to the intrachelate N3-Pd1-C4 angle of 79.6(4)˚ (Figure 1). Only one pyridyl-appended NHC ligand is able to fully chelate in the solid-state, whilst the opposing mutually *cis*-coordinated NHC resides relatively orthogonal to twist the adjoining pyridyl motif out of the chelate plane. The Pd-$N_{pyridyl}$ bond length of 2.091(8) Å is in agreement with related complexes reported in the literature.[37] It is anticipated that complex **3a** undergoes fluxional behaviour, with coordination / de-coordination of the pyridyl groups and bromide anions. This activity is reflected in both the ^{1}H and ^{13}C NMR spectra, which feature broad signals consistent with literature precedent.[38] The solid-state structure of **3c** highlights a coordination sphere around the Pd^{II} centre similar to that of **3a**. Interestingly, both Pd–$C_{carbene}$ bond lengths in **3c** are equivalent (within error) at 1.994(9) and 1.978(8) Å (Pd1-C4 and Pd1-C15, respectively); such close values may be surprising considering that one NHC chelates to afford a 5-membered ring whereas the other NHC is monodentate. Furthermore, each NHC is disposed *trans* to markedly different donor substituents (C4 to bromide, C15 to pyridyl) which may be expected to exhibit contrasting *trans*-influences. Despite each pyridyl ring housing a highly electron-withdrawing nitro function, the Pd-$N_{pyridyl}$ bond distance is 2.090(7) Å (Pd1-N3); *i.e.* almost identical to that observed for complex **3a**.

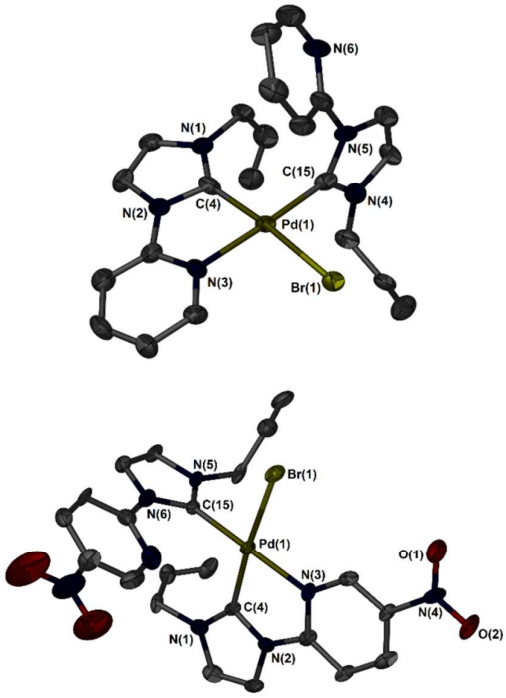


Fig. 1 Molecular structure of complexes **3a** (top) and **3c** (bottom). Ellipsoids are shown at the 50% probability level, hydrogen atoms, bromide counter anions and solvent molecules (**3a**: one molecule of MeOH; **3c**: one molecule of MeOH) are omitted for clarity. Selected bond distances (Å) and angles (˚): **3a** Pd1–C4 1.961(12), Pd1–C15 1.968(10), Pd1–Br1 2.4542(13), Pd1–N3 2.091(8), N3–Pd1–C4 79.6(4), Br1–Pd1–C4 175.1(3). **3c** Pd1–C4 1.994(9), Pd1–C15 1.978(8), Pd1–Br1 2.4508(12), Pd1–N3 2.090(7), N3–Pd1–C4 79.0(3), Br1–Pd1–C4 174.1(3).

Reaction of imidazolium bromide **1b** with 0.5 equivalents $Pd(OAc)_2$ delivered the expected 2:1 (NHC:Pd) stoichiometric complex, which was confirmed by NMR spectroscopy, high-resolution mass spectrometry and microanalysis. However, crystallisation of the complex resulted in an overall neutral $[Pd(NHC)Br_2]$ complex (Figure 2). Complex **4b** exhibits distorted square planar geometry with chelation from the adjoining pyridyl donor moiety, causing the C6-Pd1-Br1 angle to contract to 172.47(11)˚. It is postulated that complex **4b** forms in solution *via* concomitant displacement of one NHC ligand by a proximal bromide anion, implying a subtle competition between *bis*-NHC versus *mono*-NHC complexation. In our hands, it has been observed that modest electronic alterations of the pyridyl function are able to activate the Pd centre toward unique reactivity.[39] In light of this, it appears that the mild electronic donation from the 4-methyl substituent of the pyridyl ring is sufficient in activating the metal such that one imidazolium unit is lost to provide a vacant coordination site, which is subsequently occupied by a vicinal bromide anion.

Further supporting this notion, 4-methoxy substituted imidazolium bromide **1d** was treated with 0.5 equivalents $Pd(OAc)_2$ to furnish only the neutral $[Pd(NHC)Br_2]$ complex **4d**, as evidenced by microanalytical data and X-ray crystallography (Figure 2). Despite bearing a strongly electron donating

methoxy substituent at the pyridyl ring, the Pd-$N_{pyridyl}$ bond length of **4d** is 2.057(7) Å, a value in keeping with the 5-nitro substituted complex **3c**, and 4-methyl pyridyl analogue, **4b**, implying little electronic influence upon pyridyl basicity. The planar nature of complexes **4b** and **4d** leads to an extended packing structure which is largely influenced by strong π-π stacking interactions, propagating a lamellar packing assembly throughout each crystalline lattice (see Supporting Information).

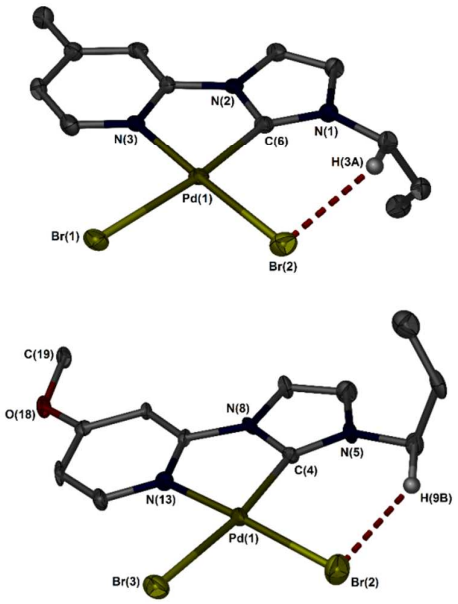
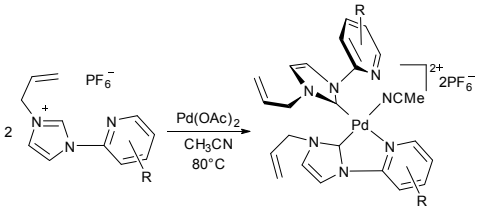


Fig. 2 Molecular structure of complexes **4b** (top) and **4d** (bottom). Ellipsoids are shown at the 50% probability level, hydrogen atoms (except H3A and H9B) are omitted for clarity. Selected bond distances (Å) and angles (°): **4b** Pd1–C6 1.982(4), Pd1–Br1 2.4820(5), Pd1–Br2 2.4266(5), Pd1–N3 2.065(3), N3–Pd1–C6 79.83(14), Br1–Pd1–C6 172.47(11). **4d** Pd1–C4 1.998(8), Pd1–Br2 2.4175(11), Pd1–Br3 2.4703(10), Pd1–N13 2.057(7), N13–Pd1–C4 80.3(3), Br3–Pd1–C4 171.9(2).

Imidazolium hexafluorophosphate salts **2a**-**2d** were prepared and treated with 0.5 equivalents $Pd(OAc)_2$ to afford *bis*-NHC coordinated Pd complexes **5a**-**5d** (Scheme 3). The ^{1}H NMR spectra of both **5a** and **5b** contain broad, yet assignable resonances. High-resolution mass spectrometry and microanalyses were also used to confirm the identity of each complex.



