N-heterocyclic carbene tethered amido complexes of palladium and platinum

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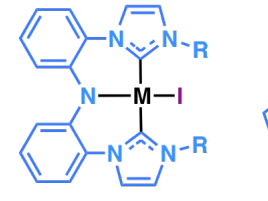
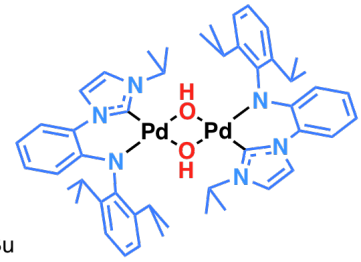


M = Pd, Pt; R = *i*-Pr, *n*-Bu

[CNC]M–I



{[C,N]Pd(μ-OH)}$_2$

The synthesis and structure of chelating amido-NHC and amido-bis(NHC) complexes of Pd and Pt are described, including the first [CNC]Pt complexes and the first Pd arylamido-NHC complex.

Abstract

With a view to applications in bifunctional catalysis, a modular cross-coupling strategy has been used to prepare amine bis(imidazolium) salts (**3a** and **3b**) and an amine mono(imidazolium) salt (**6**) as precursors to chelating amido-NHC ligands. Treating the pro-ligands **3** with 3 equivalents of the bulky base KHMDS and $Pd(OAc)_2$ or $PtCl_2(COD)$ gave the four amido bis(*N*-heterocyclic carbene) pincer complexes [CNC-R]M-I [M = Pd (**7**) or Pt (**8**); R = *i*-Pr (**a**) or *n*-Bu (**b**)], including the first examples of platinum complexes of a CNC ligand. The reaction of **7a** with AgOTf in pyridine gave the cationic complex {[CNC-*i*-Pr]Pd-py}OTf (**9a**). Heating a mixture of amine mono(imidazolium) salt **6** with $PdCl_2$ or K_2PtCl_4, K_2CO_3 and KI in pyridine at 100 °C gave the complexes [C,NH]MI_2py [M =Pd (**10**) or Pt (**11**)], in which the amine arm of the NHC ligand is not deprotonated and does not coordinate to the metal. For a solution of **10** in 1,4-dioxane, deprotonation of the amine occurred in a biphasic reaction with aqueous KOH at 40 °C, giving the dimeric amido complex {[C,N]Pd(μ-OH)}$_2$ (**12**). The more

inert Pt analogue **11** was unreactive under the same conditions. Solid-state structures of the complexes **7a**, **7b**, **9a**, **10**, **11** and **12** have been determined by single crystal X-ray diffraction.

Introduction

Bifunctional catalysis, in which an electrophilic metal and a nucleophilic ligand act in concert to activate a substrate, enables reactions to take place that are not possible using classical catalytic transformations that occur only at the metal centre.[1–3] Wide-ranging applications have been found for bifunctional catalysis, many in asymmetric synthesis, including hydrogenation under H_2,[4] transfer hydrogenation,[5,6] isomerisation of allylic alcohols,[7] alkene hydroamination,[8] hydrosilylation,[9] Michael addition,[10] C-H activation[11–15] and lactide polymerisation.[16] The most studied of these reactions is the asymmetric transfer hydrogenation between alcohols and carbonyl compounds, catalysed by half-sandwich complexes of Ru, Ir or Rh with a chiral diamine ligand such as *N*-tosyl-1,2-diphenylethylenediamine. The key steps in the catalytic cycle occur after deprotonation of the primary amine group to give a metal amido complex: subsequent transfer hydrogenation from *i*-PrOH to the M-N bond gives a metal amine-hydride complex that transfers an acidic and a basic hydrogen to the carbonyl substrate.[17] Crucially, the chelating amine ligand makes the catalyst more resistant to undesirable M-N bond cleavage.[18] Other chelating groups such as aryl,[19] phosphine[20–22] and thiol/thioether[23] have also been used to tether the reactive nitrogen to the metal in transfer hydrogenation. However, the application of *N*-heterocyclic carbene (NHC) donor groups to tether a nucleophilic amido ligand to an electrophilic metal in bifunctional catalysis has yet to be fully exploited,[24,25] and even simple coordination chemistry of multidentate amido-NHC ligands is under-explored. Of note, tridentate bis(amido)-NHC [NCN] pincer complexes of zirconium and hafnium have been reported,[26,27] and amido-bis(NHC) [CNC] and amido-NHC [C,N] complexes of some early and late transition metals are also known.[28–35] Most closely related to this work, Douthwaite has described the palladium [CNC] complex **A** and, during the course of our research, Luo has reported the Pd complexes (**B**).[36,37]

Fig. 1

As part of a research programme exploring new applications in bifunctional catalysis, we have been investigating late transition metal complexes containing amido-NHC ligands. Herein, we report tridentate amido-bis(NHC) [CNC] ligand complexes of palladium and for the first time platinum. We also report the first bidentate arylamido-NHC [C,N] ligand complex of palladium.

Results and Discussion

The synthesis of the amine bis(imidazolium) pro-ligands proceeded with a palladium catalysed amination of 2-bromoiodobenzene to give bis(2-bromophenyl)amine (**1**) using a procedure adapted from the literature (Scheme 1).[38] A copper catalysed Ullman-type reaction[39] of imidazole with **1** gave the coupled product **2** in 90% yield. Subsequent alkylation of **2** with *i*-propyliodide or *n*-butyliodide gave the imidazolium iodide salts **3a** and **3b** in 89 and 93% yields respectively. As expected, the alkylation reaction proceeded faster for the primary alkyl halide than the secondary alkyl halide. Hence, the pro-ligands **3a** and **3b** were prepared in three steps in 74-78% yield from commercially available materials.

Scheme 1.

The same methodology was also applied to prepare an analogous pro-ligand containing only one imidazolium moiety: starting instead from *N*-(2-bromophenyl)-2,6-di*iso*propylaniline (**4**),[40] the Ullman-type cross coupling with imidazole gave intermediate **5** and subsequent alkylation with *i*-propyl iodide gave the imidazolium pro-ligand **6** (Scheme 2).

Scheme 2.

A common method for the coordination of *N*-heterocyclic carbene ligands to transition metals is to prepare the silver(I) NHC complex from the reaction of an imidazolium salt and Ag_2O; subsequent transmetallation then gives the required metal-NHC complex.[41,42] Douthwaite *et al*. have shown that this is a viable route to the complex **A**.[36] However, treating our more rigid pro-ligands **3a** or **3b** with Ag_2O in DCM at room temperature gave an intractable mixture of products. Performing the reaction in refluxing THF also gave an unidentifiable mixture, as did including $Pd(OAc)_2$ or $PdCl_2(COD)$ in the reaction mixture. Conversely, Luo *et al*. have reported that treatment of an amine bis(imidazolium) salt with Ag_2O followed by $PdCl_2(MeCN)_2$ gave the corresponding [CNC]PdCl complexes **B**, although a silver complex of their ligands could not be isolated.[37] Presumably, a silver(I) NHC complex was generated *in situ*., and subsequent transmetallation to Pd was successful. For our ligands, however, this strategy also proved to be unsuccessful.

Luo reported that the preparation of [CNC] pincer complexes of palladium **B** by deprotonation of the amine bis(imidazolium) ligand with an organometallic or amide base were unsuccessful.[37] In contrast, we found that treating a DME solution of **3a** or **3b** with 3 equivalents of potassium hexamethyldisilazide (KHMDS) at 0 °C in the presence of $Pd(OAc)_2$ gave, after work-up and purification by column chromatography, the complexes [CNC-*i*-Pr]Pd-I (**7a**) and [CNC-*n*-Bu]Pd-I (**7b**) in 33 and 42% yields respectively, Scheme 3. These moderate

yields do not appear to arise from the purification procedure: the ^{1}H NMR spectrum recorded for the crude product showed several other species that could not be identified and repeating the column chromatography gave complete recovery of analytically pure material. Using $PdCl_2(COD)$ in the reaction instead of $Pd(OAc)_2$ or using THF as the solvent gave lower yields, and performing the reaction in the absence of a palladium salt gave an intractable mixture of products. Coordination of the anionic tridentate bis(*N*-heterocylic carbene) ligand to palladium was confirmed by ^{1}H and ^{13}C NMR spectroscopy: the ^{1}H NMR spectra for **7a** and **7b** lack a signal that could be assigned to the NCHN proton of an imidazolium cation (these were present as singlet resonances at δ_H 9.56 and 9.72 ppm respectively in the spectra recorded for **3a** and **3b**) and the $^{13}C\{^{1}H\}$ NMR spectra for **7a** and **7b** contained signals at δ 165.3 and 167.0 ppm respectively for the carbene bound to palladium. An unexpected feature of the ^{1}H NMR spectrum recorded for **7a** was the downfield shift observed for the *i*-Pr CH resonance, which appeared as an apparent septet at 6.35 ppm. The ligand completing the fourth coordination site at Pd was confirmed as iodide by FAB MS and microanalysis.

Scheme 3.

Crystals of **7a** and **7b** suitable for single crystal X-ray diffraction were obtained by the slow evaporation of a C_6D_6 solution of each; ORTEP figures for the solid state structures are shown in Figures 2 and 3 and selected bond lengths are shown in Table 1.

Table 1.

Fig. 2.

Fig. 3.

