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NN_{py}C- and ON_{py}C-Pincers as Functional Ligands for Palladium(II) Complexes and Assemblies

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Abstract

The pyridyl-imine, -amine and -alcohol pro-ligands, 2-(2-MeC₆H₄)-6-{CMe=N(2,6-*i*-Pr₂C₆H₃)}C₅H₃N (**HL1**), 2-(2-MeC₆H₄)-6-{CMe₂NH(2,6-*i*-Pr₂C₆H₃)}C₅H₃N (**HL2**) and 2-(2-MeC₆H₄)-6-(CMe₂OH)C₅H₃N (**HL3**), each appended with an *ortho*-tolyl unit, have been synthesized by a combination of condensation and methylation approaches, all deriving from the common acetylpyridine precursor, 2-(2-MeC₆H₄)-6-(CMe=O)C₅H₃N. Treatment of **HL1**, **HL2** and **HL3** with Pd(OAc)₂ results in cyclo-palladation *via* sp²-CH activation of the tolyl unit to give the organometallic palladium(II) NNC- or ONC-pincer complexes (**L1**)Pd(OAc) (**1a**), (**L2**)Pd(OAc) (**2a**) and (**L3**)Pd(OAc) (**3a**). Quantitative conversion of **1a**, **2a** and **3a** to their chloride derivatives, (**L1**)PdCl (**1b**), (**L2**)PdCl (**2b**) (**L3**)PdCl (**3b**), respectively, has been demonstrated. Intramolecular NH $\cdots$ O_{acetate} (**2a**) and intermolecular OH $\cdots$ O_{acetate} (**3a**) or OH $\cdots$ Cl (**3b**) hydrogen-bonding interactions are a feature of the crystal structures for **2a**, **3a** and **3b**; notably in **3a** and **3b** this leads to self-assembly into dimers with differing metal $\cdots$ metal separations. The molecular structures for **HL1**, **HL2**, **1a**, **1b** and **2b** are additionally reported as is full characterization data for both the pro-ligands and complexes.

Keywords: pincer ligands; palladium(II) complexes; hydrogen bonding; X-ray crystallography; C-H activation; organometallic chemistry; self-assembly

1. Introduction

Pincer-type complexes containing a pyridine group as the central donor have emerged as important class of inorganic species due, in large measure, to their applications in organic synthesis, homogeneous catalysis, bond activation and material science [1-7]. The capacity to vary the electronic and steric properties of the exterior donor groups of the tridentate ligand frame has no doubt contributed to the versatility of these thermodynamically stable metal complexes. Furthermore, appreciation of the aromatization-dearomatization processes that can take place at the pyridine core during certain bond activations has help provide added impetus to this research area [8-12].

In relation to palladium(II) chemistry, numerous examples have been reported based on symmetrical $LN_{py}L$ ligand sets such as PNP [13], NNN [14] and CNC [15]. On the other hand, the non-symmetrical variants, $LN_{py}L'$, incorporating inequivalent exterior donor atoms are not nearly as well documented. This can, in part, be attributed to the non-trivial synthetic routes involved in their ligand synthesis often involving multiple steps. Nevertheless, cyclometallated $C_{aryl}NN$ -Pd systems containing σ -coordinated arene groups have received a good deal of attention and in particular where the exterior N-donor is pyridine-based [16] and to a much lesser degree amine [17] or imine [18]. In stark contrast, the $C_{aryl}NO$ -Pd counterparts have, to the knowledge of the authors, been the subject of only one report [19].

Over the years we have been interested in the synthesis and applications of pyridine-based unsymmetrical pincer ligands and have demonstrated their use in a number of metal-mediated processes [21-27]. As a more recent target, the introduction of some hydrogen bonding capacity to the role of the pincer has provided an additional source of motivation. Indeed, we have shown that suitably positioned hydrogen bond donor and acceptor moieties to the arms of the pincer manifold can lead to intramolecular hydrogen bonding or even self-dimerization through intermolecular hydrogen bonding [19,28,29].

Figure 1 General structure for the target $LN_{py}C^{-1}$ -type pincer ligands; dipp = 2,6-diisopropylphenyl

Herein, we are concerned with developing pincer ligands of general formula $LN_{py}C^{-1}$ as unsymmetrical monoanionic supports for palladium(II) acetate and chloride complexes (Figure 1). In particular, we target three types of L as one of the exterior donors namely imine, amine and alcohol with the intent of forming **L1**, **L2** and **L3**. It is envisaged that NH and OH

functionalities in **L2** and **L3** could serve as a directional hydrogen bond donors that could facilitate the formation of multinuclear assemblies. For purposes of comparison, palladium complexes bearing **L1** are also being sought. Full details of the synthetic procedures employed to prepare pro-ligands **HL1**, **HL2** and **HL3** will be disclosed as will the resultant complexation and structural chemistry.

2. Results and discussion

2.1. Synthesis of **HL1**, **HL2** and **HL3**

The pyridylimine, 2-(2-MeC₆H₄)-6-{CMe=N(2,6-*i*-Pr₂C₆H₃)}C₅H₃N (**HL1**), has been prepared in good yield by the acid-catalysed condensation reaction of 2-tolyl-6-acetylpyridine with 2,6-diisopropylaniline (Scheme 1). The 2-(*o*-tolyl)-6-acetylpyridine precursor is not commercially available and could be synthesised in reasonable yield by a palladium-mediated Suzuki cross-coupling reaction of 2-bromo-6-acetylpyridine and 2-methylphenylboronic acid. Both **HL2** and **HL3** could be prepared using similar synthetic approaches based on reacting either imine **HL1** or ketone 2-(*o*-tolyl)-6-acetylpyridine with firstly trimethylaluminium to accomplish the methylation and then secondly hydrolysing the intermediate aluminium species to form the corresponding free amine (**HL2**) or alcohol (**HL3**). Compounds **HL1**, **HL2** and **HL3** have been characterized by ¹H/¹³C NMR, IR spectroscopy and by mass spectrometry. In addition, the molecular structures of **HL1** and **HL2** have been determined using single crystal X-ray diffraction.

Compounds **HL1**, **HL2** and **HL3** all show protonated molecular ions in their ESI mass spectra. In the IR spectra an imine absorption band for **HL1** is clearly visible at 1645 cm⁻¹, while the N-H and O-H bands for **HL2** and **HL3** can be seen at 3351 and 3398 cm⁻¹, respectively. The ¹H NMR spectrum of **HL1** shows a 2H septet at δ 2.71 and two closely located 6H doublets at δ 1.08 and 1.10 for the CHMe₂ methyl groups which is consistent with

some restricted rotation of each isopropyl group rendering the methyl groups inequivalent; this inequivalency is also supported in the ^{13}C NMR spectrum which reveals two different carbon signals for the corresponding methyls. By contrast, the ^1H NMR spectrum of **HL2** shows a 12H doublet for the now equivalent isopropyl methyl groups at δ 0.97, while the ^{13}C NMR spectrum shows one strong signal at δ 24.1 for the corresponding methyl carbons. In **HL3** the *gem*-dimethyl signal takes the form of a 6H singlet at δ 1.49 which compares to δ 1.42 in **HL2**. A broad singlet for the NH proton is seen at δ 4.17 for **HL2** while the OH proton for **HL3** is observed more downfield at δ 5.18.