2a: R = H
2b: R = 4-Me
2c: R = 5-NO_2
2d: R = 5-OMe

5a: R = H
5b: R = 4-Me
5c: R = 5-NO_2
5d: R = 5-OMe

Scheme 3 Preparation of Pd^{II}-*bis*-NHC dihexafluorophosphate complexes **5a–5d**.

The solid-state structure of **5c** shows a complex of the type $[Pd(NHC)_2(CH_3CN)](PF_6)_2$, whereby a solvent molecule of acetonitrile occupies a vacant coordination site at the metal centre (Figure 3). As observed in complexes **3a**-**3c**, the Pd^{II} centre of **5c** exhibits distorted square planar geometry, with one NHC ligand forming a 5-membered chelate ring. The Pd–$C_{carbene}$ bond length in **5c** (1.962(3) Å, Pd1-C4) is surprisingly similar to that of **3c** (1.994(9) Å, Pd1-C4), considering a *trans*-bromide ligand has been substituted for an acetonitrile ligand. Crystals of complex **5d** were also isolated and reveal a similar structure to **5c** (Figure 3).

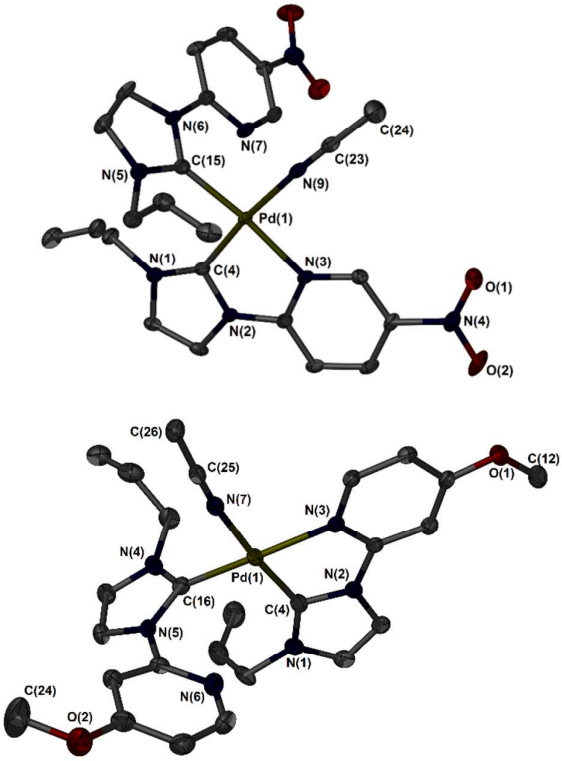


Fig. 3 Molecular structure of complexes **5c** (top) and **5d** (bottom). Ellipsoids are shown at the 50% probability level, hydrogen atoms and hexafluorophosphate counter anions are omitted for clarity. Selected bond distances (Å) and angles (°): **5c** Pd1–C4 1.962(3), Pd1–C15 1.978(3), Pd1–N9 2.055(2), Pd1–N3 2.092(2), N3–Pd1–C4 80.25(10), N9–Pd1–C4 172.81(10). **5d** Pd1–C4 1.964(4), Pd1–C16 1.989(4), Pd1–N3 2.078(3), Pd1–N7 2.059(4), N3–Pd1–C4 79.63(14), N7–Pd1–C16 91.24(15), C4-Pd1-C16 95.71(16), C4–Pd1–N7 172.42(15), C16–Pd1–N3 171.86(15).

Despite their similar solid-state structures, comparison between the ^{1}H NMR spectra of complexes **3c** and **5c** highlights a notable difference in their solution-state behaviour (Figure 4). At low temperature (238 K, top spectrum), ^{1}H NMR spectroscopic analysis of complex **3c** reveals a sequence of sharp signals, corroborating with twenty magnetically inequivalent proton resonances. Subsequent heating of the sample to ambient temperature leads to significant resonance broadening and coalescence, attributed to enhanced ligand fluxion about the metal centre. Intriguingly however, exchanging the bromide anions in **3c** for PF_6 to produce **5c** leads to much sharper resonances in the ^{1}H NMR spectrum at

room temperature, implying reduced fluxional character around Pd. Previous studies have shown that a Pd complex bearing a chelating NHC-pyridyl-NHC ligand undergoes conformer interconversion.[40] The mechanism was found to be anion dependent, with a more nucleophilic anion reversibly displacing the central pyridine unit. Unexpectedly, recording the ^{1}H NMR spectrum of complex **5c** at elevated temperature (333 K, bottom spectrum) leads to further resonance resolution, uncovering each individual magnetically inequivalent proton signal with discrete multiplicity. Ligand scrambling studies in solution on complexes **3a**, **3b** and **3c** using mass spectrometry (see Supporting Information) indicate that the fluxional behaviour in these complexes is caused only by coordination / de-coordination of the pyridyl groups, and that the NHC units remain firmly coordinated to the Pd centre. Such fluxionality in chelating NHC-pyridyl ligands has previously been reported, with the assumption that the pyridine moiety is the most labile unit.[41]

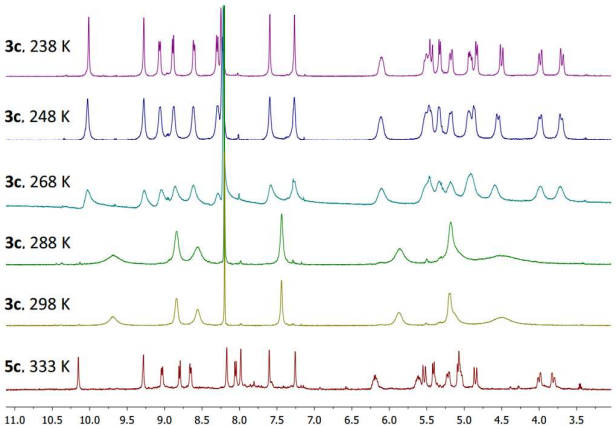
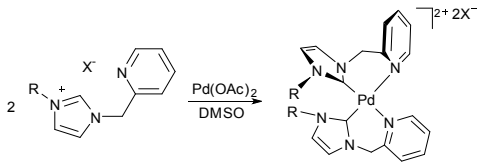


Fig. 4 VT ^{1}H NMR spectra (500 MHz, CD_3CN) of Pd^{II}-*bis*-NHC complexes **3c** (238 – 298 K) and **5c** (333 K).

A clear observation regarding Pd complexation of *N*-pyridyl-appended NHC ligands is the extent of coordinative restriction around the distorted square plane of the metal centre, as evidenced by the inability of both NHC ligands to fully chelate within Pd^{II}-*bis*-NHC assemblies. To improve conformational flexibility about the coordination sphere, *N*-picolyl substituted NHC precursors **1e**, **1f** and **2f** were synthesised (Scheme 4).

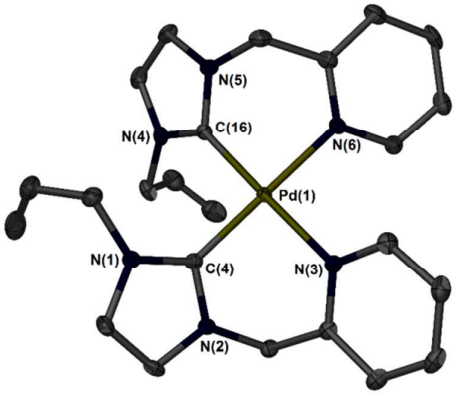


1e: R = allyl, X = Br
1f: R = picolyl, X = Br
2f: R = picolyl, X = PF_6
7e: R = allyl, X = PF_6
6f: R = picolyl, X = Br
7f: R = picolyl, X = PF_6

Scheme 4 Preparation of picolyl-substituted Pd^{II}-*bis*-NHC complexes **7e**, **6f** and **7f**.

