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Solid-state structure, solution-state behaviour and catalytic activity of electronically divergent C, N-chelating palladium-N-heterocyclic carbene complexes

Michael R. Chapman, a Benjamin R. M. Lake, a Christopher M. Pask, a Bao N. Nguyen a and Charlotte E. Willans a*

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)X]X and dicationic [Pd(NHC)X]2-X-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 2 N]Cl] 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).

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

From a catalytic viewpoint, 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 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-disopropylphenyl)imidazole-2-ylidene) in a cross-coupling reaction to produce sterically congested tetra-ortho-substituted biaryl compounds.
Results and discussion

Imidazolium bromides 1a–1d were synthesised and treated with 0.5 equivalents Pd(OAc)$_2$ under anhydrous conditions. Pd$^{1}$-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.

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)$^\circ$ (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 2.090(7) Å is in agreement with related complexes reported in the literature. 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. The solid-state structure of 3c highlights a coordination sphere around the Pd$^{2+}$ 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.

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)$^\circ$. 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. 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$_3$] 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 b acidity. The planar nature of complexes \(4b\) and \(4d\) leads to an extended packing structure which is largely influenced by strong \(\pi-\pi\) stacking interactions, propagating a lamellar packing assembly throughout each crystalline lattice (see Supporting Information).

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 \(^1H\) 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.

Despite their similar solid-state structures, comparison between the \(^1H\) 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), \(^1H\) 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 \(^1H\) 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.\textsuperscript{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.\textsuperscript{41}

\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig4.png}
\caption{VT $^1$H NMR spectra (500 MHz, CD$_2$CN) of Pd$^2$-bis-NHC complexes 3c (238 – 298 K) and 5c (333 K).}
\end{figure}

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$^2$-bis-NHC assemblies. To improve conformational flexibility about the coordination sphere, N-picoly substituted NHC precursors 1e, 1f and 2f were synthesised (Scheme 4).

\begin{scheme}
\centering
\includegraphics[width=0.5\textwidth]{scheme4.png}
\caption{Preparation of picoly-substituted Pd$^2$-bis-NHC complexes 7e, 6f and 7f.}
\end{scheme}

Reaction of two equivalents of imidazolium bromide 1e with 0.5 equivalents Pd(OAc)$_2$ led to Pd(NHC)$_2$Br$_2$ complex, which proved to be extremely hygroscopic and difficult to handle when exposed to air. Consequently, the resulting residue was immediately reacted with NH$_4$PF$_6$, 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)$^\circ$ attributed to C4-Pd1-N3, and a C4-Pd1-C16 angle of 95.25(11)$^\circ$ 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).\textsuperscript{41} Interestingly, upon sample cooling (233 K, top spectrum), two sets of 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$_2$CN; 5.87, 5.51, 5.06 and 4.73 ppm), akin to those displayed by 7e representing each diastereotopic set of methylene-bridged protons.
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.

Pd-NHC complexes, in the presence of ancillary nitrogen donor ligands, have shown remarkable activities in numerous Pd-catalysed cross-coupling reactions. 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).
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\textsuperscript{I}-\textsuperscript{mono}-NHC 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\textsuperscript{I}-\textsuperscript{mono}-NHC rivals. Highest conversions were achieved using picoly1-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.\textsuperscript{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 biaryl)s under mild reaction conditions.\textsuperscript{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).\textsuperscript{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 picoly1-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.
significant increase in catalyst performance as N-picoly substituted NHC ligands are introduced to the Pd* coordination sphere. Near-quantitative conversion to biphenyl was achieved using Pd-bis(picoly)-substituted-NHC complex 1. It is anticipated that the enhanced activity is attributed to the hemilabile nitrogen-donor ligands acting to protect and vacate more challenging cross-coupling reaction to prepare a tetra-ortho substituted biaryl. In this setting, N-picoly substituted complexes 5a-c afforded the sterically congested product in 32–36% conversion, whilst N-picoly 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, 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 P2O5. 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 CaH2 or distilled and then freeze-pump-thaw degassed prior to use. All other reagents and solvents were used as supplied.