The complexes **7a** and **7b** both display the expected square planar geometry around Pd and iodide is confirmed as the ligand filling the fourth coordination site. The [CNC] ligand is strongly distorted from planarity: the angle between the square plane around Pd and the trigonal plane around the amide nitrogen is 53.3 ° in **7a** and 57.4 ° in **7b**. Hence, the ligand adopts a helical conformation and two atropisomers arise. Complex **7a** crystallizes in the non-centrosymmetric chiral space group C222(1), and only one enantiomer is present in the unit cell. Complex **7b**, however, crystallizes in the non-centrosymmetric achiral space group Aba2, and hence both enantiomers are observed in the unit cell. Atropisomerism has been observed for pyridyl and aryl bridged NHC pincers and rapid interconversion of the atropisomers is common.[29,43,44] In addition, the [CNC]PdCl complex **A** and the related amine complex {[CN(H)C]PdCl}Cl also show interconversion of atropisomers at ambient temperature.[36,45]

Conversely, variable temperature ^{1}H NMR spectra recorded for **7a** in C_6D_6 up to 344 K showed no coalescence of the diastereotopic methyl groups or indeed any line broadening consistent with fluxionality. Hence, these [CNC] palladium complexes appear to possess greater stereochemical rigidity that could enable new strategies for the synthesis of non-racemic chiral complexes from achiral ligands.[46]

The Pd-N bond lengths in the two complexes **7a** and **7b** are typical for a Pd(II)-amide bond and the Pd-C bond lengths are also typical for two *trans* NHC ligands bound to square planar palladium.[47] These bond lengths do not differ significantly from those reported for the complexes **B** by Luo.[37] There is a large angle (**7a**: 81.3 °; **7b**: 78.3 °) between the planes of the two NHC ligands. In turn, the plane of each NHC ring lies at an angle of *ca*. 40 ° to the square plane around Pd (**7a**: 41.1 °; **7b**: 38.7, 41.2 °). Although two *trans* NHC ligands will often lie in the same plane as each other, a large angle between these two planes – either as forced by the conformation of a pincer ligand or as the result of steric interactions between bulky NHCs and the *cis* ligands - is not uncommon; the torsion angle between the two trans NHC rings has no correlation with the Pd-C bond length, as would be expected for a purely σ-bonding interaction between palladium and the carbene.[47]

In **7a** there is a very short H---I contact (2.859 Å) between the methyne hydrogen of the *i*-propyl substituent and the iodide ligand. This H-bonding interaction also appears to be present in solution, as there is a large downfield shift (δ_H 6.35 ppm) for the signal arising from this proton in the ^{1}H NMR spectrum for **7a**. Similar short H---I distances are observed for **7b** (2.789 and 2.917 Å).

We found that the coordination chemistry could be extended from palladium to platinum. Hence, reacting the imidazolium salts **3a** or **3b** with $PtCl_2$(COD) and 3 equivalents of KHMDS gave the analogous platinum pincer complexes [CNC-*i*-Pr]Pt-I (**8a**) or [CNC-*n*-Bu]Pt-I (**8b**), although the yields were poor, Scheme 3. As for **7a** and **7b**, iodide rather than chloride occupies the fourth coordination site, as confirmed for both complexes by mass spectrometry and microanalysis. Coordination of the tridentate pincer ligand to platinum gave similar NMR spectra to the Pd complexes: in particular, the ^{13}C NMR spectrum recorded contained characteristic singlets at 162.5 ppm (**8a**) and 164.0 ppm (**8b**) corresponding to the carbene. Moreover, for **8a** the apparent septet corresponding to the *i*-Pr CH was shifted downfield to 6.38 ppm, indicating that a H-bonding interaction with the iodide ligand is also present in the Pt complex. Therefore, although we have thus far been unable to grow crystals of **8a** or **8b** suitable for X-ray crystallography, the data we have obtained indicates that the complexes

have a very similar structure to those of their palladium analogues. Although several pincer carbene complexes of Pd have been reported, platinum pincer carbene complexes are surprisingly rare,[48,49] and these are the first reported platinum [CNC] complexes.

We were interested to see if the halide ligand could be replaced with a neutral donor in a cationic complex. When **7a** was dissolved in d_5-pyridine the ^{1}H NMR spectrum indicated the presence of two different complexes. One of these complexes exhibited an apparent septet attributable to the *i*-Pr group at 6.40 ppm (which we assign, by the downfield shift, as **7a**) whereas the other exhibited an apparent septet at 3.68 ppm. The addition of 1.5 equivalents of silver triflate to this solution gave quantitative conversion to the latter complex (Scheme 3), which we subsequently identified as the triflate salt {[CNC-*i*-Pr]Pd-py}OTf (**9a**) by single crystal X-ray diffraction. The solid-state structure of **9a** is shown in Figure 4 and selected bond lengths are shown in Table 1. Unfortunately the crystal was weakly diffracting and hence the data is weak; the crystal also contained disordered dichloromethane. Despite this, it is possible to discuss the prominent structural features of **9a**. The geometry around Pd is square planar, with the tridentate pincer and a molecule of pyridine bound to the metal. The triflate anion is not coordinated to Pd, and also shows significant disorder in the crystal, requiring the splitting of one of the F atoms in one of the triflate ions. It is apparent that there is still a significant twist in the [CNC] ligand: in the two independent molecules of **9a** present in the unit cell the angle between the square plane around the metal and the trigonal planar amide nitrogen is 49.9 and 49.4 ° and the torsion angle between the planes of the two *trans* NHC ligands is 72.8 and 70.5 °. There are no significant differences between the metal amide and metal carbene bond lengths in the iodide complex **7a** or the cation **9a**. Our attempts to isolate an analytically pure sample of **9a** on a larger scale were unsuccessful as it was not possible to completely separate **9a** from pyridine.

Fig. 4.

The strategy described above for the coordination of the [CNC] ligands to Pd and Pt was also attempted with the amine mono(imidazolium) pro-ligand **6**, but NHC complexes could not be isolated under these conditions. Alternatively, treating **6** with K_2CO_3, $PdCl_2$ and potassium iodide in refluxing pyridine gave [C,NH]PdI_2py (**10**) as a yellow-orange solid in 89% yield after column chromatography (Scheme 4). Performing the reaction with K_2PtCl_4 instead of $PdCl_2$ gave the platinum analogue [C,NH]PtI_2py (**11**) as yellow crystals in 47% yield. Scheme 4.

The solid-state structures of both **10** and **11** were determined by single crystal X-ray diffraction (Figures 5 and 6; selected bond lengths are given in Table 2). The structure of **10** is very

similar to the structures of *trans*-(NHC)PdI_2py complexes that have been reported previously.[50–53] The NHC-amine ligand in both complexes is only bound to the metal through the carbene; the amine nitrogen is not coordinated. The inner coordination sphere is completed by two *trans* iodide ligands and a pyridine ligand. In **10**, the bond lengths and angles around the square planar Pd are extremely similar for the two independent molecules found in the unit cell, despite the two molecules having very different angles between the mean plane of the NHC and pyridine ring (14.9 and 40.2 °). The Pd–C bond lengths (1.957(7) and 1.981(7) Å) are shorter than for the pincer complexes, demonstrating the weaker *trans* influence of the pyridine ligand in **10** compared with the NHC in **7a**, **7b** and **9a**. The unit cell for **11** also contains two unique molecules, which like **10** differ greatly with respect to the angle between the mean plane of the NHC ring and the pyridine ring (19.8 and 38.7 °). However, both of the unique molecules show very similar bond lengths around Pt (*e.g.* d(Pt–C) are 1.965(13) and 1.968(11) Å).

The signals arising from the carbene are difficult to assign in the ^{13}C NMR spectra for **10** and **11**. For **10**, the signal at 147.3 ppm is most likely the carbene resonance, as the nearby signals for 4° carbons at 146.6 and 148.0 ppm are broad like the signals we can unambiguously assign as arising from the 2,6-di*iso*propylphenyl group. Likewise for **11**, the carbene resonance appears to be the sharp signal at 143.6 ppm, rather than one of the broad 4° C signals at 147.2 and 148.2 ppm (unfortunately ^{195}Pt satellites, which would have aided the identification of the carbene resonance, could not be observed). These signals fall into the range previously reported for carbenes in *trans*-(NHC)MX_2py (M = Pd or Pt) complexes.[51,52,54]

Fig. 5.

Fig. 6.

Table 2.

Pre-catalysts of the type *trans*-(NHC)PdI_2py (PEPPSI catalysts: Pyridine-Enhanced Pre-catalyst Preparation, Stabilization and Initiation) deliver excellent activity in cross-coupling reactions;[55–57] complexes with NHC ligands that are functionalised with carbonyl (amide[50–52] and ketone[52]), alcohol and ether groups[51,53] have also been reported previously, but, to the best of our knowledge, **10** is the first amine functionalised complex of this type. Furthermore, the nucleophilic substitution reactions of alkyl or benzyl halides used to prepare the functionalised NHC ligands in these previously reported complexes contrasts with the cross-coupling strategy used to synthesise the pro-ligand **6**, which enables efficient access to aryl substituted NHC

ligands with the functional group (amine) also bound to the aromatic ring. Platinum analogues of these Pd catalysts have been reported,[54] but these are much less common.

We first attempted to deprotonate the amine group in **10** to yield an amido-NHC complex using KHMDS as the base. Surprisingly, the novel dimeric amido complex {[C,N]Pd(μ-OH)}$_2$ (**12**) was the only compound that could be isolated from this reaction. Presumably the hydroxide ligand was produced from adventitious moisture, but the reaction showed poor reproducibility, even when an excess of water was added to a rigorously dry reaction mixture. Alternatively, **12** could be isolated in good yield by stirring a solution of **10** in 1,4-dioxane with aq. KOH, Scheme 4. The IR spectrum recorded for **12** contains a weak resonance at 3601 cm^{-1} that is consistent with the bridging hydroxide ligand.

The solid-state structure of **12** was determined by single crystal X-ray diffraction (Fig. 7; selected bond lengths are given in Table 2). Two crystallographically equivalent monomer units make up the dimer in **12**, with a non-bonding Pd(1)···Pd(1') distance of 3.2348(6) Å. The Pd_2O_2 ring is almost planar, with a Pd-O-Pd-O torsion angle of 4.7 °, but the two Pd–O bond lengths are different, with the bond *trans* to the NHC (2.086(2) Å) *ca.* 0.03 Å longer than the bond *trans* to the amido ligand (2.052(2) Å) due to the stronger *trans* influence of the carbene. A search of the Cambridge Structural Database for complexes of the type [L^{1}L^{2}Pd(μ-OH)]$_2$ revealed that the Pd–O bond length tends to correlate with the Lewis basicity of the *trans* ligand.[47] Hence, the shortest Pd–O distances (2.005(2) to 2.016(3) Å) have been observed with a pyridine or imine donor *trans* to μ-OH;[58–61] the database contained no examples of NHC or amido ligands in complexes of this type, but the Pd–O bond lengths in **12** are similar to those reported for complexes with a phosphine *trans* to the μ-OH ligand,[62–64] and the longest Pd–O distance (2.126 Å) is for μ-OH *trans* to a phenyl ligand.[65]

Fig. 7.