Reaction of two equivalents of imidazolium bromide **1e** with 0.5 equivalents $Pd(OAc)_2$ delivered the corresponding $Pd(NHC)_2Br_2$ complex, which proved to be extremely hygroscopic and difficult to handle when exposed to air. Consequently, the resulting residue was immediately reacted with NH_4PF_6, furnishing the desired air- and moisture-stable $[Pd(NHC)_2](PF_6)_2$ complex, **7e**. Analysis of the solid-state structure of **7e** disclosed square planar geometry around the palladium centre, with the smallest angle of 85.97(10)˚ attributed to C4-Pd1-N3, and a C4-Pd1-C16 angle of 95.25(11)˚ between the mutually *cis*-coordinated NHCs (Figure 5). As a result of additional conformational relief from the methylene-bridged ligand, each hemilabile six-membered C,N-palladacycle adopts boat-like geometry, allowing each independent NHC unit to reside orthogonal to one another, furnishing a pair of 5,6,6-fused tricyclic ring scaffolds. Room temperature NMR spectroscopic analysis of **7e** illustrates a sequence of broad signals, which are characteristic of fluxional behaviour around a metal centre (Figure 6).[41] Interestingly, upon sample cooling (233 K, top spectrum), two sets of two doublet resonances become apparent (5.79, 5.34, 5.24 and 5.14 ppm) in the ^{1}H NMR spectrum, resulting from both methylenic and allylic protons generating diastereotopicity upon metal complexation (*cf*. imidazolium bromide **1e**). Further, sample heating (323 K, bottom spectrum) leads to coalescence of such signals to feature only two doublet resonances (5.28 and 5.22 ppm).

Reaction of imidazolium hexafluorophosphate **2f** with 0.5 equivalents $Pd(OAc)_2$ led to $[Pd(NHC)_2](PF_6)_2$ complex **7f**. The solid-state structure resembles that of complex **6f** (Figure 5). Spectroscopically, complex **7f** features a sequence of four unambiguous doublets in the ^{1}H NMR spectrum (400 MHz, CD_3CN; 5.87, 5.51, 5.06 and 4.73 ppm), akin to those displayed by **7e** representing each diastereotopic set of methylene-bridged protons.



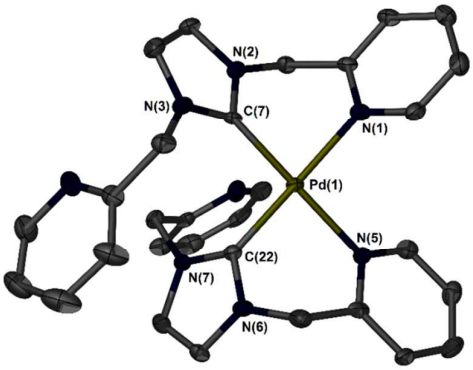


Fig. 5 Molecular structure of complexes **7e** (top) and **7f** (bottom). Ellipsoids are shown at the 50% probability level, hydrogen atoms and hexafluorophosphate counter anions are omitted for clarity. Selected bond distances (Å) and angles (°): **7e** Pd1–C4 1.979(3), Pd1–C16 1.977(3), Pd1–N3 2.101(2), Pd1–N6 2.091(2), N3–Pd1–C4 85.97(10), N6–Pd1–C16 86.22(10), C4-Pd1-C16 95.25(11), C4–Pd1–N6 176.83(10), C16–Pd1–N3 178.77(11). **7f** Pd1–C7 1.950(5), Pd1–C22 1.969(5), Pd1–N1 2.093(4), Pd1–N5 2.097(4), N1–Pd1–C7 84.85(19), N5–Pd1–C22 85.71(19), C7–Pd1–N5 178.39(19), C22–Pd1–N1 176.79(19).

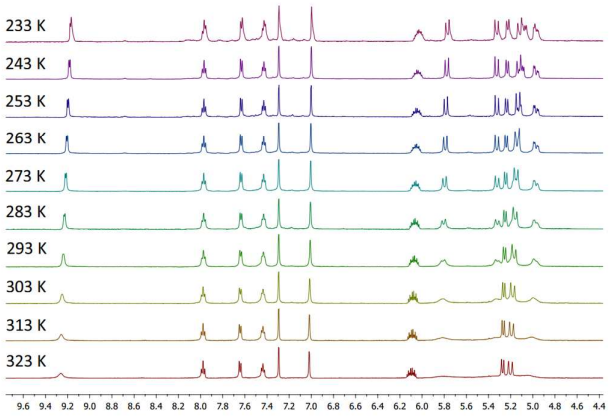


Fig. 6 VT ^{1}H NMR spectra (500 MHz, CD_3CN) of complex **7e** (233 – 323 K).

Single crystals of imidazolium bromide **1f** suitable for X-ray crystallographic study were grown *via* slow evaporation of a concentrated acetonitrile solution of the salt (see Supporting Information). Treatment of imidazolium bromide **1f** with 0.5 equivalents $Pd(OAc)_2$ afforded a complex of the type $[Pd(NHC)_2]Br_2$. The solid-state structure of **6f** revealed a geometry around the Pd^{II} centre very similar to **7f**, with each independent NHC ligand coordinating to the metal in a bidentate manner to displace bromide from the coordination sphere (Figure 7). One NHC ligand in **6f** binds to Pd with a free pyridyl arm bent into the metal coordination sphere, whilst the free pyridyl donor of the opposing NHC bends away to share favourable π-π stacking interactions with the adjacent NHC unit. The extended packing structure of complex **6f** reveals a series of solvent-accessible channels running through the crystallographic *c* axis, with an approximate diameter of 14 Å in which DMSO molecules are situated in the solid-state.

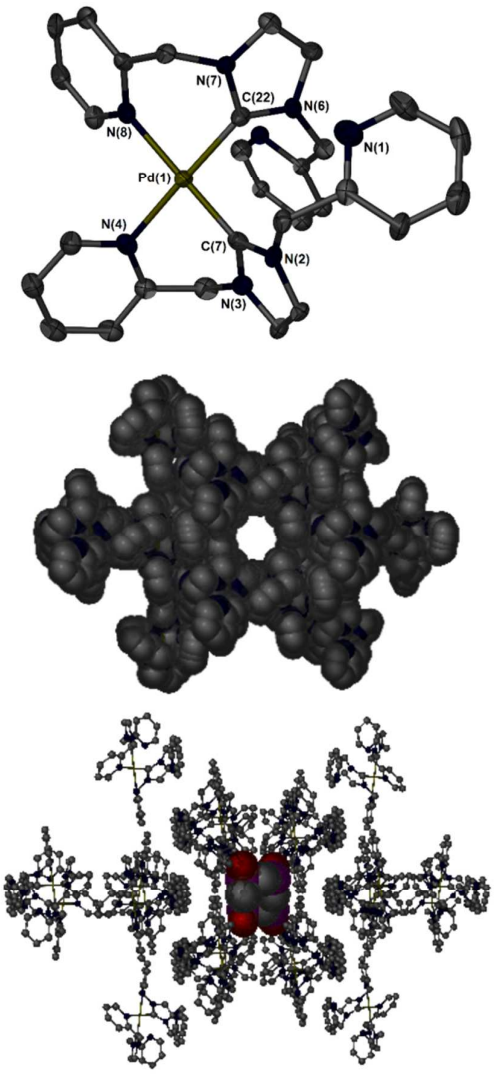
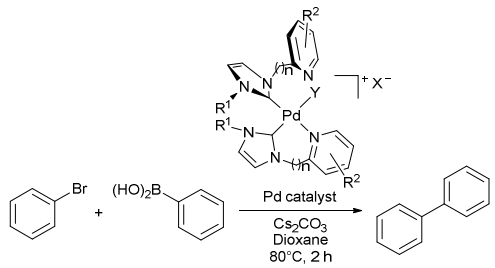


Fig. 7 Molecular structure of complex **6f** (top), space-filling diagram revealing a solvent-accessible pore running parallel to the crystallographic *c* axis (middle), and ball-and-stick diagram with space-filled model of four DMSO molecules occupying one accessible channel (bottom). Ellipsoids are shown at the 50% probability level, hydrogen atoms, bromide counter anions and solvent molecules (**6f** (top): one molecule of DMSO, only those modelled are shown below) are omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–C7 1.964(8), Pd1–C22 1.980(7), Pd1–N4 2.109(6), Pd1–N8 2.103(7), N4–Pd1–C7 85.1(3), N8–Pd1–C22 85.4(3), C7–Pd1–N8 179.5(3), C22–Pd1–N4 175.5(3).