Scheme 1 Synthesis of **HL1**, **HL2** and **HL3**

Further confirmation of the identity of **HL1** and **HL2** was provided by their X-ray structures. Single crystals of **HL1** and **HL2** were grown by the slow evaporation of methanol/dichloromethane solutions of the corresponding compound. Perspective views of **HL1** and **HL2** are shown in Figures 2a and 2b; selected bond lengths and angles are listed in Table 1. Both structures consist of a central pyridine unit substituted at the 6-position by an *ortho*-tolyl group and at its 2-position by either a $\text{CMe}=\text{N}(2,6\text{-}i\text{-Pr}_2\text{Ph})$ (**HL1**) or a saturated

CMe₂NH(2,6-*i*-Pr₂Ph) (**HL2**) unit. Comparison of the C(6)-N(2) distances in **HL1** (1.265(3) Å) and **HL2** (1.496(2) Å) confirms the presence of double and single bonds, respectively. The *ortho*-tolyl groups are tilted with respect the neighbouring pyridine [tors.: C(2)-C(1)-C(20)-C(25) 49.6° (**HL1**), 50.8° (**HL2**)], which is likely due to the steric properties of this aryl group [18a]. On the other hand, the imine and amine C(6)-N(2) vectors are inclined at 27.3 and 45.1° to the pyridine ring with the imine nitrogen adopting a configuration best described as *trans* to the pyridine nitrogen, while the amine nitrogen is closer to *cis*; the latter arrangement is likely due to the NH proton being able to undergo an intramolecular hydrogen bonding interaction with the pyridine nitrogen atom (NH...N_{pyridine} 2.248 Å).

Figure 2 ORTEP representations of (a) **HL1** and (b) **HL2**; the thermal ellipsoids are set at 50% with all hydrogen atoms (except the N-H proton) omitted for clarity.

Table 1 Selected bond distances (Å) and angles (°) for **HL1** and **HL2**.

	HL1	HL2
Bond distances (Å)		
N(2)-C(6)	1.265(3)	1.491(2)
C(5)-C(6)	1.481(3)	1.540(3)
Bond angles (°)		
N(1)-C(5)-C(6)	115.3(2)	113.37(15)
N(2)-C(6)-C(5)	116.1(2)	109.77(14)
C(6)-N(2)-C(8)	122.2(2)	120.39(14)
N(1)-C(1)-C(20)	116.7(2)	116.89(16)

2.2. Synthesis and characterization of the palladium(II) pincer complexes

Reaction of **HL1** and **HL2** with Pd(OAc)₂ in toluene at 60 °C gave, on work-up, the palladium(II) complexes, (**L1**)Pd(OAc) (**1a**) and (**L2**)Pd(OAc) (**2a**), in high yield (Scheme 2). A similar approach was employed to prepare (**L3**)Pd(OAc) (**3a**) from **HL3**, however, the yield was notably lower despite a number of attempts at varying the reaction conditions. All the new complexes have been characterized by a combination of ¹H/¹³C NMR, IR spectroscopy, mass spectrometry and microanalysis. In addition, single crystals of each complex have been the subject of X-ray diffraction studies.

In general, the ESI mass spectra of **1a** – **3a** show molecular ion peaks or fragmentation peaks corresponding to the loss of an acetate. In their IR spectra two peaks in the ranges 1373-1382 cm⁻¹ and 1558-1562 cm⁻¹ relate to the symmetric and asymmetric ν(COO) vibrations of the acetate ligand, respectively; values typical of an O-bound monodentate acetate [30]. Integration of the aromatic region in the ¹H NMR spectra (recorded in CDCl₃ at ambient temperature) reveals there to be nine aryl protons for **1a** and **2a** and six for **3a** consistent with C-H activation of *ortho*-tolyl group having occurred in all three cases.

Scheme 2 Synthesis of **1 – 3**

With specific regard to **1a**, the ^1H NMR spectrum reveals there to be two well-separated 6H doublets for the two *i*-Pr methyl groups and one 2H septet for the corresponding CH protons. As with free **HL1**, the inequivalency is consistent with some restricted rotation of each *i*-Pr group leading to distinct methyl environments; it is assumed there is a plane of symmetry along the N-2,6-diisopropylphenyl axis. In the IR spectrum, the imine absorption band has shifted from 1645 cm^{-1} in free **HL1** to 1604 cm^{-1} in **1a**, supportive of coordination to the metal center [28,29].

In the ^1H NMR spectrum of **2a** two separate septets are evident for the now inequivalent CHMe_2 protons at δ 3.26 and 3.38, a feature which can be attributed to a loss of symmetry as a result of coordination of the secondary amine nitrogen to palladium. The corresponding methyl signals are also expected to be inequivalent but due to their closeness in chemical

shift along with the additional presence of an acetate methyl resonance, the four separate doublets were not completely distinguished. Furthermore, the CMe₂ methyl groups are also inequivalent leading to clearly resolved singlet resonances at δ 1.91 and 2.57. The intact amine proton appears at δ 6.90 which was confirmed by the absence of any correlations to other protons in the COSY spectrum or to any of the carbons in the HMQC spectrum. Notably, this signal is more downfield than that observed in free HL2 (δ 4.17), a finding that is likely attributable to intramolecular hydrogen bonding between this amine proton and the acetate group (*vide infra*). The IR spectrum of the complex shows peaks at 1590 and 3230 cm⁻¹, which is in accord with the N-H bending and stretching frequencies. Unlike in **2a**, the ¹H NMR spectrum of **3a** reveals the CMe₂ methyl groups are in equivalent environments which is corroborated by the ¹³C NMR spectrum with a singlet at δ 33.1. The acetate methyl resonance for **3a** can be seen at δ 2.48 notably more downfield than that in **1a** (δ 1.63), while the OH proton is evident as a broad singlet resonance at δ 5.23.

The observed cyclo-palladation of the *ortho*-tolyl group in HL1, HL2 and HL3 is presumed to follow an acetate-assisted CH activation mechanism commonly referred to as AMLA-6 or CMD [31]. In the case of HL2 and HL3 the potential for NH or OH activation presents an alternative reaction pathway. Surprisingly, the only products that could be identified were **2a** and **3a**.

Interaction of **1a**, **1b** and **1c** with brine at room temperature followed by extraction into chloroform gave the chloride complexes (L1)PdCl (**1b**), (L2)PdCl (**2b**) (L3)PdCl (**3b**), respectively, in quantitative yield (Scheme 2). Each complex was fully characterized by ¹H, ¹³C{¹H} NMR and IR spectroscopy as well as with mass spectrometry. All three complexes have also been the subject of single crystal X-ray diffraction studies.

The absence of the acetate methyl signals in the ¹H and ¹³C NMR spectra of **1b** – **3b** was a clear indication of product formation. In addition, the ESI and FAB mass spectra show

molecular ions for all three complexes, while the IR spectra are devoid of the acetate absorptions present in their precursors. As with **1a** the ^1H NMR spectrum of **1b** shows two doublets for the inequivalent methyl groups in the isopropyl groups with the CHMe_2 protons giving rise to a single septet. By contrast, four doublets are clearly distinguishable for all four isopropyl methyl groups in **2b** along with two distinct septets for CHMe_2 protons. Otherwise, the spectroscopic data strongly resembled that observed for **1a** – **3a**.

2.3. X-ray structures

Single crystals of complexes **1a**, **1b**, **2a**, **2b**, **3a** and **3b** were grown as yellow/orange blocks or plates by layering their dichloromethane solutions with hexane followed by prolonged standing at room temperature. Each pair of complexes, **1a/1b**, **2a/2b** and **3a/3b**, are structurally similar and will be discussed together.