Table 2.

Both the metal-amide (1.998(3) Å) and metal-carbene (1.945(3) Å) distances are the shortest for all the complexes that we report herein. Unusually for a metal hydroxide, there is an absence of H-bonding in the solid state, which may be a consequence of the bulky *N*-aryl and *N*-alkyl substituents that surround the hydroxide ligand. The bridging hydroxide ligand can be clearly identified in the ^{1}H NMR spectrum for **12** at δ_H –3.97 ppm, slightly upfield of the typical range of *ca.* –0.25 to –3.5 ppm for cationic and neutral Pd(μ-OH)$_2$ moieties.[62,66–69] In the

previously reported β-diiminato complex {[Ph_2nacnac]Pd(μ-OH)}$_2$ the OH signal was observed even further upfield at –5.24 ppm, most likely as a consequence of the shielding effect of the two nearby phenyl groups of the Ph_2nacnac ligands.[69] Likewise, the 2,6-di*iso*propylphenyl group in **12** also appears to shield the bridging hydroxide, which sits *ca.* 2.54 Å above the aromatic ring in the solid state. In the ^{13}C NMR spectrum for **12**, the carbene signal could not be clearly identified as there are four signals for 4° C atoms between δ 144-148 ppm.

Palladium complexes of a bidentate amido-NHC ligand have been reported for an amido donor that is derived from deprotonation of an N-acyl group.[50] However, to the best of our knowledge, compound **12** is the first reported Pd complex of either an arylamido or alkylamido functionalised NHC ligand.

We attempted to prepare the platinum analogue of **12** by also treating a solution of **11** in 1,4-dioxane with aqueous KOH at 40 °C, but **11** was unreactive under these conditions. This observation is consistent with a mechanism where hydroxide reacts at the metal first and follows the common trend that ligand substitution reactions are slower for Pt than Pd.[70–72] Increasing the temperature of the reaction to 60 °C gave complete conversion of **11** to a mixture of products, but we were unable to isolate a pure compound from this reaction.

Conclusions

We have prepared precursors to bidentate amido-NHC [C,N] and tridentate amido-bis(NHC) [CNC] ligands in high yield using an efficient sequence of two cross-coupling reactions and an alkylation. Different strategies were required to coordinate these ligands to Pd and Pt. For the [CNC] ligands, reaction of the amine bis(imidazolium) salts **3** with KHMDS and either $Pd(OAc)_2$ or $PtCl_2$(COD) enabled the isolation of the palladium complexes [CNC-*i*-Pr]Pd-I (**7a**) and [CNC-*n*-Bu]Pd-I (**7b**) and the first [CNC] platinum complexes [CNC-*i*-Pr]Pt-I (**8a**) and [CNC-*n*-Bu]Pt-I (**8b**); treating **7a** with AgOTf in pyridine also gave the cationic complex [CNC-*i*-Pr]Pd(py)}OTf **9a** with pyridine bound in the fourth site. For the [C,N] ligand, reaction of the amine mono(imidazolium) salt **6** with $PdCl_2$ or K_2PtCl_4, K_2CO_3 and KI in pyridine at 100 °C gave the complexes [C,NH]MI_2py [M =Pd (**10**) or Pt (**11**)], in which the amine arm of the NHC ligand is not deprotonated and does not coordinate to the metal. The amine group in **10** was deprotonated in a biphasic reaction with aqueous KOH at 40 °C, giving the dimeric amido complex {[C,N]Pd(μ-OH)}$_2$ (**12**), the first reported arylamido-NHC complex of palladium. Under the same conditions, the more inert Pt analogue **11** was unreactive. We are currently investigating the reactivity of these ligands and complexes with a view to applications in

bifunctional catalysis.

Experimental

All manipulations were performed under dry, oxygen free nitrogen using standard Schlenk techniques unless otherwise stated. THF and toluene were dried by passing through a column of activated alumina and then degassed; DME was pre-dried over sodium and distilled from Na-benzophenone; anhydrous DMF was purchased from Sigma-Aldrich and used as supplied; KHMDS was purchased as a solution in toluene and titrated against 4-phenylbenzylidene benzylamine.[73] Bis(2-bromophenyl)amine (**1**),[38] *N*-(2-bromophenyl)-2,6-di*iso*propylaniline (**4**)[40] and $PtCl_2(COD)$[74] were prepared as reported in the literature. All other reagents were obtained from Sigma-Aldrich, Johnson Matthey or Alfa Aesar and used as supplied. NMR spectra were recorded on a Bruker DPX300, DRX400 or AV500 spectrometer; chemical shifts have been referenced to the residual protonated solvent peak and *J* values are given in Hz. IR spectra were run in a diamond ATR cell using a Perkin Elmer Spectrum 1 instrument. ESI mass spectra were recorded on a micromass Quattra LC spectrometer in MeCN/MeOH with a cone voltage of +50 or -25 V unless stated; FAB mass spectra were obtained on a Kratos concept spectrometer using NBA as the matrix. Elemental analyses were performed at London Metropolitan University.

Bis(2-(1*H*-imidazol-1-yl)phenyl)amine (2)

Compound **1** (2.97 g, 9.10 mmol), imidazole (1.24 g, 18.2 mmol), Cs_2CO_3 (11.86 g, 36.40 mmol), CuI (0.346 g, 1.82 mmol) and 8-hydroxyquinoline (0.264 g, 1.82 mmol) were suspended in DMF (5 mL) in a pre-dried sealable tube. The tube was sealed and heated at 125 °C for 15 h. The reaction mixture was then allowed to cool to room temperature and diluted with DCM (50 mL). The mixture was filtered through a pad of Celite and washed with a solution of 5% $LiCl_{(aq.)}$ (5 x 100 mL) and brine (2 x 50 mL). The solution was then dried ($MgSO_4$) and the volatiles removed *in vacuo* to give a green solid (2.47 g, 90%) m.p. 80-82 °C. δ_H(500 MHz, CD_2Cl_2) 5.12 (1H, s, NH), 7.11 (2H, t, *J* = 7.8, Ar CH), 7.24–7.32 (4H, m, Ar CH), 7.36 (2H, t, *J* = 7.8, Ar CH), 7.75 (br, imidazole CH); δ_C(67.9 MHz, $CDCl_3$) 119.3, 122.6, 127.6, 129.7, 137.7. u_{max}/cm^{-1} (solid) 3116 w, 3096 w, 2914 w, 1593 m, 1510 s, 1500 s, 1482 s, 1459 m, 1312 s, 1278 m, 1236 w, 1108 m, 1088 w, 1059 s, 963 m, 907 m, 821 m, 772 s. *m/z* (ESI) 302 (100%, $M+H^+$), 324 (21% $M+Na^+$); HRMS $C_{18}H_{16}N_5$ calcd. 302.1400, found 302.1414. Compound **2** could not be isolated in analytically pure form, but this did not hinder subsequent steps. Some signals are broad or not apparent in the NMR spectra; we speculate that this is

due to inter- and intramolecular H-bonding.

Bis(2-(3-*iso*-propyl-1*H*-imidazolium)phenyl)amine diiodide (3a)

In a sealable tube under an atmosphere of air, *i*-propyl iodide (0.36 mL, 3.7 mmol) was added to a green suspension of **2** (0.500 g, 1.66 mmol) in MeCN (10 mL). The tube was sealed and heated at 90 °C for 24 h, giving a red solution. The mixture was allowed to cool to RT and filtered. The volatiles were removed *in vacuo* to give an orange solid (0.951 g, 89%) m.p. 81-84 °C. δ_H(300 MHz, $CDCl_3$) 1.70 (12H, d, *J* = 6.7, CH(C*H*$_3$)$_2$), 4.97 (2H, sept, *J* = 6.7, C*H*(CH_3)$_2$), 7.14 (2H, dt, ^3J = 7.8, ^4J = 1.2, CH), 7.30 (2H, dd, ^3J = 7.9, ^4J = 1.2, CH), 7.36 (2H, dd, ^3J = 7.8, ^4J = 1.5, CH), 7.46 (2H, dt, ^3J = 7.9, ^4J = 1.5, CH), 7.53 (2H, t, *J* = 1.7, NC*H*CHN), 7.75 (2H, t, *J* = 1.7, NCHC*H*N), 9.56 (2H, t, *J* = 1.7, NC*H*N); δ_C(67.9 MHz, $CDCl_3$) 22.9 (CH(*C*H_3)$_2$), 52.8 (*C*H(CH_3)$_2$), 121.5, 122.9, 123.8, 124.2, 126.1, 127.7, 132.0, 135.6, 137.7 (aromatic C). υ_{max}/cm^{-1} (solid) 3066 w, 2978 w, 1597 m, 1546 m, 1497 s, 1458 m, 1375 w, 1305 m, 1264 w, 1192 s, 1161 w, 958 w, 875 w, 827 w, 758 vs, 681 w, 650 s. *m/z* (ESI) 514 (18%, $[M\text{-}I]^+$), 386 (100% $[M\text{-}I\text{-}HI]^+$), 344 (36%, $[M\text{-}I\text{-}HI\text{-}^iPr]^+$); HRMS $C_{24}H_{29}I_2N_5$ calcd. 514.1462, found 514.1465. Anal. Calcd. for $C_{24}H_{29}I_2N_5$: C, 44.95; H, 4.56; N, 10.92. Found C, 45.01; H, 4.27; N, 10.61%.