Pd-NHC complexes, in the presence of ancillary nitrogen donor ligands, have shown remarkable activities in numerous Pd-catalysed cross-coupling reactions.[28,29,35,42-46] To evaluate catalytic activity and examine the effect of tethered pyridyl donor basicity and flexibility on catalysis, a benchmark Suzuki–Miyaura cross-coupling reaction between phenylboronic acid and bromobenzene was examined (Table 1).

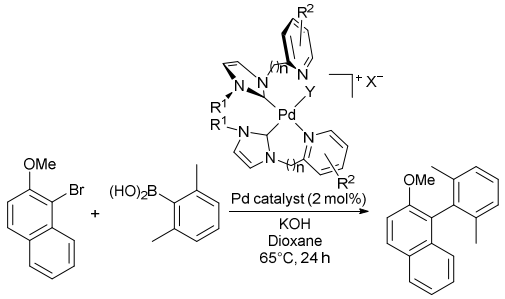


Entry	**Catalyst** (R^1, R^2, n)	X	Y	Conversion[c]
1[a]	**3a** (allyl, H, 0)	Br	Br	3
2	**3c** (allyl, 5-NO_2, 0)	Br	Br	78
3	**3a** (allyl, H, 0)	Br	Br	83
4	**3b** (allyl, 4-Me, 0)	Br	Br	86
5	**4b** (allyl, 4-Me, 0)	Neutral[d]	2Br	56
6	**4d** (allyl, 4-OMe, 0)	Neutral[d]	2Br	68
7	**5c** (allyl, 5-NO_2, 0)	2PF_6	MeCN	81
8	**5a** (allyl, H, 0)	2PF_6	MeCN	86
9	**5b** (allyl, 4-Me, 0)	2PF_6	MeCN	84
10	**7e** (allyl, H, 1)	2PF_6	Picolyl	92
11	**6f** (picolyl, H, 1)	2Br	Picolyl	94
12	**7f** (picolyl, H, 1)	2PF_6	Picolyl	94
13[b]	**7f** (picolyl, H, 1)	2PF_6	Picolyl	>99

Table 1 Suzuki-Miyaura cross-coupling of phenylboronic acid and bromobenzene. Conditions: 1.0 mmol bromobenzene, 1.5 mmol phenylboronic acid, 0.01 mmol (1 mol %) catalyst, 2.0 mmol Cs_2CO_3 and 5 mL dioxane; [a] Cs_2CO_3 omitted; [b] catalyst loading increased to 0.015 mmol (1.5 mol %); [c] GC conversions (%) are the average of three runs; [d] two bromide anions are coordinated to Pd.

Examination of entries 2-4 shows a subtle increase in conversion as an electron-withdrawing substituent on the hemilabile pyridyl ring is replaced by an electron-donating substituent. This implies that electron-rich pyridyl donor wingtips may enhance catalytic turnover. In contrast, neutral Pd^{II}-*mono*-NHC dibromide complexes **4b** and **4d** perform poorly in the coupling transformation, delivering the lowest recorded conversions to biphenyl (entries 5 and 6, respectively). Hexafluorophosphate analogues **5a–5c** afforded results comparable to their bromide derivatives (entries 7-9), indicating little enhancement of catalytic activity in the presence of bromide ligands. The presence of two potential pyridyl donors enables constant occupancy of coordination sites around the palladium centre upon removal of bromide, providing stabilisation throughout the catalytic cycle, thus offering return over their Pd^{II}-*mono*-NHC rivals. Highest conversions were achieved using picolyl-tethered NHC ligands (entries 10–12). These results imply that additional geometrical freedom of each hemilabile pyridyl donor provides greater stabilisation of Pd throughout catalysis; such a conclusion has been previously drawn with analogous complexes of Cu, Ir, Ru and Fe.[26-28] For this system, a 50% increase in catalyst loading (entry 13) led to only trace quantities of bromobenzene detectable by GC analysis after 2 hours reaction time.

One of the most challenging cross-coupling reactions involves the formation of tetra-*ortho*-substituted biaryls under mild reaction conditions.[47-49] Complexes **5a**-**5c**, **7e** and **7f** were examined in the coupling of 2,6-dimethylphenylboronic acid and 1-bromo-2-methoxynaphthalene, under the same reaction conditions as those reported for Pd-PEPPSI catalysts (Table 2).[28] Pd-PEPPSI catalysts furnished conversions of 4% (Pd-PEPPSI-IBu), 9% (Pd-PEPPSI-cPent), 41% (Pd-PEPPSI-IPr) and 91% (Pd-PEPPSI-IPent), with the authors concluding that the steric bulk around the metal must be conformationally flexible to exert a positive influence on the cross-coupling reaction. Conversions obtained in this study were similar to the sterically bulky PEPPSI catalyst, Pd-PEPPSI-IPr. Highest conversions were observed with picolyl-substituted ligands (entries 4-5), indicating that conformational flexibility does indeed have a positive effect on the outcome of these difficult cross-coupling reactions, and that steric bulk may play less of a key role.



Entry	**Catalyst** (R^1, R^2, n)	X	Y	Conversion[a]
1	**5a** (allyl, H, 0)	2PF_6	MeCN	36
2	**5b** (allyl, 4-Me, 0)	2PF_6	MeCN	33
3	**5c** (allyl, 5-NO_2, 0)	2PF_6	MeCN	32
4	**7e** (allyl, H, 1)	2PF_6	Picolyl	39
5	**7f** (picolyl, H, 1)	2PF_6	Picolyl	48

Table 2 Suzuki-Miyaura cross-coupling of 2,6-dimethylphenylboronic acid and 1-bromo-2-methoxynaphthalene. Conditions: 1.0 mmol 1-bromo-2-methoxynaphthalene, 1.2 mmol 2,6-dimethylphenylboronic acid, 0.02 mmol (2 mol %) catalyst, 3.0 mmol KOH and 3 mL dioxane; [a] GC conversions (%) are the average of three runs.

Conclusions

A family of new Pd^{II}-NHC complexes bearing electronically divergent pyridyl or picolyl wingtip substituents have been prepared, with several complexes being structurally elucidated *via* X-ray crystallography. Examples of both neutral Pd^{II}-*mono*-NHC and cationic Pd^{II}-*bis*-NHC complexes are reported, which are readily obtained in a single step *via* their corresponding imidazolium salt precursors. A combination of spectroscopic and crystallographic analyses have been used to rationalise both the solution- and solid-state behaviour of these complexes, with methylene-tethered *N*-picolyl substituted complexes demonstrating increased geometrical freedom around the Pd centre. Although varying between coordinating Br and non-coordinating PF_6 anions in the Pd^{II}-*bis*-NHC complexes has an effect on fluxionality rates in solution, the complexes appear to perform similarly in catalysis.

The Pd^{II} complexes were employed in a Suzuki-Miyaura cross-coupling reaction between phenylboronic acid and bromobenzene, highlighting subtle electronic effects and a

significant increase in catalyst performance as *N*-picolyl substituted NHC ligands are introduced to the Pd^{II} coordination sphere. Near-quantitative conversion to biphenyl was achieved using Pd^{II}-*bis*(picolyl)-substituted-NHC complex **7f**. It is anticipated that the enhanced activity is attributed to the hemilabile nitrogen-donor ligands acting to protect and vacate coordination sites at the metal centre throughout the catalytic cycle. The most promising complexes were examined in a more challenging cross-coupling reaction to prepare a tetra-*ortho*-substituted biaryl. In this setting, *N*-pyridyl substituted complexes **5a**-**c** afforded the sterically congested product in 32-36% conversion, whilst *N*-picolyl substituted complexes **7e** and **7f** highlighted increased performance with conversions of 39 and 48%, respectively. In line with conclusions drawn by Organ and co-workers,[28] a topographically 'fluid' environment around the Pd centre provides a positive effect on the cross-coupling process, with the availability of hemilabile pyridyl functions acting to stabilise oxidation state changes at the metal centre throughout the catalytic cycle.