Views of **1a** and **1b** are shown side-by-side in Figure 3; selected bond distances and angles are listed in Table 2. Each structure consists of a palladium center surrounded by one carbon and two nitrogen donors belonging to tridentate **L1** along with a monodentate O-bound acetate (**1a**) or chloride (**1b**) to complete a geometry best described as distorted square planar. While the *trans* N(2)-Pd(1)-O(1) or N(2)-Pd(1)-Cl(1) angles are close to the desired 180° in **1a** ($176.87(19)^\circ$) and **1b** ($178.38(12)^\circ$), respectively, the N(1)-Pd(1)-C(16) angles at $160.5(2)^\circ$ (**1a**) and $159.64(19)^\circ$ (**1b**) account for the distortion to the geometry; in-turn this latter observation can be attributed to the constraints imposed by the pincer ligand. Two five-membered chelate rings are a feature of the **L1Pd** interaction with the imine, pyridine and aryl moieties virtually co-planar [tors: N(1)-C(7)-C(9)-N(2) 0.39° (**1a**), 1.06° (**1b**) and tors.: N(2)-C(13)-C(14)-C(15) 1.17° (**1a**), 0.99° (**1b**)]. By contrast, there are some differences in the bond distances involving the donor atoms in **L1** with the Pd(1)_{imine} length the longest (2.171(5) (**1a**), 2.161(4) (**1b**) Å), while the Pd(1)-N_{pyridine} and Pd(1)-C_{aryl} ones are comparable

and shorter (1.958(5), 1.952(4) Å (**1a**)) and (1.952(4), 1.977(5) Å (**1b**)). The relatively short Pd-C(16) distance when compared to its *trans* imine-N(1) counterpart can be attributed to a combination of the ionic contribution to the bonding in the former and the compatibility of the soft-soft Pd-C interaction. The 2,6-diisopropylphenyl group adopts an almost perpendicular arrangement with respect to the neighbouring imine vector [C(7)-N(1) 1.280(7) Å]. Related NNC-palladium complexes have been reported and indeed **1a** and **1b** show similar features [18,19]. There are no intra- or intermolecular contacts of note in either structure.

Figure 3 ORTEP representations of (a) **1a** and (b) **1b**; the thermal ellipsoids are set at 50% with all hydrogen atoms (except the N-H proton) omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) for **1a** and **1b**.

	1a	1b
Bond distances (Å)		
Pd(1)-N(1)	2.171(5)	2.161(4)
Pd(1)-N(2)	1.958(5)	1.952(4)
Pd(1)-C(15)	1.960(7)	1.977(5)
Pd(1)-O(1)	2.034(4)	-
Pd(1)-Cl(1)	-	2.317(1)

C(7)-N(1)	1.280(7)	1.281(6)
Bond angles (°)		
N(1)-Pd(1)-N(2)	78.8(2)	78.58(16)
N(1)-Pd(1)-C(15)	160.5(2)	159.64(19)
N(1)-Pd(1)-O(1)	104.28(19)	-
N(1)-Pd(1)-Cl(1)	-	102.45(11)
N(2)-Pd(1)-C(15)	81.7(2)	81.24(19)
N(2)-Pd(1)-O(1)	176.87(19)	-
N(2)-Pd(1)-Cl(1)	-	178.38(12)
C(15)-Pd(1)-O(1)	95.2(2)	-
C(15)-Pd(1)-Cl(1)	-	97.78(16)
C(9)-C(7)-N(1)	116.8(6)	116.1(5)

Representations of **2a** and **2b** are depicted in Figure 4; selected bond distances and angles are given in Table 3. The structures are similar to that seen for **1a** and **1b** comprising a palladium center coordinated to by one carbon and two nitrogen donors in **L2** along with an acetate (**2a**) or chloride (**2b**) filling the fourth coordination site of the square planar arrangement. The Pd-C(16) and Pd-N(2)_{pyridine} distances are again the shortest (1.956(2), 1.960(3) (**2a**) Å; 1.964(3), 1.970(4) Å (**2b**)) of the three **L2**Pd interactions with Pd-N(1)_{amine} the longest (2.221(2) (**2a**), 2.205(3) (**2b**) Å). These Pd-N_{amine} distance are also notably longer than those seen for Pd-N_{imine} distances in **1a** and **1b** reflecting the weaker amine interaction with the metal. The *trans* N(2)-Pd(1)-O(1)_{acetate} angle in **2a** (174.68(9)°) is further from 180° than the N(2)-Pd(1)-Cl(1) angle in **2b** (179.05(9)°) which is likely due, in part, to the presence of an intramolecular hydrogen bonding between the pendant oxygen of the acetate and the N(1)-H proton (NH...O(1) 2.251 Å). Within the **L2** ligand, the pyridine and tolyl units in both structures are almost co-planar (tors.: C(16)-C(15)-C(14)-N(2) 2.67° (**2a**), 0.09° (**2b**)), while the CMe₂NArH group undergoes some twisting to accommodate the sp³-hybridised C(7) with the result that the CMe₂ is positioned on one side the pyridine-tolyl plane (tors.: C(7)-C(10)-C(11)-C(12) 10.87° (**2a**), 6.19° (**2b**)). Furthermore, the N-2,6-

diisopropylphenyl group is folded away from the tolyl-pyridine plane due to the pyramidal nature of the coordinated amine. There are no intermolecular interactions of note in either structure.

Figure 4 ORTEP representations of (a) **2a** and (b) **2b**; the thermal ellipsoids are set at 50% with all hydrogen atoms (except the N-H proton) omitted for clarity. The dotted line shows an NH $\cdots$ O hydrogen bond.

Table 3 Selected bond distances (Å) and angles (°) for **2a** and **2b**.

	2a	2b
Bond distances (Å)		
Pd(1)-N(1)	2.221(2)	2.205(3)
Pd(1)-N(2)	1.956(2)	1.964(3)
Pd(1)-C(16)	1.960(3)	1.970(4)
Pd(1)-O(1)	2.056(2)	-
Pd(1)-Cl(1)	-	2.313(1)
C(7)-N(1)	1.526(4)	1.530(5)
Bond angles (°)		
N(1)-Pd(1)-N(2)	81.84(10)	81.88(12)
N(1)-Pd(1)-C(16)	163.05(11)	163.45(15)
N(1)-Pd(1)-O(1)	101.47(9)	-

N(1)-Pd(1)-Cl(1)	-	97.93(9)
N(2)-Pd(1)-C(16)	81.78(11)	81.60(15)
N(2)-Pd(1)-O(1)	174.68(9)	-
N(2)-Pd(1)-Cl(1)	-	179.05(9)
C(16)-Pd(1)-O(1)	95.19(11)	-
C(16)-Pd(1)-Cl(1)	-	98.56(12)
C(10)-C(7)-N(1)	110.7(2)	109.6(3)

Perspective views of **3a** and **3b** are illustrated in Figures 5 and 6; selected bond distances and angles are compiled in Table 4. Within the unit cell of each structure there are two independent molecules (*A* and *B*) that are essentially the same. Interestingly, both *A* and *B* in **3a** and **3b** are independently linked through OH $\cdots$ O_{acetate} (**3a**) or OH $\cdots$ Cl (**3b**) hydrogen bonds (see below) with symmetry generated molecules. For the purposes of this discussion only molecule *A* in each structure will be discussed in detail; bond parameters for *B* are however presented in Table 4. Within each molecule each palladium is bound by **L3** through its oxygen, nitrogen and carbon donors and is additionally bound by an acetate (**3a**) or a chloride (**3b**) to furnish square planar geometries. As with previous structures in this study there are some differences in the bond lengths of the donor atoms within the pincer, in particular, Pd(1)-O(1) (2.174(4) Å) >> Pd(1)-N(1) (1.948(4) Å) > Pd(1)-C(11) (1.938(6) Å). Furthermore, there is significant difference in the two Pd-O distances in **3b** with Pd(1)-O(2)_{acetate} (2.042(4) Å) considerably shorter than the Pd(1)-O(1), a finding that can be related to the ionic contribution to the bonding in the former and dative bonding in the latter. The pyridine and tolyl groups are once again essentially co-planar (tors. C(11)-C(6)-C(5)-N(1) 6.58° (**3a**), 1.64° (**3b**)) and this *pseudo*-planarity is extended to the *gem*-dimethyl carbon (tors.: C(12)-C(1)-C(2)-C(3) 4.12° (**3a**), 5.16° (**3b**)). Unlike in **2a**, the hydrogen bonding is now intermolecular and involves the OH proton as the donor with the acceptor atom being either a pendant acetate oxygen in the neighbouring molecule (**3a**, O(1)-H(1) $\cdots$ O(3AA))

1.852 Å) or the bound chloride ligand in the neighbouring molecule (**3b**, O(1)-H(1)···Cl(1C) 2.057 Å). This difference in the location of the acceptor atom has an additional effect on the M···M separation with a distance of 6.388 Å in **3a** and 3.282 Å in **3b**. Notably in **3b** the molecules units align in an anti-parallel fashion allowing the two metal centers to efficiently approach to a separation close to the sum of the van der Waals radii (3.26 Å); related assemblies have been reported elsewhere [28,29].