Bis(2-(3-butyl-1*H*-imidazolium)phenyl)amine diiodide (3b)

In an identical procedure to that used for **3a**, **3b** was prepared from *n*-butyl iodide (0.940 g, 5.11 mmol) and **2** (0.700 g, 2.33 mmol) in MeCN (10 mL). The tube was sealed and heated at 90 °C for 15 h, giving a red solution. The mixture was allowed to cool to RT and filtered. The volatiles were removed *in vacuo* to give **3b** as a light brown solid (1.450 g, 93%) m.p. 56-57 °C. δ_H(400 MHz, $CDCl_3$) 0.95 (6H, t, *J* = 7.5, CH_3), 1.36 (4H, apparent sext, *J* = 7.5, CH_2), 1.92 (4H, apparent quint, *J* = 7.5, CH_2), 4.40 (4H, t, *J* = 7.5, CH_2), 7.10 (2H, t, *J* = 7.6, CH), 7.25 (2H, d, *J* = 7.6, CH), 7.39 (2H, d, *J* = 8.2, CH), 7.44 (2H, t, *J* = 8.2, CH), 7.56 (2H, t, *J* = 1.5, NC*H*CHN), 7.66 (2H, t, *J* = 1.5, NCHC*H*N), 9.72 (2H, s, NC*H*N); δ_C(100 MHz, $CDCl_3$) 13.6 CH_3, 19.6 CH_2, 31.6 CH_2, 50.5 CH_2, 122.8, 123.6, 123.8, 123.9, 126.1, 127.6, 132.1, 136.7, 137.7 (aromatic C). υ_{max}/cm^{-1} (solid) 3066 w, 2978 w, 1597 m, 1546 m, 1497 s, 1458 m, 1375 w, 1305 m, 1264 w, 1192 s, 1161 w, 958 w, 875 w, 827 w, 758 vs, 681 w, 650 s. *m/z* (ESI) 542 (34%, $[M\text{-}I]^+$), 414 (100% $[M\text{-}I\text{-}HI]^+$), 358 (30%, $[M\text{-}I\text{-}HI\text{-}Bu]^+$); HRMS $C_{26}H_{33}IN_5$ calcd. 542.1781, found 542.1770. Anal. Calcd. for $C_{26}H_{33}I_2N_5$: C, 46.65; H, 4.97; N, 10.46. Found C, 46.25; H, 4.70; N, 10.13%.

***N*-(2-(1*H*-imidazol-1-yl)phenyl)-2,6-di*iso*propylaniline (5)**

Compound **4** (2.00 g, 6.01 mmol), imidazole (0.409 g, 6.01 mmol), Cs_2CO_3 (3.916 g, 12.02 mmol), CuI (0.114 g, 0.601 mmol) and 8-hydroxyquinoline (0.087 g, 0.60 mmol) were suspended in DMF (10 mL) in a pre-dried sealable tube. The tube was sealed and heated at 125 °C for 72 h. The reaction mixture was then allowed to cool to room temperature and diluted with DCM (75 mL). The mixture was filtered through a pad of Celite and washed with a solution of 5% $LiCl_{(aq.)}$ (4 x 100 mL) and brine (100 mL). The solution was then dried ($MgSO_4$) and the volatiles removed *in vacuo* to give a green residue that was redissolved in DCM (30 mL). Hexane (70 mL) was then added and a solid precipitate removed by filtration. Volatiles were removed *in vacuo* to give **5** as a pale yellow powder (1.592 g, 83%) m.p. 142-144 °C. δ_H(300 MHz, d_4-MeOH) 1.11 (12H, d, *J* = 6.8, CH(C*H*$_3$)$_2$), 3.11 (2H, sept, *J* =6.8, C*H*(CH$_3$)$_2$), 5.83 (1H, br s, NH), 6.17 (1H, d, *J* = 8.2, ArH), 6.74 (1H, t, *J* = 7.2, ArH), 7.10 – 7.32 (m, 6H, ArH), 7.50 – 8.40 (2H, br, ArH); δ_C(75 MHz, $CDCl_3$) 23.0 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 112.7, 117.3, 124.0, 127.2,127.9, 130.1, 133.6, 143.6, 147.4 (aromatic C); u_{max}/cm^{-1} (solid) 3205 w, 2961 w, 2868 w, 1603 m, 1586 w, 1511 s, 1493 m, 1465 m, 1453 m, 1310 m, 1057 m. *m/z* (ESI) 320 (100%, M+H$^+$); HRMS (FAB) $C_{21}H_{25}N_3$ calcd. 320.21202, found 320.21208. Anal. Calcd. for $C_{21}H_{25}N_3$: C, 78.96; H, 7.89; N, 13.15. Found C, 79.03; H, 7.48; N, 13.04%. Some signals are broad or not apparent in the NMR spectra; we speculate that this is due to inter- and intramolecular H-bonding.

_N_-(2-(3-_iso_-propyl-1_H_-imidazolium)phenyl)-2,6-di_iso_propylaniline iodide (6)

In a sealable tube under an atmosphere of air, *i*-propyl iodide (0.35 mL, 3.4 mmol) was added to a green suspension of **5** (1.00 g, 3.14 mmol) in MeCN (10 mL). The tube was sealed and heated at 90 °C for 48 h, giving a red solution. The mixture was allowed to cool to RT and filtered through Celite. The volatiles were removed *in vacuo* to give a brown solid that was purified by two precipitations from MeOH (5 mL) upon addition of Et_2O (80 mL), giving **6** (1.138 g, 74%) as a white solid m.p. 228-230 °C. δ_H(300 MHz, $CDCl_3$) 1.11 (6H, d, *J* = 6.8, CH(C*H*$_3$)$_2$), 1.21 (6H, d, *J* = 6.8, CH(C*H*$_3$)$_2$), 1.75 (6H, d, *J* = 6.7, NCH(C*H*$_3$)$_2$), 3.14 (2H, sept, *J* = 6.8, C*H*(CH$_3$)$_2$), 5.19 (1H, sept, *J* = 6.7, C*H*(CH$_3$)$_2$, 6.27 (1H, s, NH), 6.34 (1H, d, *J* = 8.4, ArH), 6.80 (1H, td, ^3J = 7.6, ^4J = 1.1, ArH), 7.20 (1H, t, *J* = 8.4, ArH), 7.21 (2H, d, *J* = 7.0, ArH), 7.28 – 7.34 (2H, m, ArH), 7.54 (1H, ap t, *J* = 1.7, NCHC*H*N), 7.64 (1H, ap t, *J* = 1.7, NC*H*CHN), 9.36 (1H, br s, NCHN); δ_C(75 MHz, $CDCl_3$) 22.7 (CH(*C*H$_3$)$_2$), 23.4 (CH(*C*H$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 54.0 (N*C*H(CH$_3$)$_2$), 115.3, 118.1, 120.0, 122.0, 123.4, 124.2, 127.4, 127.9, 131.8, 133.4, 135.3, 143.0, 147.3 (aromatic C). u_{max}/cm^{-1} (solid) 3215 w, 3070 w, 2962 m, 2867 w, 1608 m, 1563 w, 1549 w, 1505 s, 1463 m, 1432 w, 1303 m, 1199 w, 1120 w, 1048 w, 797 m, 743 vs. *m/z* (ESI) 362 (100 % [M-I]$^+$); HRMS (FAB) $C_{24}H_{32}N_3$ calcd.

362.25882, found 362.25878. Anal. Calcd. for $C_{24}H_{32}IN_3$: C, 58.90; H, 6.59; N, 8.59. Found C, 59.07; H, 6.29; N, 8.69%.

Palladium bis(2-(3-*iso*-propylimidazolin-2-yliden-1-yl)phenyl)amide iodide, [CNC-*i*-Pr]PdI (7a)

A solution of $Pd(OAc)_2$ (0.026 g, 0.12 mmol) and the imidazolium salt **3a** (0.075 g, 0.12 mmol) in DME (15 mL) was cooled to 0 °C and a solution of 1 M KHMDS in toluene (0.36 mL, 0.36 mmol) added dropwise with stirring. The flask was stirred for 6 h at 0 °C and then allowed to warm to RT overnight. The crude reaction mixture was filtered through Celite and the solvent removed *in vacuo* to give a red-brown solid. The solid was dissolved in DCM (*ca*. 20 mL) and the solution decanted to remove insoluble material. Purification by flash column chromatography (33% EtOAc/pet. ether) gave **7a** (0.024 g, 33%) as an orange solid m.p. 272-275 °C, R_f = 0.37 (33% EtOAc/pet. ether). Crystals of **7a** suitable for structure determination by X-ray diffraction were obtained by slow evaporation of a solution of **7a** in C_6D_6. δ_H(300MHz, C_6D_6) 0.71 (6H, d, *J* = 6.7, CH_3), 1.32 (6H, d, *J* = 6.7, CH_3), 6.23 (2H, d, *J* = 1.8, NC*H*CHN), 6.35 (2H, apparent sept, *J* = 6.7, C*H*(CH_3)$_2$), 6.60 (2H, t, *J* = 7.8, CH), 6.71 (2H, d, *J* = 1.8, NC*H*CHN), 6.81 (2H, t, *J* = 7.8, CH), 6.99 (2H, d, *J* = 7.8, CH), 7.09 (2H, d, *J* = 7.8, CH); δ_C(75MHz, C_6D_6) 23.2 (CH(*C*H_3)$_2$), 23.7 (CH(*C*H_3)$_2$), 53.5 (*C*H(CH_3)$_2$), 117.7, 118.9 (N*C*HCHN), 119.2 (N*C*HCHN), 121.3, 122.8, 127.4, 133.5, 144.7, 165.3 (N_2C-Pd); υ_{max}/cm^{-1} (solid) 2962w, 2926w, 2870w, 1587w, 1487s, 1449m, 1403m, 1334s, 1266m, 1216m, 1132m, 1077w, 1039w, 882w, 842w, 743s, 728s, 682s. *m/z* (ESI) 490 (65%, $[M-I]^+$), 531 (100%, $[M-I+MeCN]^+$); (FAB) 617 $[M]^+$; HRMS $C_{24}H_{26}N_5Pd$ ($[M-I]^+$) calcd. 490.1227, found 490.1239. Anal. Calcd for $C_{24}H_{26}IN_5Pd$: C, 46.66, H, 4.24, N, 11.34. Found: C, 46.70, H, 4.22, N, 11.37%.