Experimental

General methods. Where stated, manipulations were performed under an atmosphere of dry nitrogen by means of standard Schlenk line or Glovebox techniques. The gas was dried by passing through a twin-column drying apparatus containing molecular sieves (4 Å) and P_2O_5. Anhydrous solvents were prepared by passing the solvent over activated alumina to remove water, copper catalyst to remove oxygen and molecular sieves to remove any remaining water, *via* the Dow-Grubbs solvent system. Deuterated chloroform, acetonitrile and DMSO were dried over CaH_2, cannula-filtered or distilled and then freeze-pump-thaw degassed prior to use. All other reagents and solvents were used as supplied.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on either a Bruker DPX300 or a Bruker AV500 spectrometer. The values of the chemical shifts are given in ppm and values for coupling constants (J) in Hz. All resonances in the $^{13}C\{^1H\}$ NMR spectra appear as singlet resonances. Assignment of some ^1H NMR spectra was aided by the use of 2D $^1H^1H$ COSY experiments, and the assignment of some $^{13}C\{^1H\}$ NMR spectra was aided by $^{13}C\{^1H\}$ DEPT 135 experiments. Mass spectra were collected on a Bruker Daltonics (micro TOF) instrument operating in the electrospray mode. Microanalyses were performed using a Carlo Erba Elemental Analyzer MOD 1106 spectrometer. GC analyses were performed using a Bruker 430-GC equipped with a CP-8400 autosampler. X-ray diffraction data were collected on either a Bruker Nonius X8 diffractometer fitted with an Apex II detector with Mo-Kα radiation (λ = 0.71073 Å), or an Agilent SuperNova diffractometer fitted with an Atlas CCD detector with Mo-Kα radiation (λ = 0.71073 Å) or Cu- Kα radiation (λ = 1.5418 Å). Crystals were mounted under oil on glass or nylon fibres. Data sets were corrected for absorption using a multiscan method, and the structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F2 using ShelXL-97, interfaced through the program X-Seed. Molecular graphics for all structures were generated using POV-RAY in the X-Seed program.

Imidazolium salts **1a–e** and **2a–f** were prepared as previously reported.[29] Imidazolium bromide **1f** was prepared using a modified synthetic procedure and can be found in the Supporting Information.

Bis[1-allyl-3-(2-pyridyl)imidazol-2-ylidene]palladium(II) dibromide (3a). 1-Allyl-3-(2-pyridyl)imidazolium bromide **1a** (0.19 g, 0.70 mmol) and $Pd(OAc)_2$ (79 mg, 0.35 mmol) were added to a flame-dried Schlenk flask and dried *in vacuo*. To these was added anhydrous acetonitrile (30 mL) and the resultant mixture stirred vigorously at 70 °C for 24 hours under an inert atmosphere. After this time, an excess of diethyl ether (100 mL) was added to the mixture in a single portion, with the resulting solid collected *via* vacuum filtration and washed further with cold diethyl ether (50 mL), followed by drying *in vacuo* to give the title compound as a microcrystalline yellow solid. Yield: 0.13 g, 0.20 mmol, 58%. Mp decomp. at 222–223 °C. ^1H NMR (300 MHz, CD_3CN): δ (ppm) 9.27 (br s), 8.67 (br s), 8.52 (br s), 8.39 – 8.12 (br m), 8.08 (s), 7.51 (br s), 7.27 (br s), 6.14 (br s), 5.90 – 4.53 (br m), 3.87 (br s). Unambiguous assignment of the resonances is hampered by broadening of the spectrum. For this reason, a $^{13}C\{^1H\}$ NMR spectrum was not obtained. HRMS (ESI+): *m/z* 555.0120 $[C_{22}H_{22}N_6BrPd]^+$, calcd. $[M - Br]^+$ 555.0119. Anal. calcd. (%) for $C_{22}H_{22}N_6Br_2Pd\cdot 2/3CH_3CN$: C 40.73, H 3.63, N 12.96; found C 40.50, H 3.35, N 12.75. Crystals of complex **3a** suitable for X-ray diffraction analysis were grown *via* slow evaporation of a saturated methanol solution.

Bis[1-allyl-3-(2-(4-methyl)pyridyl)imidazole-2-ylidene]palladium(II) dibromide (3b). 1-Allyl-3-(2-(4-methyl)pyridyl)imidazolium bromide **1b** (0.21 g, 0.75 mmol) and $Pd(OAc)_2$ (84 mg, 0.38 mmol) were charged to a flame-dried ampoule under an inert atmosphere and stirred vigorously in anhydrous dimethylsulfoxide (8 mL) at 100 °C for 16 hours. After this time, the crude reaction mixture was filtered through a Celite plug and rinsed with one aliquot of dichloromethane (10 mL) to give a golden brown solution. The solution was added to a separating funnel, extracted with water (3 x 30 mL) and the organic fraction dried over anhydrous magnesium sulfate. After filtration, the resulting organic solution was concentrated under reduced pressure to furnish a pale yellow residue. Recrystallisation of the crude residue from acetonitrile / diethyl ether, followed by repeated washes with cold chloroform (3 x 10 mL) delivered the pure title compound as a bright yellow solid which was collected *via* vacuum filtration. Yield: 0.20 g, 0.30 mmol, 77%. Mp decomp. 222–224 °C. ^1H NMR (500 MHz, CD_3CN): δ (ppm) 9.39 (br d, J = 5.5 Hz, 1H, imH), 9.09 (br m, 1H, pyrH), 8.68 (br d, J = 5.5 Hz, 1H, imH), 8.44 (br m, 1H, pyrH), 8.07 (br m, 1H, pyrH), 7.83 (br d, J = 4.5 Hz, 1H, imH), 7.73 (br d, J = 4.5 Hz, 1H, imH), 7.52 – 7.11 (br m, 3H, pyrH), 5.49 (br d, J = 5.0 Hz, 2H, C=CH), 5.30 – 5.24 (br m, 2H, $C=CH_{trans}$), 4.98 (br s, 2H, $C=CH_{cis}$) 3.92 – 3.77 (br m, 4H, NCH_2), 2.51 (br s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN): δ (ppm) 160.8, 155.8, 155.1, 153.8, 151.0, 150.1, 150.6, 149.5, 148.6, 148.3, 133.6, 131.9, 131.6, 128.2, 125.0, 124.6, 124.1, 122.8, 122.5, 120.7, 54.3, 51.3, 21.4, 20.6. HRMS

(ESI+): *m/z* 585.0650 $[C_{24}H_{26}N_6PdBr]^+$, calcd. $[M - Br]^+$ 585.0417. Anal. calcd. (%) for $C_{24}H_{26}N_6Br_2Pd \cdot 1/2CHCl_3$: C 40.62, H 3.69, N 11.60; found C 40.70, H 3.70, N 11.80. Complex **4b** was formed *via* dissolution of **3b** into hot acetonitrile (5 mL), followed by filtration through a short silica plug. To this, an excess of diethyl ether (30 mL) was added to precipitate a yellow solid which was collected *via* vacuum filtration and dried *in vacuo* to afford the desired compound. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 9.39 (br d, J = 8.0 Hz, 1H, imH), 8.67 (br d, J = 8.0 Hz, 1H, imH), 7.80 (br d, J = 2.8 Hz, 1H, pyrH), 7.77 (br d, J = 2.8 Hz, 1H, pyrH), 7.62 (br s, 1H, pyrH), 6.14 – 6.01 (m, 1H, $CH=CH_2$), 5.49 (br d, J = 7.6 Hz, 2H, NCH_2), 5.31 – 5.22 (m, 2H, $CH=CH_2$), 2.51 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (125 MHz, d_6-DMSO): δ (ppm) 181.4, 155.3, 153.8, 149.6, 133.6, 128.2, 121.5, 112.7, 111.5, 98.5, 54.4, 52.3. HR-MS (ESI+): *m/z* 383.9333 $[C_{12}H_{13}N_3BrPd]^+$, calcd. $[M - Br]^+$ 383.9322. Anal. calcd. (%) for $C_{12}H_{13}N_3Br_2Pd \cdot H_2O$: C 29.80, H 3.10, N 8.69; found C 29.40, H 2.70, N 8.70. Crystals of **4b** were grown *via* the vapour diffusion of diethyl ether into a saturated dichloromethane / dimethylsulfoxide solution.