Figure 5 ORTEP representation of **3a**; the thermal ellipsoids are set at 50% with all hydrogen atoms (except the O-H proton) omitted for clarity. Dotted lines represent the hydrogen bonds.

Figure 6 ORTEP representation of **3b**; the thermal ellipsoids are set at 50% with all hydrogen atoms (except the O-H proton) omitted for clarity. Dotted lines represent the hydrogen bonds.

Table 4 Selected bond distances (Å) and angles (°) for **3a** and **3b**.

	3a		3b	
	Molecule <i>A</i>	Molecule <i>B</i>	Molecule <i>A</i>	Molecule <i>B</i>
Bond distances (Å)				
Pd(1)-N(1)	1.948(4)	1.962(5)	1.966(3)	1.971(3)
Pd(1)-O(1)	2.174(4)	2.161(4)	2.211(3)	2.204(3)
Pd(1)-C(11)	1.938(6)	1.944(7)	1.948(4)	1.960(4)
Pd(1)-O(2)	2.042(4)	2.055(4)	-	-
Pd(1)-Cl(1)	-	-	2.334(1)	2.320(1)
C(12)-O(1)	1.420(7)	1.415(6)	1.457(5)	1.461(5)
Bond angles (°)				
N(1)-Pd(1)-O(1)	77.80(18)	77.62(18)	79.48(12)	80.01(12)
N(1)-Pd(1)-C(11)	83.0(2)	82.2(3)	81.96(15)	81.81(16)
N(1)-Pd(1)-O(2)	177.33(19)	176.52(18)	-	-
N(1)-Pd(1)-Cl(1)	-	-	176.87(9)	176.14(10)
O(1)-Pd(1)-C(11)	159.3(2)	158.0(2)	160.91(14)	161.27(15)
O(1)-Pd(1)-O(2)	104.83(17)	103.41(15)	-	-
O(1)-Pd(1)-Cl(1)	-	-	100.34(8)	97.93(8)
C(11)-Pd(1)-O(2)	94.4(2)	96.3(2)	-	-
C(11)-Pd(1)-Cl(1)	-	-	98.43(12)	100.48(13)
C(1)-C(12)-O(1)	107.1(5)	107.2(5)	110.6(3)	109.7(3)

3. Conclusions

Cyclo-palladation has been successfully employed to convert the *o*-tolyl-substituted pyridyl-imine, **HL1**, and -amine, **HL2**, into their corresponding NNC-palladium(II) pincer complexes, **1a** and **2a**, as their acetate derivatives in excellent yields. Similarly, the ONC-bearing **3a** has been obtained from the *o*-tolyl-substituted pyridyl-alcohol, **HL3**, albeit in lower yield. All three complexes, **1a** – **3a**, undergo ready acetate/chloride exchange to form chlorides **1b** – **3b**. In addition to spectroscopic and spectrometric characterization, single crystal X-ray

diffraction has been performed on all six complexes revealing distorted square planar arrangements. Interestingly, the OH donor arm of the pincer ligands in **3a** and **3b** undergoes $\text{OH}\cdots\text{O}_{\text{acetate}}$ or $\text{OH}\cdots\text{Cl}$ intermolecular hydrogen bonding leading to the formation of dimeric assemblies. By contrast, the NH donor arm in **2a** facilitates intramolecular $\text{NH}\cdots\text{O}_{\text{acetate}}$ hydrogen bonding; no such interaction was observed in **2b**.

4. Experimental

4.1. General

All air sensitive reactions were carried out using standard Schlenk techniques under an atmosphere of dry, oxygen-free, nitrogen unless otherwise stated. Unless otherwise indicated, toluene, tetrahydrofuran (THF) and diethylether were dried by heating at reflux over sodium and benzophenone and then distilled prior to use. All NMR spectroscopic data were collected on a Bruker ARX-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C) or a Bruker Avance III 500 spectrometer (500 MHz for ^1H , 125 MHz for ^{13}C), at ambient temperature unless otherwise stated; chemical shifts (ppm) are reported with relation to residual protio solvent peaks while coupling constants are expressed in hertz (Hz). Electrospray mass spectrometry (ESMS) data were collected by means of a micromass Quattro LC mass spectrometer with MeOH as a solvent. High resolution FAB (fast atom bombardment) mass spectra were recorded using a Kratos Concept spectrometer (xenon gas, 7kV) with NBA as the matrix. The infrared spectra were recorded in the solid state with Universal ATR sampling accessories on a Perkin Elmer Spectrum One FTIR instrument. Elemental analyses were performed at the Science Technical Support Unit, London Metropolitan University.

All compounds, including n-BuLi (1.6 M in hexane), trimethylaluminium (2 M solution in toluene) and 2,6-diisopropylaniline were purchased from Sigma Aldrich and rigorously maintained under a nitrogen atmosphere. Palladium(II) acetate was purchased from Alfa-

Aesar and used as obtained. Tetrakis(triphenylphosphine)palladium(0) [32], 2-bromo-6-acetylpyridine [33] and 2-methylphenylboronic acid [34] were synthesized by literature routes. NMR solvents were kept over molecular sieves and were not distilled prior to use.

4.2. Synthesis of 2-(2-MeC₆H₄)-6-(CMe=O)C₅H₃N

A 500 mL oven-dried three-necked round bottomed flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was loaded with 2-bromo-6-acetylpyridine (2.32 g, 11.68 mmol), Pd(PPh₃)₄ (0.27 g, 0.234 mmol, 0.02 eq.), toluene (40 mL) and an aqueous 2 M solution of potassium carbonate (11.68 mL, 23.36 mmol, 2 eq.). The solution was stirred for 15 min followed by the addition of the 2-methylphenylboronic acid (2.06 g, 15.18 mmol, 1.3 eq.) in ethanol (22 mL). Following stirring and heating the solution at 90 °C for 48 h, the mixture was allowed to cool to room temperature and 30% hydrogen peroxide (0.8 mL) added. The solution was left to stir at room temperature for a further 1 h. The product was extracted using diethylether (2 x 100 mL) and the organic extracts washed with brine (3 x 50 mL). The aqueous layer was then washed with chloroform (3 x 30 mL). All organic extracts were combined and dried over magnesium sulphate and the volatiles removed under reduced pressure to give a brown residue. The catalyst residues were removed using a short silica column employing dichloromethane:hexane (70:30) as the eluting solvent. After removing the solvent under reduced pressure, the product, 2-{2-MeC₆H₄}-6-CMeO-C₅H₃N, was obtained as a yellow oil (2.457 g, 99%). ¹H NMR (CDCl₃, 400 MHz): δ 2.37 (s, 3H, Ar-CH₃), 2.65 (s, 3H, Py-C(O)CH₃), 7.16-7.26 (m, 3H, Ar-H), 7.34 (d, 1H, ³J_{HH} 7.2, Ar-H), 7.48 (d, 1H, ³J_{HH} 7.8, *m*-Py-H), 7.76 (t, 1H, ³J_{HH} 7.8, *p*-Py-H), 7.91 (d, 1H, ³J_{HH} 7.8, *m*-Py-H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 20.7 (Py-C(O)-CH₃), 25.9 (o-Ar-CH₃), 119.4 (CH), 126.1 (CH), 127.4 (CH), 128.7 (CH), 129.8 (CH), 131.2 (CH), 136.3 (C), 137.2 (CH), 139.5 (C), 152.9 (C), 159.4 (C), 200.5 (Py-C(O)-CH₃). IR (cm⁻¹): 759 ν(C-H bend), 819 ν(C-

H bend), 1581 $\nu(\text{C}=\text{N})_{\text{pyridine}}$, 1696 $\nu(\text{C}=\text{O})_{\text{ketone}}$, 2926 $\nu(\text{C}-\text{H stretch})$. ESIMS (+ve, MeOH): m/z 212 $[\text{M}+\text{H}]^+$, 234 $[\text{M}+\text{Na}]^+$. HRMS (TOF): calculated for $\text{C}_{14}\text{H}_{14}\text{NO}$ $[\text{M}+\text{H}]^+$ 212.1036, found 212.1075.