Palladium bis(2-(3-*n*-butylimidazolin-2-yliden-1-yl)phenyl)amide iodide, [CNC-*n*-Bu]PdI (7b)

Complex **7b** was prepared in an identical procedure to that for **7a**, using $Pd(OAc)_2$ (0.067 g, 0.30 mmol), **3b** (0.200 g, 0.299 mmol), DME (15 mL) and a solution of KHMDS in toluene (1 M, 0.90 mL, 0.90 mmol). Purification by flash column chromatography (33% EtOAc/pet. ether) gave **7b** (0.082 g, 42%) as an orange solid m.p. 106-108 °C, R_f = 0.37 (33% EtOAc/pet. ether). Crystals of **7b** suitable for structure determination by X-ray diffraction were obtained by slow evaporation of a solution of **7b** in C_6D_6. δ_H(300 MHz, C_6D_6) 0.72 (6H, t, J= 7.4, CH_3), 0.96-1.24 (4H, m, $NCH_2CH_2C\mathit{H}_2CH_3$), 1.25-1.43 (2H, m, $NCH_2C\mathit{H}_2CH_2CH_3$), 1.70-1.87 (2H, m, $NCH_2C\mathit{H}_2CH_2CH_3$), 4.12-4.24 (2H, m, $NC\mathit{H}_2CH_2CH_2CH_3$), 4.61-4.73 (2H, m,

NC*H*$_2$CH$_2$CH$_2$CH$_3$), 6.10 (2H, d, *J* = 2.0, NC*H*$_2$CH$_2$N), 6.61 (2H, t, *J* = 7.6, C*H*), 6.64 (2H, d, *J* = 2.0, NC*H*$_2$CH$_2$N), 6.81 (2H, t, *J* = 7.6, C*H*), 7.00 (2H, d, *J* = 7.6, C*H*), 7.03 (2H, d, *J* = 7.6, C*H*); δ_C(75MHz, C_6D_6) 14.2 (CH_3), 19.9 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 33.8 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 52.7 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 118.0 (N*C*H$_2$CH$_2$N), 119.2, 121.7, 123.0, 123.2, 127.9, 134.1, 145.2, 167.0 (N_2C-Pd); u_{max}/cm^{-1} (solid) 2952 w, 2868 w, 1588 w, 1487 s, 1451 m, 1416 m, 1336 m, 1269 m, 1133 w, 1073 w, 1039 w, 952 w, 880 w, 745 s, 724 s, 696 s, 683 s. *m/z* (ESI) 518 (20%, [M-I]$^+$), 559 (100%, [M-I+MeCN]$^+$) (FAB) 645 [M]$^+$; HRMS $C_{26}H_{30}N_5Pd$ ([M-I]$^+$) calcd. 518.1557, found 518.1517; Anal. Calcd for $C_{26}H_{30}IN_5Pd$: C, 48.35; H, 4.68; N, 10.84. Found C, 48.41; H, 4.68; N, 10.74%.

Platinum bis(2-(3-*iso*-propylimidazolin-2-yliden-1-yl)phenyl)amide iodide, [CNC-*i*-Pr]PtI (8a)

A solution of $PtCl_2$(cod) (0.292 g, 0.780 mmol) and **3a** (0.500 g, 0.780 mmol) in THF (15 mL) was cooled to -78 °C and a solution of 0.55 M KHMDS in toluene (5.00 mL, 2.73 mmol) added dropwise with stirring. The flask was stirred for 8 h at -78 °C and then allowed to warm to RT overnight. The crude reaction mixture was filtered through Celite and the solvent removed under reduced pressure to give a yellow-orange solid. The solid was dissolved in DCM (*ca*. 20 mL) and the solution decanted to remove insoluble salts. Purification by flash column chromatography (20% EtOAc/hexane) gave **8a** (0.043 g, 9%) as a yellow solid m.p. 287-289 °C, R_f = 0.26 (20% EtOAc/hexane). δ_H(300 MHz, C_6D_6) 0.73 (6H, d, *J* = 6.9, CH_3), 1.37 (6H, d, *J* = 6.9, CH_3), 6.19 (2H, d, *J* = 2.2, NC*H*CHN), 6.38 (2H, apparent sept, *J* = 6.9, C*H*(CH_3)$_2$), 6.60 (2H, t, *J* = 7.8, CH), 6.68 (2H, d, *J* = 2.2, NC*H*CHN), 6.78 (2H, t, *J* = 7.8, CH), 6.95 (2H, d, *J* = 7.8, CH), 7.09 (2H, d, *J* = 7.8, CH); δ_C(125MHz, CD_2Cl_2) 23.4 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$-), 53.2 (*C*H(CH$_3$)$_2$), 118.5, 118.8 (N*C*HCHN), 119.4 (N*C*HCHN), 121.0, 122.2, 127.1, 133.1, 144.0, 162.5 (N_2C-Pt); u_{max}/cm^{-1} (solid) 3061 w, 2971 w, 1563 w, 1489 s, 1451 m, 1401 m, 1340 s, 1268 m, 1214 m, 1131 w, 1079 w, 1037 w, 951 w, 889 w, 723 s, 690 s. *m/z* (ESI) 620 (25%, [M-I+MeCN]$^+$), 579 (100% [M-I]$^+$); *m/z* (FAB) 706 [M]$^+$; Anal. Calcd. for $C_{24}H_{26}IN_5Pt$: C, 40.80; H, 3.71; N, 9.91. Found C, 40.82; H, 3.75; N, 9.91%.

Platinum bis(2-(3-*n*-butyl-imidazolin-2-yliden-1-yl)phenyl)amide iodide, [CNC-*n*-Bu]PtI (8b)

Complex **8b** was prepared in an identical procedure to that for **8a**, using $PtCl_2$(cod) (0.280 g, 0.747 mmol), **3b** (0.500 g, 0.747 mmol), THF (15 mL) and a solution of 1M KHMDS in toluene (2.24 mL, 2.24 mmol). Purification by flash column chromatography (33% EtOAc/pet. ether) gave **8b** (0.057 g, 12%) as a yellow solid m.p. 169-171 °C, R_f = 0.25 (33% EtOAc/pet.

ether). δ_H(500MHz, CD_2Cl_2) 0.84 (6H, t, *J*= 7.4, CH_3), 1.27 (4H, m, C*H*$_2$CH$_3$), 1.74 (2H, m, C*H*$_2$CH$_2$CH$_3$), 1.98 (2H, m, C*H*$_2$CH$_2$CH$_3$), 4.52 (4H, m, C*H*$_2$CH$_2$CH$_2$CH$_3$), 6.76 (2H, t, *J* = 7.3, CH), 6.92 (4H, m, CH), 7.12 (2H, d, *J* = 2.0, NC*H*CHN), 7.37 (2H, d, *J* = 8.0, CH), 7.45 (2H, d, *J* = 2.0, NC*H*CHN); δ_C(125 MHz, CD_2Cl_2) 14.0 (CH_3), 19.9 (*C*H$_2$CH$_3$), 33.5 (*C*H$_2$CH$_2$CH$_3$), 52.5 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 118.7, 118.8 (N*C*HCHN), 121.3, 122.4, 123.1 (N*C*HCHN), 127.4, 133.4, 144.2, 164.0 (N_2C-Pt); υ_{max}/cm^{-1} (solid) 2957 w, 2872 w, 1587 w, 1562 w, 1487 s, 1448 m, 1414 m, 1387 m, 1327 s, 1270 s, 1232 m, 1134 w, 1041 w, 951 m, 888 w, 717 s, 685 s. *m/z* (ESI) 735 (10%, $[M+H]^+$), 607 (100%, $[M-I]^+$); Anal. Calcd. for $C_{26}H_{30}IN_5Pt$: C, 42.51; H, 4.12; N, 9.53. Found C, 42.55; H, 4.17; N, 9.57%.

Pyridyl palladium bis(2-(3-*iso*-propylimidazolin-2-yliden-1-yl)phenyl)amide triflate, {[CNC-*i*-Pr]Pd-(d$_5$-py)}OTf (9a)

Iodide complex **7a** (0.012g, 0.019 mmol) was dissolved in d_5-pyridine and AgOTf added (0.007g, 0.03 mmol). Crystals of **9a** suitable for structure determination by X-ray diffraction were obtained by diffusion of pentane into this solution. Attempts to isolate an analytically pure sample of **9a** on a larger scale were unsuccessful as it was not possible to completely separate **9a** from pyridine. δ_H(400 MHz, d_5-pyridine) 0.72 (6H, d, *J* = 6.7, CH_3), 0.90 (6H, d, *J* = 6.7, CH_3), 3.68 (2H, apparent sept, *J* = 6.7, C*H*(CH_3)$_2$), 6.96 (2H, t, *J* = 7.9, CH), 7.08 (2H, t, *J* = 7.9, CH), 7.17 (2H, d, *J* = 7.9, CH), 7.64 (2H, d, *J* = 2.1, NC*H*CHN), 7.76 (2H, d, *J* = 7.9, CH), 8.14 (2H, d, *J* = 2.1, NC*H*CHN); δ_C(125 MHz, d_5-pyridine) 21.9 (CH_3), 23.8 (CH_3), 51.7 (*C*H(CH_3)$_2$), 119.3, 120.2, 120.3, 121.8, 124.6, 128.1, 132.3, 143.8, 163.8 (N_2C-Pd); ^{19}F NMR (282 MHz, d_5-pyridine) δ -77.2. *m/z* (ESI) 490 (65%, $[M-OTf-py]^+$), 531 (100%, $[M-OTf-py+MeCN]^+$).