Bis[1-allyl-3-(2-(5-nitro)pyridyl)imidazole-2-ylidene]palladium(II) dibromide (3c). 1-Allyl-3-(2-(5-nitro)pyridyl)imidazolium bromide **1c** (0.47 g, 1.51 mmol) and $Pd(OAc)_2$ (0.17 g, 0.75 mmol) were added to a flame-dried Schlenk flask and dried *in vacuo*. To these was added anhydrous acetonitrile (35 mL) and the resultant mixture stirred vigorously at 70 °C for 24 hours. After this time, an excess of cold diethyl ether (100 mL) was added in a single portion to precipitate a yellow solid which was collected *via* vacuum filtration. Hot acetonitrile (100 mL) was passed through the filter to dissolve the product into the filtrate and the solvent was removed *in vacuo* to afford the title compound as a yellow crystalline solid. Yield: 0.27 g, 0.38 mmol, 50%. Mp decomp. 229–231 °C. ^{1}H NMR (500 MHz, CD_3CN, 238 K): δ (ppm) 10.01 (s, 1H, imH), 9.28 (s, 1H, imH), 9.08 (d, J = 8.5 Hz, 1H, pyrH), 8.90 (d, J = 8.5 Hz, 1H, pyrH), 8.62 (d, J = 8.5 Hz, 1H, pyrH), 8.31 (d, J = 8.5 Hz, 1H, pyrH), 8.25 (s, 1H, imH), 8.21 (s, 1H, imH), 7.60 (s, 1H, pyrH), 7.27 (s, 1H, pyrH), 6.11 (m, 1H, C=CH), 5.50 (m, 1H, C=C'H), 5.46 (d, J = 17.0 Hz, 1H, C=CH), 5.34 (d, J = 10.0 Hz, 1H, C=C'H), 5.19 (m, 1H, C=CH), 4.94 (m, 1H, C=C'H), 4.85 (d, J = 10.0 Hz, 1H, NCH), 4.52 (d, J = 17.0 Hz, 1H, NCH), 4.00 (d, J = 17.0 Hz, 1H, NCH), 3.71 (d, J = 17.0 Hz, 1H, NCH). Unambiguous assignment of the resonances is hampered by broadening of the spectrum. For this reason, a $^{13}C\{^1H\}$ NMR spectrum was not obtained. HRMS (ESI+): *m/z* 644.9833 $[C_{22}H_{20}N_8O_4BrPd]^+$, calcd. $[M - Br]^+$ 644.9823. Anal. calcd. (%) for $C_{22}H_{20}N_8O_4Br_2Pd$: C 36.36, H 2.77, N 15.42; found C 36.40, H 2.70, N 15.30. Crystals of complex **3c** were obtained *via* the vapour diffusion of diethyl ether into a concentrated solution of the product in a mixture of methanol / dimethylsulfoxide.

[1-Allyl-3-(2-(4-methoxy)pyridyl)imidazole-2-ylidene]palladium(II) dibromide (4d). 1-Allyl-3-(2-(4-methoxy)pyridyl)imidazolium bromide **1d** (0.10 g, 0.39 mmol) and $Pd(OAc)_2$ (88 mg, 0.39 mmol) were charged to a flame-dried ampoule under an inert atmosphere and stirred in anhydrous acetonitrile (20 mL) at 80 °C for 48 hours. After this time, the mixture was cooled to room temperature, filtered through a Celite plug and solvents removed *in vacuo* to give a crude yellow residue. The residue was dissolved in acetonitrile (5 mL) and further filtered through a silica plug directly into an excess of diethyl ether (30 mL) to precipitate a bright yellow solid, which was collected *via* vacuum filtration and dried *in vacuo* to give the pure title compound. Yield: 43 mg, 0.089 mmol, 26%. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm) 9.35 (br d, J = 6.5 Hz, 1H, imH), 7.83 (br d, J = 6.5 Hz, 1H, imH), 7.24 (br d, J = 2.0 Hz, 1H, pyrH), 7.19 (br d, J = 2.0 Hz, 1H, pyrH), 6.98 (br dd, J = 6.5, 2.0 Hz, 1H, pyrH), 6.12 – 6.04 (m, 1H, $CH=CH_2$), 5.49 (br d, J = 5.5 Hz, 2H, NCH_2), 5.31 – 5.23 (m, 2H, $CH=CH_2$), 4.02 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (125 MHz, d_6-DMSO): δ (ppm) 169.6, 152.7, 142.0, 133.6, 124.5, 118.3, 117.4, 109.6, 98.7, 98.2, 57.4, 52.3. HRMS (ESI+): *m/z* 379.0381 $[C_{14}H_{17}N_4O_2Pd]^+$, calcd. $[M + MeCN + OH - 2Br]^+$ 379.0381. Anal. calcd. (%) for $C_{12}H_{13}N_3OBr_2Pd$: C 29.93, H 2.72, N 8.73; found C 29.65, H 2.70, N 8.50. Crystals of **4d** were grown *via* the vapour diffusion of diethyl ether into a solution of the complex in dichloromethane / dimethylsulfoxide.

Bis[1-allyl-3-(2-pyridyl)imidazol-2-ylidene]palladium(II) dihexafluorophosphate (5a). 1-Allyl-3-(2-pyridyl)imidazolium hexafluoro-phosphate **2a** (0.30 g, 0.91 mmol) and $Pd(OAc)_2$ (0.112 g, 0.50 mmol) were charged to a flame-dried ampoule under an inert atmosphere and stirred in anhydrous acetonitrile (15 mL) at 70 °C for 48 hours. After this time, the reaction mixture was cooled to room temperature, filtered through a Celite plug and solvents removed *in vacuo*. Recrystallisation from acetone / pentane delivered a pale yellow solid which was subsequently washed repeatedly with cold chloroform (3 x 20 mL) and dried *in vacuo* to give the title compound as a pale yellow solid. Yield: 0.18 g, 0.23 mmol, 50%. Mp decomp. at 215–216 °C. ^{1}H NMR (300 MHz, CD_3CN): δ (ppm) 9.24 (br d, J = 6.0 Hz, 2H, imH), 7.98 (t, J = 6.0 Hz, 2H, pyrH), 7.66 (d, J = 6.0 Hz, 2H, pyrH), 7.46 (t, J = 6.0 Hz, 2H, pyrH), 7.30 (d, J = 6.0 Hz, 2H, pyrH), 7.01 (br s, 2H, imH), 6.13 – 6.01 (m, 2H, C=CH), 5.83 – 5.78 (m, 2H, $C=CH_{trans}$), 5.39 – 5.14 (m, 4H, NCH_2), 4.99 (br s, 2H, $C=CH_{cis}$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN): δ (ppm) 150.2, 143.5, 143.2, 132.4, 126.0, 125.7, 125.4, 124.9, 124.8, 122.8, 119.8, 119.0, 112.6, 56.3, 54.6. HRMS (ESI+): *m/z* 238.0471 $[C_{22}H_{22}N_6Pd]^{2+}$, calcd. $[M - 2PF_6]^{2+}$ 238.0465. Anal. calcd. (%) for $C_{22}H_{22}N_6P_2F_{12}Pd \cdot CHCl_3$: C 31.17, H 2.62, N 9.99; found C 31.55, H 2.70, N 10.50.