4.3. Synthesis of **HL1**

To a dry one-necked 50 mL round bottomed flask equipped with stir bar was added 2-(2-MeC₆H₄)-6-CMeO-C₅H₃N (4.00 g, 18.95 mmol), ethanol (25 mL) and 2,6-diisopropylaniline (6.72 g, 37.9 mmol, 2 eq.). After stirring the solution at reflux for 5 min, five drops of formic acid were added to the flask and a reflux condenser attached. Following stirring and heating at reflux for five days, the reaction mixture was cooled to room temperature and the resulting suspension filtered, washed with cold ethanol and dried to yield **HL1** as a pale yellow solid (5.10 g, 73%). Mp: 138-141 °C. ¹H NMR (CDCl₃, 400 MHz): δ 1.08 (d, 6H, ³J_{HH} 6.6, CH(CH₃)_{2b}), 1.10 (d, 6H, ³J_{HH} 6.6, CH(CH₃)_{2a}), 2.16 (s, 3H, Py-C(N)-CH₃), 2.43 (s, 3H, o-Ar-CH₃), 2.71 (sept, 2H, ³J_{HH} 6.6, CH-(CH₃)₂), 6.99-7.12 (m, 3H, Py/Ar-H), 7.21-7.31 (m, 3H, Py/Ar-H), 7.41-7.49 (m, 2H, Py/Ar-H), 7.80 (t, 1H, ³J_{HH} 7.8, Py/Ar-H), 8.24 (d, 1H, ³J_{HH} 8.0, Py/Ar-H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 17.5 (Py-C(N)-CH₃), 20.8 (o-Ar-CH₃), 23.0 (Ar-CH-CH_{3(a)}), 23.3 (Ar-CH-CH_{3(b)}), 28.4 (Ar-CH-(CH₃)₂), 119.1 (CH), 123.1 (CH), 123.6 (CH), 125.0 (CH), 126.1 (CH), 128.5 (CH), 130.0 (CH), 131.2 (CH), 135.9 (C), 136.3 (C), 136.8 (CH), 140.1 (C), 146.7 (C), 155.8 (C), 158.9 (C), 167.5 (Py-C(N)-CH₃). IR (cm⁻¹): 765 $\nu(\text{C}-\text{H bend})$, 822 $\nu(\text{C}-\text{H bend})$, 1587 $\nu(\text{C}=\text{N})_{\text{pyridine}}$, 1645 $\nu(\text{C}=\text{N})_{\text{imine}}$, 2926 $\nu(\text{C}-\text{H stretch})$. ESIMS (+ve, MeOH): m/z 371 $[\text{M}+\text{H}]^+$, 393 $[\text{M}+\text{Na}]^+$. HRMS (TOF): calculated for $\text{C}_{26}\text{H}_{30}\text{N}_2$ $[\text{M}+\text{H}]^+$ is 371.2437, found 371.2487.

4.4. Synthesis of **HL2**

A clean and dry Schlenk flask equipped with a stir bar was evacuated and backfilled with nitrogen. To the flask was added **HL1** (0.555 g, 1.5 mmol) which was dissolved in dry toluene (30 mL). A 2 M solution of trimethylaluminium (2.3 mL, 4.5 mmol, 3 eq.) in toluene was introduced dropwise and the reaction mixture stirred and heated to 95 °C overnight. The mixture was cooled to room temperature and water (30 mL) added carefully. The mixture was stirred for 1 h and then the organic phase separated. The aqueous layer was washed with chloroform (2 × 30 mL) and then all organic extracts combined, washed with brine and dried over magnesium sulphate. The solvent was removed under reduced pressure to give **HL2** as a yellow oily solid (0.525 g, 91%). Mp: 81-84 °C. ¹H NMR (CDCl₃, 400 MHz): δ 0.97 (d, 12H, ³J_{HH} 6.9, CH-(CH₃)₂), 1.42 (s, 6H, HN-(CH₃)₂), 2.37 (s, 3H, o-Ar-CH₃), 3.17 (sept, 2H, ³J_{HH} 6.9, CH-(CH₃)₂), 4.17 (br s, 1H, HN-(CH₃)₂), 6.94-7.01 (m, 1H, Py/Ar-H), 7.04-7.25 (m, 6H, Py/Ar-H), 7.35-7.42 (m, 2H, Py/Ar-H), 7.63 (t, 1H, ³J_{HH} 7.73, Py/Ar-H). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 20.8 (o-Ar-CH₃), 24.1 (Ar-CH-(CH₃)₂), 28.3 (Ar-CH-(CH₃)₂), 29.3 (Py-C(NH)-(CH₃)₂), 59.5 (Py-C(NH)-(CH₃)₂), 117.1 (CH), 121.6 (CH), 123.0 (CH), 124.5 (CH), 125.9 (CH), 128.2 (CH), 129.9 (CH), 130.9 (CH), 136.1 (C), 136.5 (C), 140.6 (CH), 140.9 (C), 146.6 (C), 158.7 (C), 167.7 (C). IR (cm⁻¹): 794 ν(C-H bend), 815 ν(C-H bend), 1576 ν(C=N)_{pyridine}, 2926 ν(C-H stretch), 3351 ν(N-H)_{amine}. ESIMS (+ve, MeOH): m/z 387 [M+H]⁺. HRMS (FAB): calculated for C₂₇H₃₅N₂ [M+H]⁺ 387.2747, found 387.2796.

4.5. Synthesis of **HL3**

A small dry Schlenk flask was evacuated and backfilled with nitrogen. The flask was charged with 2-{2-MeC₆H₄}-6-CMeO-C₅H₃N (0.253 g, 1.2 mmol) and the contents dissolved in toluene (10 mL). A 2M solution of trimethylaluminium in toluene (2.0 ml, 4.0 mmol, 3.3 eq.) was added dropwise and the reaction stirred and heated to 95 °C overnight. The reaction

mixture was cooled to room temperature and water (10 mL) carefully added. The mixture was then stirred vigorously for 2 h. The organic layer was separated and the aqueous layer washed with dichloromethane (3×15 mL). The organic layers were combined and washed with brine (1×30 mL) and dried over MgSO_4 . Following filtration, the solvent was removed using a rotary evaporator and then under reduced pressure for 24 h to give **HL3** as a white solid (0.248 g, 91%). Mp: 113-116 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 1.49 (s, 6H, Py-C- $(\text{CH}_3)_2$), 2.29 (s, 3H, *o*-Ar- CH_3), 5.18 (s, broad, 1H, C- $(\text{CH}_3)_2$ -OH), 7.16-7.22 (m, 5H, Py/Ar-H), 7.32 (d, 1H, $^3J_{\text{HH}}$ 6.8, Py/Ar-H), 7.64 (t, 1H, $^3J_{\text{HH}}$ 7.8, Py/Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 20.7 (*o*-Ar- CH_3), 30.8 (Py-C- $(\text{CH}_3)_2$), 71.8 (Py-C- $(\text{CH}_3)_2$), 116.6 (CH), 122.1 (CH), 125.9 (CH), 128.5 (CH), 129.8 (CH), 131.0 (CH), 136.1 (C), 137.4 (CH), 139.9 (C), 157.8 (C), 165.3 (C). IR (cm^{-1}): 801 ν (C-H bend), 1563 ν (C=N)_{pyridine}, 3398 ν (O-H bond). ESIMS (+ve, MeOH): m/z 216 $[\text{M}+\text{H}]^+$, 238 $[\text{M}+\text{Na}]^+$. HRMS (FAB): calculated for $\text{C}_{14}\text{H}_{17}\text{NO}$ $[\text{M}+\text{H}]^+$ 216.2911, found 216.2914.