Pyridyl palladium *N*-(2-(3-*iso*-propylimidazolin-2-yliden-1-yl)phenyl)-2,6-di*iso*propylaniline diiodide, [C,NH]PdI$_2$py (10)

Imidazolium salt **6** (0.150 g, 0.307 mmol), $PdCl_2$ (0.050 g, 0.28 mmol), K_2CO_3 (0.193 g, 1.40 mmol) and KI (0.232 g, 1.40 mmol) were suspended in pyridine (10 mL) and heated at 100 °C for 18 h. After cooling to RT, the reaction mixture was diluted with DCM (30 mL), filtered through Celite and the volatiles removed *in vacuo*. Purification by flash column chromatography (17% EtOAc/pet. ether) gave **10** as a yellow-orange solid (0.199 g, 89%) m.p. 122-123 °C, R_f = 0.18 (17% EtOAc/pet. ether). Crystals suitable for structure determination by X-ray diffraction were obtained by diffusion of hexane into a saturated DCM solution of **10**. δ_H(300 MHz, CD_2Cl_2) 1.11 (12H, br d, *J* = 6.8, CH(C*H*$_3$)$_2$), 1.62 (6H, d, *J* = 6.8, NCH(C*H*$_3$)$_2$), 3.15 (1H, br, C*H*(CH_3)$_2$), 3.48 (1H, br, C*H*(CH_3)$_2$), 5.27 (1H, s, NH), 5.79 (1H, sept, *J* = 6.8,

NC*H*(CH_3)$_2$), 6.32 (1H, d, *J* = 8.2, ArH), 6.94 (1H, t, *J* = 7.6, ArH), 7.17-7.35 (8H, m), 7.74 (1H, t, *J* = 7.6, pyH), 7.16 (1H, d, *J* = 7.9, ArH), 8.88 (2H, br d, *J* = 4.9, pyH); δ_C(125.8 MHz, C_6D_6) 21.9 (NCH(*C*H_3)$_2$), 22.3 (CH(*C*H_3)$_2$), 22.7 (CH(*C*H_3)$_2$), 25.0 (CH(*C*H_3)$_2$), 25.5 (CH(*C*H_3)$_2$), 28.5 (*C*H(CH_3)$_2$), 28.7 (*C*H(CH_3)$_2$), 53.9 (N*C*H(CH_3)$_2$), 116.1, 117.7, 118.8, 123.8, 124.2, 124.9, 125.1, 127.0, 127.6, 130.4, 131.5, 135.4, 136.8, 144.0, 146.6 (Ar/py C), 147.3 (N_2CPd), 148.0 (Ar C), 154.1 (py CH). u_{max}/cm^{-1} (solid) 3386 w (NH), 2965 m, 2865 w, 1603 m, 1506 m, 1444 m, 1430 m, 1362 w, 1326 m, 1300 m, 1240 w, 1210 m, 1111 w, 1070 w, 1045 w, 1020 w, 957 w, 937 w, 880 w, 803 m, 754 s, 726 m, 685 s. *m/z* (ESI) 466 (100 % [M-I-HI-py]$^+$); 507 (70 % [M-I-HI-py+MeCN]$^+$). Anal. Calcd. for $C_{29}H_{36}I_2N_4Pd$: C, 43.49; H, 4.53; N, 7.00. Found C, 43.51; H, 4.45; N, 7.12%.

Pyridyl platinum *N*-(2-(3-*iso*-propylimidazolin-2-yliden-1-yl)phenyl)-2,6-di*iso*propylaniline diiodide, [C,NH]PtI$_2$py (11)

Imidazolium salt **6** (0.400 g, 0.818 mmol), K_2PtCl_4 (0.309 g, 0.744 mmol), K_2CO_3 (0.513 g, 3.72 mmol) and KI (0.617 g, 3.72 mmol) were suspended in pyridine (15 mL) and heated at 100 °C for 48 h. After cooling to RT, the reaction mixture was diluted with DCM (30 mL), filtered through Celite and the volatiles removed *in vacuo*. Purification by flash column chromatography (13% EtOAc/pet. ether) followed by crystallisation from Et_2O/pentane gave **11** (0.313 g, 47%) as yellow crystals m.p. 206-208 °C (dec.), R_f = 0.3 (13% EtOAc/pet. ether). Crystals suitable for structure determination by X-ray diffraction were obtained by slow evaporation of a saturated DCM solution of **11**. δ_H(300 MHz, CD_2Cl_2) 1.11 (12H, d, *J* = 6.5, CH(C*H*$_3$)$_2$), 1.60 (6H, d, *J* = 6.7, NCH(C*H*$_3$)$_2$), 3.10 (1H, br, C*H*(CH_3)$_2$), 3.53 (1H, br, C*H*(CH_3)$_2$), 5.99 (1H, sept, *J* = 6.7, NC*H*(CH_3)$_2$), 6.30 (1H, d, *J* = 8.2, ArH), 6.90 (1H, t, *J* = 7.6, ArH), 7.14-7.33 (8H, m, CH), 6.73 (1H, t, *J* = 7.6, pyH), 8.01 (1H, d, *J* = 7.9, ArH), 8.90 (2H, d, *J* = 5.3, pyH); δ_C(125.8 MHz, CD_2Cl_2) 22.4 (NCH(*C*H_3)$_2$), 22.8 (CH(*C*H_3)$_2$), 24.4 (CH(*C*H_3)$_2$), 25.0 (CH(*C*H_3)$_2$), 25.5 (CH(*C*H_3)$_2$), 28.2 (*C*H(CH_3)$_2$), 28.8 (*C*H(CH_3)$_2$), 53.1 (N*C*H(CH_3)$_2$), 115.1, 117.3, 117.9, 124.2, 124.6, 125.2, 126.7, 127.6, 129.9, 131.2, 135.1, 136.7, 137.9 (Ar/py C), 143.6 (N_2CPt), 147.2, 148.2 (Ar C), 154.1 (py C). u_{max}/cm^{-1} (solid) 3389 w (NH), 2966 m, 2866 w, 1605 m, 1445 m, 1416 m, 1370 w, 1328 m, 1300 m, 1240, 1210 m, 1117 w, 1071 w, 1043 w, 1022 w, 958 w, 938 w, 883 w, 800 m, 758 s, 730 m, 693 s. *m/z* (ESI) 555 (100 % [M-I-HI-py]$^+$); 634 (10 % [M-I-HI-py+MeCN]$^+$). Anal. Calcd. for $C_{29}H_{36}I_2N_4Pt$: C, 39.16; H, 4.08; N, 6.30. Found C, 39.27; H, 4.17; N, 6.18%.

Hydroxy palladium *N*-(2-(3-*iso*-propylimidazolin-2-yliden-1-yl)phenyl)-2,6-di*iso*propylphenylamide dimer, {[C,N]Pd(μ-OH)}$_2$ (12)

A solution of complex **10** (0.100 g, 0.125 mmol) in 1,4-dioxane (18 mL) was stirred vigorously with a solution of KOH (0.350g, 6.250 mmol) in H_2O (3 mL) at 40 °C for 24 h. After cooling to RT, the volatiles were removed *in vacuo*. The crude solid was re-dissolved in DCM (15 mL), dried ($MgSO_4$) and filtered through Celite. Removing the solvent under reduced pressure gave **12** (0.076 g, 63%) as an orange/red powder m.p. 190 °C (dec.). Crystals suitable for structure determination by X-ray diffraction were obtained by slow evaporation of an Et_2O/pentane solution of **12**. δ_H(300 MHz, CD_2Cl_2) -3.97 (2H, s, OH), 0.96 (12H, d, *J* = 6.9, CH(C*H*$_3$)$_2$), 1.11 (12H, d, *J* = 6.7, NCH(C*H*$_3$)$_2$), 1.46 (12H, d, *J* = 6.9, CH(C*H*$_3$)$_2$), 3.49 (4H, sept, *J* = 6.9, C*H*(CH$_3$)$_2$), 5.17 (2H, sept, *J* = 6.7, NC*H*(CH$_3$)$_2$), 5.80 (2H, d, *J* = 8.1, CH), 6.23 (2H, t, *J* = 7.7, CH), 6.63 (2H, t, *J* = 8.1, CH), 7.02 (2H, d, *J* = 2.2, NC*H*CHN), 7.08 (6H, br s, 2,6-^{i}Pr$_2$C$_6$*H*$_3$), 7.22 (2H, d, *J* = 7.7, CH), 7.50 (2H, d, *J* = 2.2, NC*H*CHN); δ_C(75 MHz, C_6D_6) 23.8 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 25.5 (CH(*C*H$_3$)$_2$), 28.1 (*C*H(CH$_3$)$_2$), 50.1 (N*C*H(CH$_3$)$_2$), 110.8, 117.4, 117.7, 117.8, 118.9 (ArCH), 122.9 (ArC), 124.7, 125.2, 126.7 (ArCH), 144.7, 145.7, 147.4, 147.5 (4°C). u_{max}/cm^{-1} (solid) 3601 w (OH), 2961 m, 2863 w, 1598 m, 1493 s, 1455 m, 1426 m, 1410 m, 1356 s, 1337 s, 1284 m, 1221 m, 1161 w, 1124 w, 1081 w, 1055 m, 952 w, 850 s, 825 m, 801 m, 767 m, 735 s, 723 s, 713 s, 693 m, 672 s. *m/z* (ESI, 25 V) 466 (100% [(C,N)Pd]$^+$), 500 (100% [(C,N)Pd(OH)$_2$]$^-$). Anal. Calcd. for $C_{48}H_{62}N_6O_2Pd_2$: C, 59.56; H, 6.46; N, 8.68. Found C, 59.47; H, 6.30; N, 8.73 %.

X-ray Crystallographic Studies

All single crystal diffraction data were collected using graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å) on a Bruker APEX 2000 CCD diffractometer at 150 K. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. Structures were solved by Patterson methods and structures refined by least-squares full-matrix refinement against F^2 employing SHELXTL version 6.10.[75] Hydrogen atoms were included in calculated positions (d(C-H) = 0.95 to 0.99 Å) riding on the bonded atom with isotropic displacement parameters set to 1.5 U_{eq}(C) for methyl H atoms and 1.2 U_{eq}(C) for all other C atoms. All non-H atoms were refined with anisotropic displacement parameters.

Crystal data for 7a·(2C$_6$H$_6$). $C_{36}H_{38}IN_5Pd$, M_w = 774.01 gmol^{-1}, T = 150(2) K, orthorhombic space group C222(1), a = 10.8012(19) Å, b = 19.746(4), c = 15.230(3) Å, α = β = γ = 90°, V = 3248.2(10) Å^3, Z = 4, ρ_{calcd} = 1.583 Mgm^{-3}, μ = 1.555 mm^{-1}, F(000) = 1552, crystal size 0.33 x 0.26 x 0.21 mm^3, 13040 reflections collected, 3336 unique [R(int) = 0.0341] which were used in all calculations. Empirical absorption correction made, T_{min} and T_{max} 0.831 and 0.646 respectively. GOF = 1.064, final R indices [I>2σI] R_1 = 0.0260, wR_2 = 0.0661, R indices (all

data) R_1 = 0.0277, wR_2 = 0.0667. Largest diff. peak and hole 0.692 and –0.554 e Å^{-3}.