Bis[1-allyl-3-(2-(4-methyl)pyridyl)imidazole-2-ylidene]palladium(II) dihexafluorophosphate (5b). 1-Allyl-3-(4-methyl)pyridyl imidazolium hexafluorophosphate **2b** (0.18 g, 0.52 mmol) and $Pd(OAc)_2$ (59 mg, 0.26 mmol) were charged to a flame-dried ampoule under an inert atmosphere and stirred in anhydrous acetonitrile (10 mL) at 80 °C for 48 hours. After this time, the mixture was cooled to room temperature, filtered through a Celite plug and solvents removed *in vacuo* to give a crude yellow residue. Dissolution of the residue *via* a binary mixture of methanol / dichloromethane followed by dropwise addition to an excess of cold diethyl ether precipitated a pale yellow solid, which was subsequently washed with chloroform (2 x 10 mL) to deliver the pure title compound as an off-yellow solid. Yield: 0.13 g, 0.15 mmol,

56%. Mp decomp. 211–213 °C. ^{1}H NMR (300 MHz, d_6-DMSO): δ (ppm) 7.64 – 7.54 (br m, 4H, imH), 7.27 – 7.10 (br m, 2H, pyrH), 6.97 – 6.67 (br m, 4H, pyrH), 5.67 – 3.19 (br m, 6H, CH_2=CH), 2.50 (br s, 6H, CH_3), 1.25 – 0.98 (br m, 4H, CH_2). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN): δ (ppm) 153.7, 150.0, 147.5, 134.9, 132.1, 131.2, 127.8, 124.4, 122.5, 120.6, 115.6, 53.1, 21.2. HRMS (ESI+): *m/z* 252.0623 $[C_{24}H_{26}N_6Pd]^{2+}$, calcd. [M – MeCN – $2PF_6$]$^{2+}$ 252.0621. Anal. calcd. (%) for $C_{26}H_{29}N_7P_2F_{12}Pd\cdot 3/4CHCl_3$: C 34.72, H 3.24, N 10.59; found C 34.80, H 3.30, N 10.30.

Bis[1-allyl-3-(2-(5-nitro)pyridyl)imidazole-2-ylidene]palladium(II) dihexafluorophosphate (5c). 1-Allyl-3-(2-(5-nitro)pyridyl)imidazolium hexafluorophosphate **2c** (0.45 g, 1.20 mmol) and $Pd(OAc)_2$ (0.134 g, 0.60 mmol) were charged to a flame-dried Schlenk flask under an inert atmosphere and stirred vigorously in anhydrous acetonitrile (20 mL) at 80 °C for 18 hours. After this time, the reaction mixture was cooled to room temperature, filtered through a Celite plug and solvents removed *in vacuo* to afford a pale yellow residue. Dissolution of the crude oil in acetonitrile followed by dropwise addition to a solution of cold diethyl ether furnished the pure title compound as a pale yellow solid which was collected *via* vacuum filtration. Yield: 0.43 g, 0.47 mmol, 79%. Mp decomp. 211–212 °C. ^{1}H NMR (500 MHz, CD_3CN, 333 K): δ (ppm) 10.15 (s, 1H, imH), 9.28 (s, 1H, imH), 9.04 (d, J = 8.5 Hz, 1H, pyrH), 8.81 (d, J = 9.0 Hz, 1H, pyrH), 8.67 (d, J = 9.0 Hz, 1H, pyrH), 8.17 (s, 1H, imH), 8.06 (d, J = 8.5 Hz, 1H, pyrH), 7.98 (s, 1H, imH), 7.60 (s, 1H, pyrH), 7.26 (s, 1H, pyrH), 6.18 (m, 1H, C=CH), 5.61 (m, 1H, C=C'H), 5.55 (d, J = 17.0 Hz, 1H, C=CH), 5.42 (d, J = 10.5 Hz, 1H, C=C'H), 5.22 (m, 1H, C=CH), 5.07 (m, 2H, C=C'H), 4.87 (d, J = 17.0 Hz, 1H, NCH), 4.01 (d, J = 10.0 Hz, 1H, NCH), 3.83 (d, J = 10.0 Hz, 1H, NCH), 1.97 (s, 3H, coord CH_3CN). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 298 K): δ (ppm) 155.9, 154.0, 146.4, 144.9, 138.6, 132.0, 126.7, 121.9, 120.0, 115.3, 66.3, 55.0, 15.7. HRMS (ESI+): *m/z* 585.0634 $[C_{22}H_{21}N_8O_5Pd]^+$, calcd. [M – MeCN – $2PF_6$ + OH]$^+$ 585.0668. Anal. calcd. (%) for $C_{24}H_{23}N_9P_2F_{12}O_4Pd\cdot 1/3H_2O$: C 31.89, H 2.64, N 13.95; found C 31.60, H 2.50, N 13.60. Crystals of complex **5c** were obtained *via* slow evaporation of a concentrated acetonitrile solution.

Bis[1-allyl-3-(2-(4-methoxy)pyridyl)imidazole-2-ylidene]palladium(II) dihexafluorophosphate (5d). 1-Allyl-3-(4-methoxy)pyridyl imidazolium hexafluorophosphate **2d** (0.25 g, 0.69 mmol) and $Pd(OAc)_2$ (77.7 mg, 0.35 mmol) were charged to a flame-dried ampoule under an inert atmosphere and stirred in anhydrous acetonitrile (20 mL) at 80 °C for 48 hours. After this time, the mixture was cooled to room temperature, filtered through a Celite plug and solvents removed *in vacuo* to give a crude yellow residue. The crude product was dissolved in acetone and purified *via* flash chromatography on silica gel (saturated acetone solution of NH_4PF_6 as eluent) to afford a pale yellow residue. Dissolution of the residue in acetonitrile followed by dropwise addition to cold diethyl ether delivered the pure title compound as an off-yellow solid. Yield: 0.32 g, 0.35 mmol, 50%. Mp decomp. at 209–211 °C. ^{1}H NMR (300 MHz, CD_3CN): δ (ppm) 7.95 (br d, J = 2.1 Hz, 1H, imH), 7.82 (br d, J = 2.1 Hz, 1H, imH), 7.77 (br d, J = 16.5 Hz, 2H, pyrH), 7.76 (br d, J = 16.5 Hz, 2H, pyrH), 7.26 (d, J = 2.1 Hz, 1H, imH), 7.25 (d, J = 2.1 Hz, 1H, imH), 7.19 (d, J = 2.7 Hz, 1H, pyrH), 7.08 (d, J = 2.7 Hz, 1H, pyrH), 6.64 (br m, 2H, $CHCH_2$), 5.91 (br d, J = 9.0 Hz, 2H, $CH=CH_{cis}$), 5.47 (br dd, J = 3.3, 9.0 Hz, 2H, $CH=CH_{trans}$), 4.58 (br d, J = 2.7 Hz, 4H, NCH_2), 3.47 (br s, 6H, OCH_3). ^{13}C{^{1}H} NMR (75 MHz, CD_3CN): δ (ppm) 170.8, 152.7, 151.1, 151.0, 132.5, 125.4, 121.8, 119.8, 111.5, 101.6, 57.8, 54.6. HRMS (ESI+): *m/z* 573.0836 $[C_{24}H_{26}N_6O_2ClPd]^+$, calcd. [M – $2PF_6$ – Cl]$^+$ 573.0834. Anal. calcd (%) for $C_{24}H_{26}N_6O_2P_2F_{12}Pd$: C 34.86, H 3.17, N 10.29; found: C 34.90, H 3.15, N 10.65. Crystals of complex **5d** were isolated *via* the slow diffusion of diethyl ether vapours into a concentrated acetonitrile solution.