4.6. Synthesis of **1a**

A clean dry Schlenk flask equipped with a magnetic stir bar was evacuated and backfilled with nitrogen. The flask was then charged with $\text{Pd}(\text{OAc})_2$ (0.182 g, 0.81 mmol) and **HL1** (0.300 g, 0.81 mmol, 1 eq.) and the contents dissolved in toluene (30 mL). The solution was stirred and heated to 60 °C for 48 h. On cooling to room temperature, the reaction mixture was filtered through a thin layer of celite and dried under reduced pressure to give **1a** as a deep yellow solid (0.416 g, 96%). Mp: > 270 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 1.04 (d, 6H, $^3J_{\text{HH}}$ 6.9, Ar-CH- $\text{CH}_{3(a)}\text{CH}_{3(b)}$), 1.31 (d, 6H, $^3J_{\text{HH}}$ 6.7, Ar-CH- $\text{CH}_{3(a)}\text{CH}_{3(b)}$), 1.63 (s, br, 3H, OCOCH_3), 2.13 (s, 3H, Py-C(N)- CH_3), 2.53 (s, 3H, *o*-Ar- CH_3), 3.08 (sept, 2H, $^3J_{\text{HH}}$ 6.8, CH- $(\text{CH}_3)_2$), 6.77 (d, 1H, $^3J_{\text{HH}}$ 7.4, Py/Ar-H), 6.91 (t, 1H, $^3J_{\text{HH}}$ 7.6, Py/Ar-H), 7.04 (d, 1H, $^3J_{\text{HH}}$ 7.8, Py/Ar-H), 7.11-7.21 (m, 3H, Py/Ar-H), 7.35-7.40 (m, 1H, Py/Ar-H),

7.83-7.88 (m, 1H, Py/Ar-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 17.6 (Py-C(N)- CH_3), 23.3 (*o*-Ar- CH_3), 23.5 (Ar-CH- CH_3 (a)), 24.0 (Ar-CH- CH_3 (b)), 28.7 (Ar-CH-(CH_3)₂), 29.7 (OCOCH₃), 120.8 (CH), 123.4 (CH), 123.5 (CH), 124.4 (CH), 127.1 (CH), 129.3 (C), 130.1 (CH), 131.3 (CH), 135.6 (C), 136.4 (C), 138.7 (CH), 141.1 (C), 145.5 (C), 154.0 (C), 155.4 (C), 166.1 (Py-C(N)- CH_3), 172.9 (OCOCH₃). IR (cm^{-1}): 766 ν (C-H bend), 801 ν (C-H bend), 1382 ν (COO)_{symm.}, 1558 ν (COO)_{asym.}, 1586 ν (C-N)_{pyridine}, 1604 ν (C=N)_{imine}, 2958 ν (C-H stretch). ESIMS (+ve, MeOH): m/z 475 $[\text{M-OAc}]^+$. HRMS (TOF): calculated for $\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_2\text{Pd} [\text{M}]^+$ 534.1509, found 534.1510. Anal. calc. for ($\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_2\text{Pd}\cdot 0.5\text{CH}_2\text{Cl}_2$): C 59.28, H 5.76, N 4.85. Found C 59.31, H 5.07, N 4.87%.

4.7. Synthesis of **2a**

Using a procedure and molar ratios similar to that given for **1a** but with HL**2** (0.500 g, 1.3 mmol) as the pro-ligand gave **2a** as a light brown solid (0.736 g, 88%). Mp: 255-258 °C. ^1H NMR (CDCl_3 , 500 MHz): δ 0.81 (d, 3H, $^3J_{\text{HH}}$ 7.0, CH(CH_3)₂), 1.15-1.33 (m, 12H, Pd-OCOCH₃, CH(CH_3)₂), 1.91 (s, 3H, Py-C(NH)-(CH₃)₂), 1.97 (s, 3H, *o*-Ar-CH₃), 2.57 (s, 3H, Py-C(NH)-(CH₃)₂), 3.26 (sept, 1H, $^3J_{\text{HH}}$ 7.0, CH-(CH₃)₂), 3.38 (sept, 1H, $^3J_{\text{HH}}$ 7.1, CH-(CH₃)₂), 6.84 (d, 1H, $^3J_{\text{HH}}$ 7.2, Py/Ar-*H*), 6.89 (s, 1H, NH), 6.92-7.10 (m, 5H, Py/Ar-*H*), 7.15-7.21 (m, 1H, Py/Ar-*H*), 7.69 (d, 1H, $^3J_{\text{HH}}$ 8.2, Py/Ar-*H*), 7.75 (t, 1H, $^3J_{\text{HH}}$ 8.0, Py/Ar-*H*). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 22.7 (Py-C(N)- CH_3), 23.2 (*o*-Ar-CH₃), 23.4 (Ar-CH-(CH₃)₂), 24.1 (Ar-CH-(CH₃)₂), 24.9 (Ar-CH-(CH₃)₂), 25.1 (Ar-CH-(CH₃)₂), 27.1 (Ar-CH-(CH₃)₂), 28.1 (Py-C(NH)-(CH₃)₂), 28.7 (Py-C(NH)-(CH₃)₂), 35.1 (Pd-OCOCH₃), 68.1 (Py-C(NH)-(CH₃)₂), 116.9 (CH), 120.4 (CH), 124.5 (CH), 124.7 (C), 126.2 (CH), 128.8 (CH), 128.8 (CH), 130.6 (C), 135.3 (CH), 137.1 (CH), 138.3 (C), 143.9 (C), 144.1 (CH), 144.9 (C), 153.9 (C), 164.2 (C), 169.5 (C), 178.9 (Pd-OCOCH₃). IR (cm^{-1}): 781 ν (C-H bend), 805 ν (C-H bend), 1373 ν (COO)_{symm.}, 1455 ν (C=N)_{pyridine}, 1566 ν (COO)_{asym.}, 1590 ν (N-H)_{amine bend},

2926 $\nu(\text{C-H stretch})$, 3230 $\nu(\text{N-H})_{\text{amine stretch}}$. ESIMS (+ve, MeCN): m/z 532 $[(\text{M-OAc})+\text{MeCN}]^+$, 491 $[\text{M-OAc}]^+$, 550 $[\text{M}]^+$. HRMS (TOF): calculated for $\text{C}_{27}\text{H}_{33}\text{N}_2\text{Pd} [\text{M-OAc}]^+$ 491.1667, found 491.1678.