Disordered C_6H_6 was omitted using the SQUEEZE option of PLATON.[76] The solvent accessible voids are 1128.7 Å^3 with an estimated 375e/cell to be added. Eight solvent C_6H_6 molecules/unit cell accounting for 336e were included in the formula, FWt, (000) and density calculations.

Crystal data for 7b·(C_6H_6). $C_{32}H_{36}IN_5Pd$, M_w = 723.96 gmol^{-1}, T = 150(2) K, orthorhombic space group Aba2, a = 29.370(5) Å, b = 20.178(3) Å, c = 10.3042(17) Å, α = β = γ = 90°, V = 6106.4(18) Å^3, Z = 8, ρ_{calcd} = 1.575 Mgm^{-3}, μ = 1.648 mm^{-1}, F(000) = 2896, crystal size = 0.15 x 0.14 x 0.10 mm^3, 23246 reflections collected, 5940 unique [R(int) = 0.0843] which were used in all calculations. Empirical absorption correction made, T_{min} and T_{max} 0.802 and 0.628 respectively. GOF = 0.934, final R indices [I>2σI] R_1 = 0.0457, wR_2 = 0.0751, R indices (all data) R_1 = 0.0594, wR_2 = 0.0790. Largest diff. peak and hole 0.894 and -1.009 e Å^{-3}.

Crystal data for 9a·(0.75CH_2Cl_2). $C_{30.75}H_{32.50}Cl_{1.50}F_3N_6O_3PdS$, M_w = 782.76 gmol^{-1}, T = 150(2) K, triclinic space group P-1, a = 10.372(4) Å, b = 11.933(5) Å, c = 26.284(11) Å, α = 101.593(10)°, β = 94.150(9)°, γ = 95.257(10)°, V = 3159(2) Å^3, Z = 4, ρ_{calcd} = 1.646 Mgm^{-3}, μ = 0.842 mm^{-1}, F(000) = 1590, crystal size 0.22 x 0.13 x 0.02 mm^3, 25010 reflections collected, 12296 unique [R(int) = 0.2109] (completeness to theta = 26.00° 98.9 %). Empirical absorption correction made, T_{min} and T_{max} = 0.802 and 0.338 respectively. GOF = 0.795, final R indices [I>2σI] R_1 = 0.0910, wR_2 = 0.1639, R indices (all data) R_1 = 0.1872, wR_2 = 0.1958. Largest diff. peak and hole 1.347 and -2.118 e Å^{-3}.

Disordered CH_2Cl_2 was omitted using the SQUEEZE option of PLATON.[76] The solvent accessible voids are 207.5 Å^3 with an estimated 124 e/cell to be added. Three solvent CH_2Cl_2 molecules/unit cell accounting for 126 e were included in the formula, FWt, (000) and density calculations. The CF_3 group of one of the triflate anions was disordered and one of the F atoms has been split; attempts to split other atoms failed.

Crystal data for 10·(0.5CH_2Cl_2)(0.25C_6H_{14}). $C_{31}H_{40.50}ClI_2N_4Pd$, M_w = 864.82 gmol^{-1}, T = 150(2) K, triclinic space group P-1, a = 13.616(9) Å, b = 15.293(10) Å, c = 18.724(13) Å, α = 73.804(12)°, β = 73.014(12)°, γ = 64.088(12)°, V = 3302(4) Å^3, Z = 4, ρ_{calcd} = 1.740 Mgm^{-3}, μ = 2.539 mm^{-1}, F(000) = 1694, crystal size 0.20 x 0.20 x 0.13 mm^3, 25832 reflections collected, 12785 unique [R(int) = 0.0875] (completeness to theta = 26.00° 98.6 %). Empirical absorption correction made, T_{min} and T_{max} = 0.831 and 0.455 respectively. GOF = 0.952, final R indices [I>2σI] R_1 = 0.0589, wR_2 = 0.1341, R indices (all data) R_1 = 0.0825, wR_2 = 0.1428. Largest diff.

peak and hole 2.244 and -0.858 e $Å^{-3}$.

Disordered CH_2Cl_2 and C_6H_{14} were omitted using the SQUEEZE option of PLATON.[76] The solvent accessible voids are 325.1 $Å^3$ with an estimated 144e/cell to be added. Two solvent CH_2Cl_2 molecules and one C_6H_{14} molecule/unit cell accounting for 134e were included in the formula, FWt, (000) and density calculations.

Crystal data for 11. $C_{29}H_{36}I_2N_4Pt$, M_w = 889.51 gmol-1, T = 150(2) K, triclinic space group P-1, a = 13.412(3) Å, b = 15.242(3) Å, c = 18.357(4) Å, α= 95.858(4)°, β= 104.069(4)°, γ = 114.812(4)°, V = 3214.0(12) $Å^3$, Z = 4, ρ_{calcd} = 1.838 Mgm^{-3}, μ = 6.309 mm^{-1}, F(000) = 1688, crystal size 0.23 x 0.08 x 0.04 mm^3, 25327 reflections collected, independent reflections 12490 [R(int) = 0.0920] (completeness to theta = 26.00° 98.80%). Empirical absorption correction made, T_{min} and T_{max} = 0.831 and 0.518 respectively. GOF = 0.897, final R indices [I>2σI] R_1 = 0.0602, wR_2 = 0.1004, R indices (all data) R_1 = 0.1104, wR_2 = 0.1130. Largest diff. peak and hole 3.255 and -1.506 e.$Å^{-3}$.

Crystal data for 12·(C_5H_{12}). $C_{53}H_{74}N_6O_2Pd_2$, M_w = 1039.98 $gmol^{-1}$, T = 150(2) K, tetragonal space group I4(1)/a, a = 19.443(2) Å, b = 19.443(2) Å, c = 25.426(4) Å, α= 90°, β= 90°, γ = 90°, V = 9612(2) $Å^3$, Z = 8, ρ_{calcd} = 1.437 Mgm^{-3}, μ = 0.796 mm-1, F(000) = 4336, crystal size 0.31 x 0.24 x 0.15 mm^3, 37121 reflections collected, independent reflections 4713 [R(int) = 0.0767] (completeness to theta = 26.00° 100.00%). Empirical absorption correction made, T_{min} and T_{max} = 0.802 and 0.634 respectively. GOF = 1.029, final R indices [I>2σI] R_1 = 0.0378, wR_2 = 0.0914, R indices (all data) R_1 = 0.0497, wR_2 = 0.0960. Largest diff. peak and hole 0.690 and -0.388 e.$Å^{-3}$.

Disordered pentane (C_5H_{12}) was omitted using the SQUEEZE option of PLATON.[76] The solvent accessible voids are 1135.0 $Å^3$ with an estimated 332e/cell to be added. Eight solvent C_5H_{12} molecules/unit cell accounting for 336e were included in the formula, FWt, (000) and density calculations.

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Supplementary information

X-ray crystallographic data (CIF) for compounds **7a**, **7b**, **9a**, **10**, **11** and **12**; ^1H and ^{13}C NMR

spectra for all compounds.

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Ilustrations

Fig. 1. Pd [CNC] complexes similar to those reported herein.

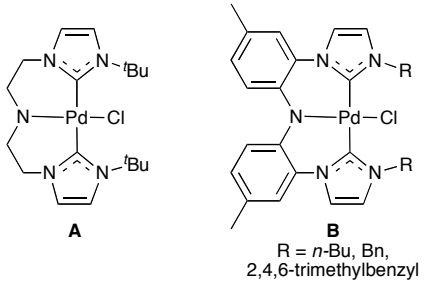


Fig. 2. ORTEP view of **7a** (ellipsoids drawn at 50% probability). Hydrogen atoms except H(10) have been omitted for clarity.

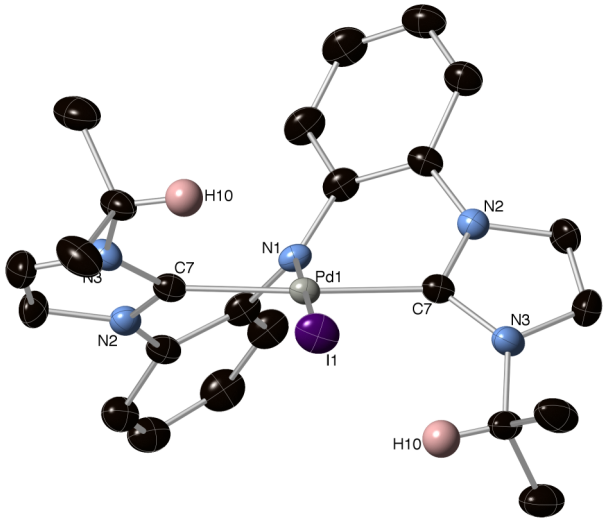


Fig. 3. ORTEP view of **7b** (ellipsoids drawn at 50% probability). Hydrogen atoms have been omitted for clarity.

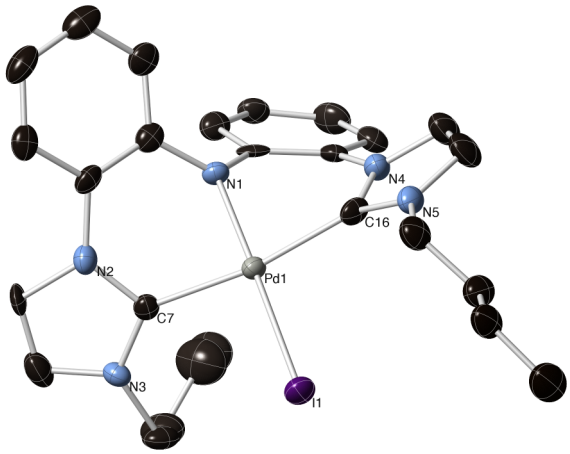


Fig. 4. ORTEP view of one of the independent cations of **9a** (ellipsoids drawn at 50% probability). Hydrogen atoms have been omitted for clarity.