Bis[1,3-(2-methylpyridyl)imidazol-2-ylidene]palladium(II) dibromide (6f). 1,3-Bis(2-methylpyridyl)imidazolium bromide **1f** (0.50 g, 1.51 mmol) and $Pd(OAc)_2$ (0.17 g, 0.76 mmol) were charged to a flame-dried Schlenk flask under an inert atmosphere and stirred vigorously in anhydrous dimethylsulfoxide (20 mL) at 80 °C for 2 hours, followed by further heating at 100 °C for 24 hours. After this time, a highly insoluble dark brown solid precipitated from solution which was removed *via* filtration over Celite. The resultant light brown filtrate was further filtered through a Celite plug which was rinsed with an aliquot of dichloromethane (20 mL) to give a yellow solution. Addition of cold diethyl ether (50 mL) in a single portion led to the precipitation of a bright yellow solid which was collected *via* vacuum filtration and washed repeatedly with cold chloroform (3 x 30 mL) to afford the pure title compound as a yellow solid. Yield: 0.24 g, 0.31 mmol, 41%. Mp decomp. 248–250 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) 9.56 (br s, 1H, imH), 9.37 (br s, 1H, imH), 8.53 – 8.40 (br m, 2H, imH), 8.24 – 7.17 (br m, 16H, pyrH), 5.74 (br s, 4H, NCH_2), 5.47 (br s, 4H, $N'CH_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN): δ (ppm) 118.6, 118.0, 116.1, 114.7, 113.8, 103.1, 102.1, 92.5, 88.5, 87.1, 86.7, 86.3, 83.4, 80.9, 16.5, 15.5, 14.5. HRMS (ESI+): *m/z* 687.0652 $[C_{30}H_{28}N_8BrPd]^+$, calcd. [M – Br]$^+$ 687.0629. Anal. calcd. (%) for $C_{30}H_{28}N_8Br_2Pd\cdot CHCl_3$: C 41.02, H 3.50, N 12.64; found C 41.20, H 3.80, N 12.70. Single crystals of **6f** were obtained *via* slow vapour diffusion of diethyl ether into a concentrated solution of the complex in a dichloromethane / dimethylsulfoxide solution.

Bis[1-allyl-3-(2-methylpyridyl)imidazol-2-ylidene]palladium(II) dihexafluorophosphate (7e). $Pd(OAc)_2$ (0.20 g, 0.89 mmol) and 1-allyl-3-(2-methylpyridyl)imidazolium bromide **1e** (0.50 g, 1.79 mmol) were added to a flame-dried Schlenk flask and stirred in anhydrous dimethylsulfoxide (20 mL) at 70 °C for 2 hours, 90 °C for 6 hours and 120 °C for 12 hours. After this time, the crude reaction mixture was filtered through a Celite plug and solvents removed *in vacuo* to give a crude brown solid. Recrystallisation from chloroform / diethyl ether produced an off-white solid which proved extremely hygroscopic when exposed to air. The solid was re-dissolved in water (50 mL) and stirred vigorously with NH_4PF_6 (0.70 g, 5.26 mmol). The resulting off-white precipitate was filtered and washed with cold water (3 x 30 mL) followed by diethyl ether (3 x 30 mL) and dried *in vacuo* to deliver pure title compound as an off-yellow crystalline solid. Yield: 0.25 g, 0.31 mmol, 35%. Mp decomp. at 243–244 °C. ^{1}H NMR (500 MHz, CD_3CN, 233 K):

δ (ppm) 9.18 (d, J = 5.5 Hz, 2H, imH), 7.97 (t, J = 15.0, 7.5 Hz, 2H, pyrH), 7.64 (d, J = 7.5 Hz, 2H, pyrH), 7.43 (t, J = 12.5, 6.5 Hz, 2H, pyrH), 7.30 (s, 2H, imH), 7.00 (s, 2H, pyrH), 6.02 (m, 2H, C=CH), 5.79 (d, J = 15.0 Hz, 2H, CH_2), 5.34 (d, J = 15.0 Hz, 2H, CH_2), 5.24 (d, J = 10.0 Hz, 2H, $C=CH_{cis}$), 5.14 (d, J = 21.0 Hz, 2H, $C=CH_{trans}$), 5.09 (m, 2H, NCH), 5.06 (m, 2H, NCH). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 157.1, 154.6, 153.5, 142.6, 133.1, 127.1, 126.8, 124.7, 123.7, 119.9, 56.3, 53.8. HRMS (ESI+): *m/z* 649.0903 $[C_{24}H_{26}N_6F_6PPd]^+$, calcd. $[M - PF_6]^+$ 649.0902. Anal. calcd. (%) for $C_{24}H_{26}N_6P_2F_{12}Pd$: C 36.30, H 3.30, N 10.59; found C 36.50, H 3.30, N 10.65. Single crystals suitable for X-ray diffraction analysis were isolated *via* the vapour diffusion of diethyl ether into a concentrated solution of **7e** in acetonitrile.

Bis[1,3-(2-methylpyridyl)imidazol-2-ylidene]palladium(II) dihexafluorophosphate (7f). 1,3-Bis(2-methylpyridyl)imidazolium hexafluorophosphate **2f** (1.25 g, 3.16 mmol) and $Pd(OAc)_2$ (0.35 g, 1.58 mmol) were charged to a flame-dried ampoule under an inert atmosphere and stirred in anhydrous dimethylsulfoxide (15 mL) at 100 °C for 24 hours. Upon completion, the crude reaction mixture was filtered through a Celite plug and rinsed with one aliquot of dichloromethane (20 mL) to give a light brown solution. The solution was added to a separating funnel, extracted with water (3 x 30 mL) and the organic fraction dried over anhydrous magnesium sulfate. After filtration, the resulting organic solution was concentrated under reduced pressure to furnish a pale yellow residue. Dissolution of the residue in acetonitrile followed by dropwise addition to a solution of cold diethyl ether delivered the pure title compound as a light brown solid which was collected *via* vacuum filtration. Yield: 1.10 g, 1.23 mmol, 39%. Mp decomp. 231–232 °C. ^1H NMR (400 MHz, CD_3CN): δ (ppm) 8.71 – 8.51 (m, 4H, imH), 8.12 – 7.08 (m, 16H, pyrH), 5.87 (d, J = 20.0 Hz, 2H, NCH_2), 5.51 (d, J = 20.0 Hz, 2H, NCH_2), 5.06 (d, J = 21.2 Hz, 2H, NCH_2), 4.73 (d, J = 21.2 Hz, 2H, NCH_2). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ (ppm) 199.4, 160.9, 158.0, 155.0, 154.6, 154.2, 153.9, 153.1, 150.5, 150.4, 142.3, 142.0, 138.2, 136.2, 132.7, 126.9, 126.8, 126.7, 126.6, 124.7, 124.5, 123.9, 123.4, 122.9, 56.2, 56.0, 55.6, 54.0. HRMS (ESI+): *m/z* 751.1138 $[C_{30}H_{28}N_8F_6PPd]^+$, calcd. $[M - PF_6]^+$ 751.1108. Anal. calcd. (%) for $C_{30}H_{28}N_8P_2F_{12}Pd \cdot 1/2H_2O$: C 39.00, H 3.38, N 12.13; found C 38.95, H 3.00, N 12.00. Crystals of **7f** were isolated *via* vapour diffusion of diethyl ether into a concentrated solution of the complex in acetonitrile.

General Procedure for Cross-Coupling Reactions.

Cross-coupling reaction 1: Phenylboronic acid (0.18 g, 1.5 mmol), bromobenzene (0.16 g, 1.0 mmol), Pd 'catalyst' (see Table 1) and Cs_2CO_3 (0.65 g, 2.0 mmol) were charged to a carousel tube and briefly dried *in vacuo*. To these was added anhydrous dioxane (5 mL) *via* syringe. The resulting mixture was stirred at 80 °C for 2 hours. After this time, the mixture was cooled and a 100 µL aliquot was withdrawn and quenched into a CH_2Cl_2 solution of *p*-cymene (2 mL, 9.52 mM). The resulting solution was filtered through Celite and subsequently analysed *via* GC.

Cross-coupling reaction 2: 2,6-Dimethylphenylboronic acid (0.18 g, 1.2 mmol), 1-bromo-2-methoxynapthalene (0.24 g, 1.0 mmol), Pd 'catalyst' (see Table 2) and KOH (0.17 g, 3.0 mmol) were charged to a carousel tube and briefly dried *in vacuo*. To these was added anhydrous dioxane (3 mL) *via* syringe. The resulting mixture was stirred at 65 °C for 24 hours. After this time, the mixture was cooled and a 100 µL aliquot was withdrawn and quenched into a CH_2Cl_2 solution of *p*-cymene (2 mL, 17.5 mM). The resulting solution was filtered through Celite and subsequently analysed *via* GC.

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