4.8. Synthesis of **3a**

Using a procedure and molar ratios similar to that given for **1a** but with **HL3** (0.116 g, 0.515 mmol) as the pro-ligand gave **3a** as a deep yellow solid (0.126 g, 59%). Mp: 234-237 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 1.73 (s, 3H, $o\text{-Ar-CH}_3$), 2.10 (s, 6H, $\text{Py-C-(CH}_3)_2$), 2.48 (s, broad, 3H, OCOCH_3), 5.23 (s, br, 1H, $\text{C-(CH}_3)_2\text{-OH}$), 6.79-7.20 (m, 4H, Py/Ar-H), 7.59 (d, 1H, $^3J_{\text{HH}}$ 8.1, Py/Ar-H), 7.81 (t, 1H, $^3J_{\text{HH}}$ 8.1, Py/Ar-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ 22.3 ($o\text{-Ar-CH}_3$), 27.8 (OCOCH_3), 33.1 ($\text{Py-C-(CH}_3)_2$), 79.3 ($\text{Py-C-(CH}_3)_2$), 116.8 (CH), 120.4 (CH), 128.4 (C), 128.7 (CH), 130.2 (CH), 135.1 (CH), 138.0 (C), 145.3 (CH), 153.6 (C), 163.3 (C), 166.8 (C), 170.9 (OCOCH_3). IR (cm^{-1}): 778 $\nu(\text{C-H bend})$, 1378 $\nu(\text{COO})_{\text{symm.}}$, 1559 $\nu(\text{C-N})_{\text{pyridine}}$, 1562 $\nu(\text{COO})_{\text{asym.}}$. ESIMS (+ve, MeOH): m/z 380 $[\text{M+H}]^+$, 402 $[\text{M+Na}]^+$. HRMS (FAB): calculated for $\text{C}_{16}\text{H}_{20}\text{NO}_3\text{Pd} [\text{M+H}]^+$ 380.3270, found 380.3274.

4.9. Synthesis of **1b**

To a round bottomed flask, equipped with a stir bar and open to the air, was added **1a** (0.056 g, 0.10 mmol) and brine (10 mL). The mixture was then stirred vigorously overnight to obtain a brown coloured reaction mixture. CHCl_3 (10 mL) was then introduced and the reaction mixture stirred for 5 min. The organic phase was then separated and the aqueous layer washed with CHCl_3 (2×10 mL). The organic extracts were combined and dried over magnesium sulphate. The solvent was removed under reduced pressure to give **1b** as a light brown solid (0.054 g, 99%). Mp > 270 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 1.07 (d, 6H, $^3J_{\text{HH}}$ 6.9, $\text{Ar-CH-CH}_{3(a)}\text{CH}_{3(b)}$), 1.31 (d, 6H, $^3J_{\text{HH}}$ 6.7, $\text{Ar-CH-CH}_{3(a)}\text{CH}_{3(b)}$), 2.12 (s, 3H, Pyr-C(N)-

CH_3), 2.56 (s, 3H, *o*-Ar- CH_3), 2.97 (sept, 2H, $^3J_{HH}$ 6.8, $CH-(CH_3)_2$), 6.81 (d, 1H, $^3J_{HH}$ 7.5, Py/Ar- H), 6.92 (t, 1H, $^3J_{HH}$ 7.6, Py/Ar- H), 7.13-7.22 (m, 3H, Py/Ar- H), 7.44 (d, 1H, $^3J_{HH}$ 7.3, Py/Ar- H), 7.74 (d, 1H, $^3J_{HH}$ 7.7, Py/Ar- H), 7.86-7.96 (m, 2H, Py/Ar- H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 17.8 (Py-C(N)- CH_3), 23.0 (*o*-Ar- CH_3), 23.8 (Ar-CH-(CH_3) $_2$), 28.7 (Ar-CH-(CH_3) $_2$), 120.6 (CH), 123.4 (CH), 124.4 (CH), 126.9 (CH), 129.2 (C), 130.1 (CH), 135.3 (C), 136.1 (C), 138.4 (CH), 138.8 (CH), 141.0 (C), 145.1 (C), 154.0 (C), 163.0 (CH), 166.1 (C), 172.3 (Py-C(N)- CH_3). IR (cm^{-1}): 764 ν (C-H bend), 798 ν (C-H bend), 1582 ν (C-N)_{pyridine}, 1614 ν (C=N)_{imide}, 2953 ν (C-H stretch). ESIMS (+ve, MeOH): m/z 511 $[M]^+$. HRMS (FAB): calculated for $C_{26}H_{29}N_2ClPd$ $[M]^+$ 510.1131, found 510.1151.

4.10. Synthesis of **2b**

Using a procedure similar to that described for **1b** with **2a** (0.050 g, 0.090 mmol) as the palladium(II) acetate starting material gave **2b** as a brown solid (0.047 g, 99%). Mp: > 270 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.86 (d, 3H, $^3J_{HH}$ 6.8, Ar-CH(CH_3) $_2$), 1.28 (s, 3H, Py-C(NH)(CH_3) $_2$), 1.29 (d, 3H, $^3J_{HH}$ 6.8, Ar-CH(CH_3) $_2$), 1.31 (d, 3H, $^3J_{HH}$ 6.8, Ar-CH(CH_3) $_2$), 1.37 (d, 3H, $^3J_{HH}$ 6.8, Ar-CH(CH_3) $_2$), 1.90 (s, 3H, Py-C(NH)-(CH $_3$) $_2$), 2.57 (s, 3H, *o*-Ar- CH_3), 3.01 (sept, 1H, $^3J_{HH}$ 6.8, CH(CH_3) $_2$), 3.32 (sept, 1H, $^3J_{HH}$ 6.8, CH(CH_3) $_2$), 5.18 (s, 1H, NH), 6.84 (d, 1H, $^3J_{HH}$ 7.6, Py/Ar- H), 6.93 (t, 1H, $^3J_{HH}$ 7.6, Py/Ar- H), 6.99 (d, 1H, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.4, Py/Ar- H), 7.02-7.12 (m, 3H, Py/Ar- H), 7.72 (dd, 1H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.1, Py/Ar- H), 7.74-7.84 (m, 2H, Py/Ar- H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 22.8 (Ar-CH-(CH $_3$) $_2$), 23.4 (Py-C(NH)-(CH $_3$) $_2$), 23.6 (Py-C(NH)-(CH $_3$) $_2$), 23.7 (Ar-CH-(CH $_3$) $_2$), 24.9 (Ar-CH-(CH $_3$) $_2$), 26.8 (Ar-CH-(CH $_3$) $_2$), 28.9 (Ar-CH-(CH $_3$) $_2$), 29.0 (Ar-CH-(CH $_3$) $_2$), 35.9 (*o*-Ar- CH_3), 68.9 (Py-C(NH)-(CH $_3$) $_2$), 116.9 (CH), 120.9 (CH), 123.6 (CH), 125.1 (C), 126.4 (CH), 128.8 (CH), 128.9 (CH), 134.2 (C), 135.5 (CH), 137.1 (CH), 138.7 (C), 141.9 (C), 143.2 (CH), 145.4 (C), 154.0 (C), 164.3 (C), 168.2 (C). IR (cm^{-1}): 789 ν (C-H bend), 802 ν (C-H bend), 1452 ν (C-

N)_{pyridine}, 1590 $\nu(\text{N-H})_{\text{amine bend}}$, 2926 $\nu(\text{C-H stretch})$, 3341 $\nu(\text{N-H})_{\text{amine stretch}}$. ESIMS (+ve, MeCN): m/z 526 $[\text{M}]^+$. HRMS (FAB): calculated for $\text{C}_{25}\text{H}_{31}\text{N}_2\text{PdCl}$: $[\text{M}]^+$ 526.1078, found 526.1082. Anal. calc. for $(\text{C}_{27}\text{H}_{33}\text{N}_2\text{ClPd})$: C 61.48, H 6.31, N 5.31. Found C 61.42, H 6.38, N 5.29%.