1H and 13C{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 13C{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 13C{1H} NMR spectra was aided by 13C{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 SHELXL-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. 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 decompos at 222–223°C. 1H NMR (300 MHz, CD2CN): 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 13C{1H} NMR spectrum was not obtained. HRMS (ESI+): m/z 555.0120 [C32H23N9BrPd]+, calcd. [M – Br]+ 555.0119. Anal. calc. (%) for C32H23N9BrPd-2/3CD2CN: 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)imidazol-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 decompos 222–224°C. 1H NMR (500 MHz, CD2CN): 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), 4.98 (br s, 2H, C=CH2), 3.92 – 3.77 (br m, 4H, NCH2), 2.51 (br s, 6H, CH3). 13C{1H} NMR (125 MHz, CD2CN): 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
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. 1H NMR (400 MHz, CD3CN): 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=CH2), 5.49 (br d, J = 7.6 Hz, 2H, NCH2), 5.31 – 5.22 (m, 2H, CH=CH2), 2.51 (s, 3H, OCH3). 13C{1H} NMR (125 MHz, D2O): δ (ppm) 181.4, 155.3, 153.8, 149.6, 133.6, 128.2, 121.5, 111.5, 98.5, 54.4, 52.3. HR-MS (ESI+): m/z 383.9333 [C12H13N3BrPd], calcd. [M – Br] 383.9322. Anal. calcld. (% for C12H13N3BrPd2O2: C 38.90, H 2.90, N 18.60. 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)imidazolylidene)palladium 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 (15 mL) at 70 °C was passed through the solvent was removed in vacuo via filtration and dried in vacuo. 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%. 1H NMR (400 MHz, CD3CN): δ (ppm) 9.35 (br d, J = 6.5 Hz, 1H, imH), 7.83 (br d, J = 6.5 Hz, 1H, pyrH), 7.24 (br d, J = 2.0 Hz, 1H, pyrH), 5.19 (br d, J = 2.0 Hz, 1H, pyrH), 6.98 (br d, J = 6.5, 2.0 Hz, 1H, pyrH), 6.12 – 6.04 (m, 1H, CH=CH2), 5.49 (br d, J = 5.5 Hz, 2H, NCH2), 5.31 – 5.23 (m, 2H, CH=CH2), 4.02 (s, 3H, OCH3). 13C{1H} NMR (125 MHz, D2O-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 [C24H14N2O2Pd2], calcd. [M + MeCN + OH – 2Br] 379.0381. Anal. calcld. (% for C24H14N2O2Br2Pd: C 59.62, H 2.72, N 8.73; found C 59.65, 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)imidazo[2,1-c]pyridine]palladium(II) hexafluoro phosphate (5a).** 1-Allyl-3-(2-pyridyl)imidazolium hexafluorophosphate 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. 1H NMR (300 MHz, CD3CN): δ (ppm) 9.24 (br d, J = 6.0 Hz, 2H, imH), 7.98 (t, J = 6.0 Hz, 2H, pyrH), 7.66 (t, 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, CH=CH2), 5.83 – 5.78 (m, 2H, CH=CH2trans), 5.39 – 5.14 (m, 4H, NCH2), 4.99 (br s, 2H, CH2CH2), 135C{1H} NMR (75 MHz, CD2CN): δ (ppm): 150.0, 143.5, 135.4, 132.4, 126.0, 126.7, 125.4, 124.9, 124.8, 122.8, 119.8, 119.0, 112.6, 56.3, 54.6. HRMS (ESI+): m/z 238.0471 [C22H22P2F12], calcd. [M – 2PF6]2+ 238.0465. Anal. calcld. (% for C22H22P2F12: 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)imidazo[2,1-c]pyridine]palladium(II) dihexafluorophosphate (5b).** 1-Allyl-3-(2-(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,

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Dissolution of the crude oil in acetonitrile followed by 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 decom. 211–212 °C. \(^1\)H NMR (500 MHz, CD$_3$CN, 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=CH), 5.55 (d, J = 17.0 Hz, 1H, C=CH), 5.42 (d, J = 10.5 Hz, 1H, C=CH), 5.22 (m, 1H, C=CH), 5.07 (m, 2H, C=CH), 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$_2$CN). \(^{13}\)C\(^{1}\)H NMR (125 MHz, CD$_3$CN, 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$_{29}$H$_{23}$N$_{6}$O$_{5}$P$_{2}$Pd$^{+}$], calculated [M – MeCN – 2PF$_{6}$ + OH$^{-}$] m/z 585.0668. Anal. calcld. (%) for C$_{29}$H$_{23}$N$_{6}$O$_{5}$P$_{2}$Pd: C 41.02, H 3.50, N 12.64; found: C 41.19, H 3.50, N 12.65.

**Bis[1-allyl-3-(2-(5-nitro)pyridyl)imidazol-2-ylidine]palladium(II) dihexafluorophosphate (5d).** 1-Allyl-3-(2-(5-nitro)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$_4$PF$_6$ 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%.

**Bis[1-allyl-3-(2-(4-methoxy)pyridyl)imidazol-2-ylidine]palladium(II) dihexafluorophosphate (5e).** Pd(OAc)$_2$ (0.20 g, 0.89 mmol) and 1-allyl-3-(2-(4-methoxy)pyridyl)imidazolium hexafluorophosphate 2d (0.25 g, 0.69 mmol) were charged 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 title compound was re-dissolved in water (50 mL) and stirred vigorously with NH$_4$PF$_6$ (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%.

**Bis[1-allyl-3-(2-(5-nitro)pyridyl)imidazol-2-ylidine]palladium(II) dihexafluorophosphate (7e).** Pd(OAc)$_2$ (0.20 g, 0.89 mmol) and 1-allyl-3-(2-(5-nitro)pyridyl)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 concentrated solution of the complex in a dichloromethane / dimethylsulfoxide solution.
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=C=CH), 5.79 (d, J = 15.0 Hz, 2H, CH₂), 5.34 (d, J = 15.0 Hz, 2H, CH₂), 5.24 (d, J = 10.0 Hz, 2H, C=CH₃), 5.14 (d, J = 21.0 Hz, 2H, C=CH₂), 5.09 (m, 2H, NCH₂), 4.73 (d, J = 21.2 Hz, 2H, NCH), 5.06 (m, 2H, NCH).

Upon completion, the crude reaction mixture was filtered through a Celite plug and subsequently dried via a 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) dihexafluorophosphatetrifluoroborate (7f)

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