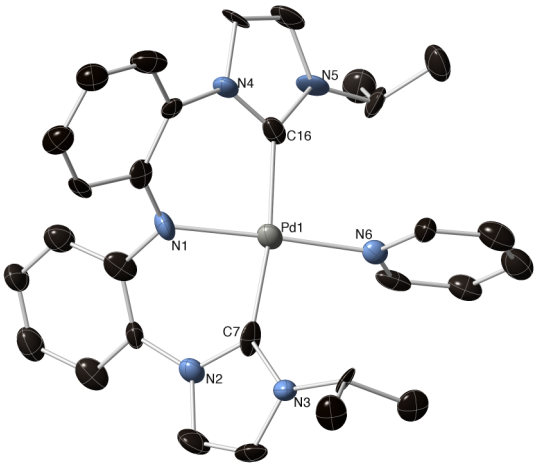


Fig. 5. ORTEP view of one of the independent molecules of **10** (ellipsoids drawn at 50% probability). Hydrogen atoms except H(1) have been omitted for clarity.

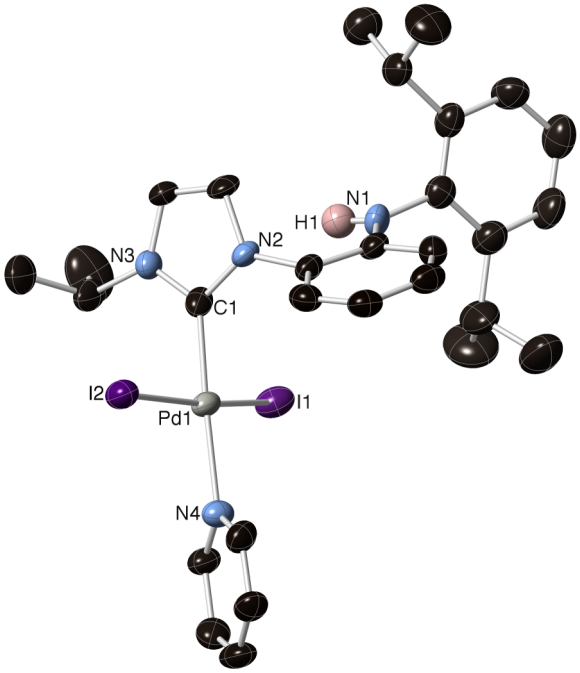


Fig. 6. ORTEP view of one of the independent molecules of **11** (ellipsoids drawn at 50% probability). Hydrogen atoms except H(1) have been omitted for clarity.

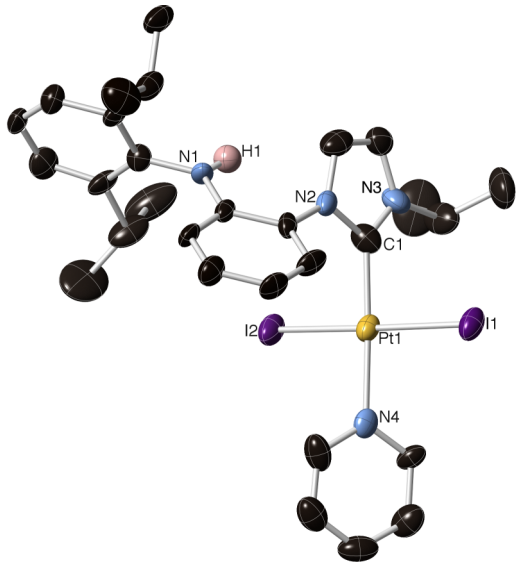
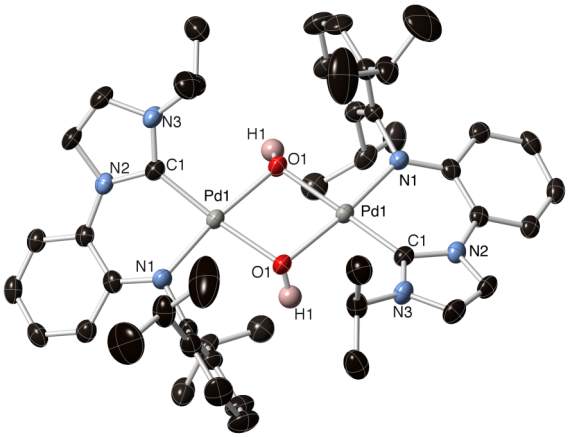
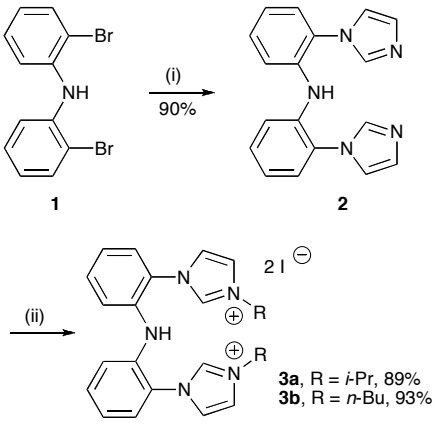


Fig. 7. ORTEP view of **12** (ellipsoids drawn at 50% probability). Hydrogen atoms except H(1) have been omitted for clarity.

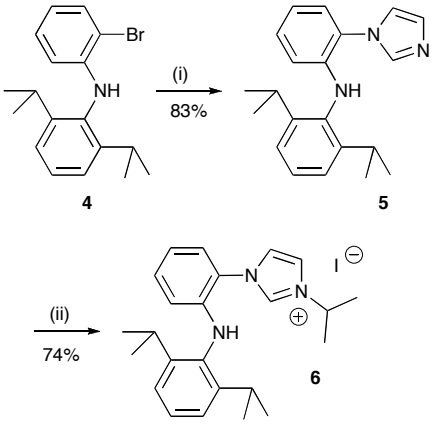


Scheme 1. Synthesis of the amine bis(imidazolium) pro-ligands **3a** and **3b**.[a]



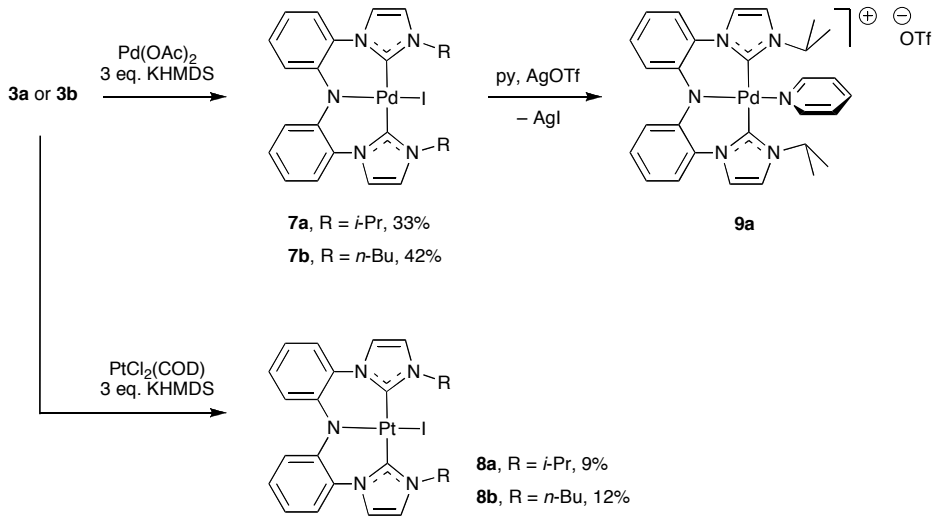
[a]Reaction conditions: (i) 2 eq. imidazole, Cs_2CO_3, CuI (10 mol%), 8-hydroxyquinoline (10 mol%), DMF, 125 °C, 24 h;
(ii) 2.2 eq. RI, MeCN, 90 °C, 24-48 h

Scheme 2. Synthesis of the amine imidazolium pro-ligand **6**.[a]



[a]Reaction conditions: (i) 1 eq. imidazole, Cs_2CO_3, CuI (10 mol%), 8-hydroxyquinoline (10 mol%), DMF, 125 °C, 72 h;
(ii) 1.1 eq. *i*-PrI, MeCN, 90 °C, 48 h

Scheme 3. Synthesis of palladium and platinum [CNC] complexes.



Scheme 4. Synthesis of amine-NHC complexes **10** and **11** and the amido-NHC complex **12**.

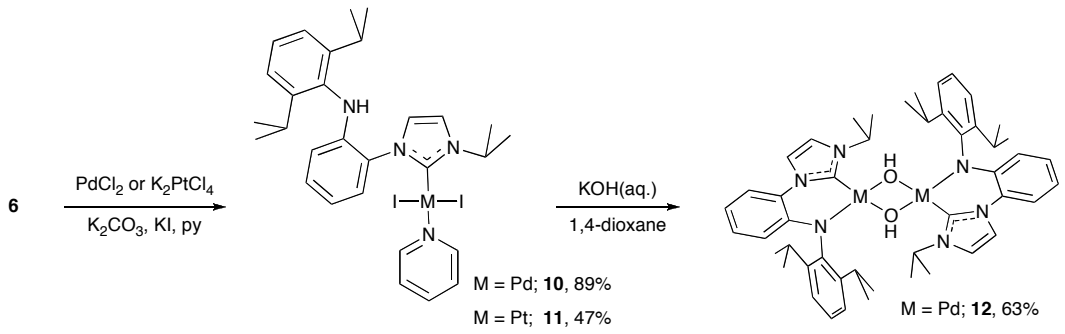


Table 1. Selected bond lengths (Å) for **7a**, **7b** and **9a**.

	7a	**7b**	**9a** molecule 1	molecule 2
M-N(amide)	2.023(3)	2.020(4)	2.022(8)	2.016(8)
M-C(NHC)	2.024(3)	2.020(6)	2.00(1)	2.027(11)
	2.024(3)	2.019(6)	2.036(9)	2.034(10)
M-N(py)	–	–	2.054(8)	2.072(11)
M-I	2.5887(6)	2.6034(6)	–	–

Table 2. Selected bond lengths (Å) for **10**, **11** and **12**.

	10 molecule 1	molecule 2	**11** molecule 1	molecule 2	**12**
M-N(amide)	–	–	–	–	1.998(3)
M-C(NHC)	1.957(7)	1.981(7)	1.965(13)	1.968(11)	1.945(3)
M-N(py)	2.121(6)	2.086(6)	2.094(10)	2.102(8)	–
M-I	2.5902(18)	2.5889(16)	2.5901(10)	2.5969(11)	–
	2.6063(17)	2.6054(15)	2.6024(10)	2.6060(10)	–
M-O1	–	–	–	–	2.052(2)
M-O1’	–	–	–	–	2.086(2)