4.11. Synthesis of **3b**

Using a procedure similar to that described for **1b** with **3a** (0.035 g, 0.09 mmol) as the palladium(II) acetate starting material gave **3b** as a brown solid (0.033 g, 99%). Mp: > 270 °C. ^1H NMR (CDCl_3 , 400 MHz): δ 1.76 (s, 6H, Py-C-(CH_3)₂), 2.34 (s, 3H, *o*-Ar- CH_3), 6.42 (t, 1H, $^3J_{\text{HH}}$ 7.7, Py/Ar-H), 6.61 (d, 1H, $^3J_{\text{HH}}$ 7.6, Py/Ar-H), 6.86 (d, 1H, $^3J_{\text{HH}}$ 8.0, Py/Ar-H), 6.91 (s, broad, 1H, C-(CH_3)₂-OH), 7.05 (d, 1H, $^3J_{\text{HH}}$ 7.7, Py/Ar-H), 7.21 (d, 1H, $^3J_{\text{HH}}$ 8.1, Py/Ar-H), 7.50 (t, 1H, $^3J_{\text{HH}}$ 8.1, Py/Ar-H). A $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum could not be obtained due to the poor solubility of the sample in common NMR solvents. IR (cm^{-1}): 749 $\nu(\text{C-H bend})$, 1602 $\nu(\text{C=N})_{\text{pyridine}}$. ESIMS (+ve, MeOH): m/z 368 $[\text{M}+\text{H}]^+$, 390 $[\text{M}+\text{Na}]^+$. HRMS (FAB): calculated for $\text{C}_{15}\text{H}_{17}\text{NOPdCl}$ $[\text{M}+\text{H}]^+$ 368.7471, found 368.7475.

4.12. Crystallographic Studies

Data for HL1, HL2, **1a**, **1b**, **2a**, **2b**, **3a** and **3b** were collected on a Bruker APEX 2000 CCD diffractometer. Details of data collection, refinement and crystal data are listed in Tables 6 and 7. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. Structure solution by direct methods and structure refinement based on full-matrix least-squares on F^2 employed SHELXTL version 6.10 [35]. Hydrogen atoms were included in calculated positions ($\text{C-H} = 0.96 - 1.00 \text{ \AA}$) riding on the bonded atom with isotropic displacement parameters set to 1.5 $\text{Ueq}(\text{C})$ for methyl H atoms and 1.2 $\text{Ueq}(\text{C})$ for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters.

Table 6 Crystallographic and data processing parameters for **HL1**, **HL2**, **1a** and **1b**.

Compound	HL1	HL2	1a	1b
Chemical formula	C ₂₆ H ₃₀ N ₂	C ₂₇ H ₃₄ N ₂	C ₅₇ H ₆₆ Cl ₂ N ₄ O ₄ Pd ₂	C ₅₃ H ₆₀ Cl ₄ N ₄ Pd ₂
Formula weight	370.52	386.56	1154.84	1107.65
Crystal size (mm ³)	0.26 x 0.16 x 0.09	0.34 x 0.23 x 0.16	0.12 x 0.10 x 0.07	0.21 x 0.11 x 0.05
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Crystal system	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	P-1	P-1	Pbcn	C2/c
<i>a</i> (Å)	8.203(3)	8.980(2)	10.676(3)	22.889(4)
<i>b</i> (Å)	9.638(4)	11.466(3)	20.786(5)	9.7814(17)
<i>c</i> (Å)	13.752(5)	12.013(3)	23.803(5)	22.312(4)
α (°)	75.438(8)	81.463(5)	90	90
β (°)	79.299(8)	74.086(4)	90	102.300(4)
γ (°)	80.671(7)	73.187	90	90
<i>V</i> (Å ³)	1026.4(7)	1135.4(5)	5282(2)	4880.8(15)
<i>Z</i>	2	2	4	4
Density (mg/m ³)	1.199	1.131	1.452	1.507
μ (mm ⁻¹)	0.070	0.065	0.832	0.996
F(000)	400	420	2376	2264
Reflections collected	7562	8341	39340	18673
Independent reflections	3590	3982	5195	4784
R(int)	0.0756	0.0598	0.1969	0.1331
Restraints / parameters	0 / 259	0 / 269	0 / 318	0 / 291
Final R indices [I > 2σ(I)]	R1 = 0.0628, wR2 = 0.1454	R1 = 0.0549, wR2 = 0.1228	R1 = 0.0600, wR2 = 0.0990	R1 = 0.0558, wR2 = 0.0910
R indices [all data]	R1 = 0.0994, wR2 = 0.1685	R1 = 0.0780, wR2 = 0.1348	R1 = 0.1375, wR2 = 0.1168	R1 = 0.0912, wR2 = 0.1015
Goodness-of-fit on <i>F</i> ²	0.950	0.956	0.888	0.882

Data in common: graphite-monochromated Mo-K α radiation, λ = 0.71073 Å; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o^2) + (aP)^2]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$, where *a* is a constant adjusted by the program; goodness of fit = $[\Sigma(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ where *n* is the number of reflections and *p* the number of parameters.

Table 7 Crystallographic and data processing parameters for **2a**, **2b**, **3a** and **3b**.

Compound	2a	2b	3a	3b
Chemical formula	C ₂₉ H ₃₆ N ₂ O ₂ Pd	C _{27.75} H _{34.50} Cl _{2.50} N ₂ Pd	C ₁₇ H ₂₂ N O _{4.50} Pd	C ₁₅ H ₁₆ Cl N O Pd
Formula weight	551.00	591.10	418.76	368.14

Crystal size (mm ³)	0.26 x 0.25 x 0.04	0.26 x 0.17 x 0.13	0.45 x 0.16 x 0.05	0.43 x 0.21 x 0.19
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	P2(1)/n	P-1	P2(1)/c	Pca2(1)
<i>a</i> (Å)	10.0969(18)	9.4219(18)	19.368(4)	12.471(3)
<i>b</i> (Å)	15.771(3)	10.957(2)	11.946(3)	12.978(3)
<i>c</i> (Å)	16.881(3)	13.941(3)	16.027(3)	17.840(4)
α (°)	90	90.712(3)	90	90
β (°)	102.798(3)	107.959(3)	113.956(4)	90
γ (°)	90	95.861(3)	90	90
<i>V</i> (Å ³)	2621.3(8)	1360.5(5)	3388.9(12)	2887.4(11)
<i>Z</i>	4	2	8	8
Density (mg/m ³)	1.396	1.443	1.641	1.694
μ (mm ⁻¹)	0.736	0.946	1.118	1.461
F(000)	1144	607	1704	1472
Reflections collected	20200	10723	25850	23015
Independent reflections	5154	5286	6648	6252
R(int)	0.0768	0.0386	0.1081	0.0445
Restraints / parameters	0 / 315	0 / 314	0 / 405	1 / 349
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.0751	R1 = 0.0444, wR2 = 0.1159	R1 = 0.0551, wR2 = 0.1040	R1 = 0.0318, wR2 = 0.0624
R indices [all data]	R1 = 0.0550, wR2 = 0.0793	R1 = 0.0522, wR2 = 0.1210	R1 = 0.0979, wR2 = 0.1149	R1 = 0.0367, wR2 = 0.0639
Goodness-of-fit on <i>F</i> ²	0.943	1.055	0.904	0.988

Data in common: graphite-monochromated Mo-K α radiation, λ = 0.71073 Å; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = [\sigma^2(F_o)^2 + (aP)^2]$, $P = [\max(F_o^2, 0) + 2(F_c^2)]/3$, where *a* is a constant adjusted by the program; goodness of fit = $[\Sigma(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ where *n* is the number of reflections and *p* the number of parameters.

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Appendix A. Supplementary data

CCDC **x – y** contain the supplementary crystallographic data for **HL1**, **HL2**, **1a**, **1b**, **2a**, **2b**, **3a** and **3b**. This data can be obtained free of charge via

<http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 554 033; or e-mail: deposit@ccdc.cam.ac.uk.

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NN_{py}C- and ON_{py}C-Pincer as Functional Ligands for Palladium(II) Complexes and Assemblies

The primary alcohol unit within a ON_{py}C pincer, has been employed as a hydrogen bond donor to direct the self-assembly of dimeric palladium(II) complexes with metal···metal separations between 6.388 and 3.282 Å; conversely with the corresponding imine- or amine-based NN_{py}C pincer, discrete monomeric square planar palladium species are accessible.